

Syntheses and structures of lithiated sulfones $\text{Li}[\text{CR}(\text{R}')\text{SO}_2\text{Ph}] - \text{C}$ versus O bound lithium. $[\{\text{Li}\{\text{CH}(\text{Me})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty] -$ The structure of a C-bound derivative

Matthias Linnert, Clemens Bruhn, Christoph Wagner, Dirk Steinborn *

Institut für Anorganische Chemie der Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle (Saale), Germany

Received 31 August 2005; received in revised form 19 December 2005; accepted 23 December 2005

Available online 20 February 2006

Abstract

Sulfones $\text{RCH}(\text{R}')\text{SO}_2\text{Ph}$ were reacted with *n*-BuLi in *thf/n*-hexane ($\text{R}/\text{R}' = \text{H}/\text{Me}$, Me/Et , $\text{H}/\text{CH}_2\text{Ph}$) and toluene/*n*-hexane ($\text{R}/\text{R}' = \text{Me}/\text{Ph}$) yielding under deprotonation $\text{Li}[\text{CR}(\text{R}')\text{SO}_2\text{Ph}]$ which reacted with Me_3SiCl and *n*-Bu₃SnCl forming the requisite trimethylsilyl and tri(*n*-butyl)tin substituted derivatives $\text{R}_3'\text{E}-\text{C}(\text{R})\text{R}'\text{SO}_2\text{Ph}$ ($\text{R}_3'\text{E} = \text{Me}_3\text{Si}$, *n*-Bu₃Sn). Performing the reactions of $\text{RCH}(\text{R}')\text{SO}_2\text{Ph}$ with *n*-BuLi in *n*-hexane (instead of *thf/n*-hexane) and toluene/*n*-hexane, respectively, resulted in the precipitation of the organo lithium compounds $\text{Li}[\text{CR}(\text{R}')\text{SO}_2\text{Ph}]$ (**1–4**) which were isolated as strongly moisture-sensitive yellow powders in essentially quantitative yields. Their identities were confirmed by ¹H and ¹³C NMR spectroscopic measurements in *thf-d*₈. Solutions of each **1**, **3**, and **4** in *thf/n*-hexane and *thf/n*-pentane afforded crystals of each $[\{\text{Li}\{\text{CH}(\text{Me})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty]$ (**1a**), $[\{\text{Li}\{\text{CH}(\text{CH}_2\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty]$ (**3a**), and $[\{\text{Li}\{\text{CMe}(\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})_2\}_2]$ (**4a**), respectively, whose structures were determined by single-crystal X-ray crystallography. The compounds **1a** and **3a** crystallize in 1D polymeric ladder-like structures. The strands of **1a** are built-up by eight-membered $\text{Li}_2\text{C}_2\text{S}_2\text{O}_2$ rings having direct Li–C bonding interactions (Li–C 2.215(5) Å). The donor set of Li is completed by three oxygen atoms, one from the *thf* ligand and two from SO_2 groups of neighboring $\text{Li}\{\text{CH}(\text{Me})\text{SO}_2\text{Ph}\}(\text{thf})$ entities. The strands of **3a** are built-up of alternating $\text{Li}_2\text{S}_2\text{O}_4$ eight- and Li_2O_2 four-membered rings. Each lithium atom is coordinated to three oxygen atoms, two from $\text{O}_2\text{S}(\text{Ph})\text{CHCH}_2\text{Ph}$ groups and one from *thf* oxygen atom. There is no Li–C bonding. Compound **4a** crystallizes in dimers consisting of eight-membered $\text{Li}_2\text{S}_2\text{O}_4$ rings in which the two lithium atoms are bridged by two $\text{O}_2\text{S}(\text{Ph})\text{CHMePh}$ groups. The coordination sphere of lithium is completed by two oxygen atoms of the *thf* ligands.
© 2006 Elsevier B.V. All rights reserved.

Keywords: α -Sulfonyl functionalized alkyl carbanions; Lithiated alkyl phenyl sulfones; Oxygen versus carbon coordination; Structures of organo lithium compounds

1. Introduction

Lithium-coordinated α -sulfonyl functionalized alkyl carbanions are widely used in organic synthesis as versatile building blocks for a wide range of organic compounds [1]. Since the carbanions are dipole stabilized [2], the α -C–H bonds in the requisite sulfones are acidic (cf. $\text{p}K_{\text{a}}(\text{CH}_3\text{SO}_2\text{Ph}) = 29.0$ in DMSO [3]) and can be easily deproto-

nated. Some derivatives with chiral carbanionic centers exhibit a relatively high conformational stability [4,5]. Thus, such carbanions have not only received experimental interest but also considerable attention from the theoretical point of view. Structurally characterized compounds $\text{Li}[\text{CR}(\text{R}')\text{SO}_2\text{R}'']$ (R , $\text{R}' = \text{alkyl}$, aryl , H ; $\text{R}'' = \text{alkyl}$, aryl) contain in the most cases *tmeda* or *diglyme* coligands and were found to be dimeric in the solid state [4]. The central structural units in these dimers are eight-membered $\text{Li}_2\text{S}_2\text{O}_4$ rings in which the SO_2 groups bridge the two lithium atoms. There are Li–O bonds only and no Li–C bonds. The lone pairs of electrons on the “free” carbanions were

* Corresponding author. Tel.: +49 345 5525620; fax: +49 345 5527028.
E-mail address: dirk.steinborn@chemie.uni-halle.de (D. Steinborn).

found to be bisecting the O–S–O angle. In a single case, the crystal structure of a thf adduct was obtained, $[\{\text{Li}(\text{thf})_2\}\{\text{CPh}(\text{CH}_2\text{Ph})\text{SO}_2\text{CF}_3\}]_2$ [6], which was also found to be dimeric as described above. On the other hand, in the case of α -sulfonyl functionalized lithiumalkyls LiCH_2SR the structures are strongly dependent on the coligand. Tmeda adducts are dimeric with six-membered $\text{Li}_2\text{C}_2\text{S}_2$ or four-membered Li_2C_2 rings [7] whereas the thf adducts were found to be dimeric or polymeric [8].

Here, we describe the synthesis of solvate-free compounds $\text{Li}[\text{CR}(\text{R}')\text{SO}_2\text{Ph}]$ ($\text{R}/\text{R}' = \text{H}/\text{Me}$, Me/Et , $\text{H}/\text{CH}_2\text{Ph}$, Me/Ph) from which we prepared the tetrahydrofuran adducts. Furthermore, we succeeded to obtain well-shaped crystals and single-crystal X-ray investigations showed both an usual dimeric structure ($\text{R}/\text{R}' = \text{Me}/\text{Ph}$) and 1D polymeric structures ($\text{R}/\text{R}' = \text{H}/\text{Me}$, $\text{H}/\text{CH}_2\text{Ph}$), one of which (H/Me) has an unusual Li–C bond.

2. Results and discussion

2.1. Syntheses and characterization

It is well known that alkyl phenyl sulfones and their derivatives can be easily deprotonated yielding α -(phenylsulfonyl) substituted carbanions. Consequently, reactions of $\text{RCH}(\text{R}')\text{SO}_2\text{Ph}$ with $n\text{-BuLi}$ in thf/ n -hexane at -78°C resulted in the formation of the lithium-coordinated α -sulfonyl functionalized alkyl carbanions **1–4** (Scheme 1, a). Their formation could be unambiguously proven by reactions with Me_3SiCl yielding the requisite trimethylsilyl substituted derivatives **5–8** in isolated yields between 90 and 95% (Scheme 1, b). Analogous reactions with the less reactive $n\text{-Bu}_3\text{SnCl}$ resulted in the formation of tri(n -butyl)tin substituted derivatives **9–11**, respectively, in yields between 60 and 85% (Scheme 1, c). $\text{MeCH}(\text{Ph})\text{SO}_2\text{Ph}$ did not react in this way in thf/ n -hexane but the reaction in toluene/ n -hexane resulted in the formation of **12** (yield: 49%). The identities of the silyl and tin compounds **5–12** have been unequivocally established by ^1H , ^{13}C , and ^{119}Sn NMR spectroscopic measurements (see Section 3).

Performing the reactions of $\text{RCH}(\text{R}')\text{SO}_2\text{Ph}$ with $n\text{-BuLi}$ in n -hexane instead of a thf/ n -hexane mixture (Scheme 1, a) resulted in the precipitation of the organo lithium compounds $\text{Li}[\text{CR}(\text{R}')\text{SO}_2\text{Ph}]$ (**1–3**) which were isolated as strongly moisture-sensitive yellow powders in essentially quantitative yields. $\text{MeCH}(\text{Ph})\text{SO}_2\text{Ph}$ was found not to react with $n\text{-BuLi}$ in hexane obviously due to its insolubility in n -hexane. In toluene/ n -hexane $\text{MeCH}(\text{Ph})\text{SO}_2\text{Ph}$ reacted with $n\text{-BuLi}$ yielding **4** in 89% yield. Selected ^1H and ^{13}C NMR spectroscopic data of the lithium compounds **1–4** in thf- d_8 solutions are given in Table 1. Comparison with the corresponding data of the sulfones demonstrates that lithiation gives rise to highfield shifts of the α -carbon resonances by 8.8–13.7 ppm. In complexes **1** and **3** the α -hydrogen resonances are highfield shifted by 1.41 and 1.15 ppm, respectively.

2.2. Structures of α -lithiated alkyl phenyl sulfones

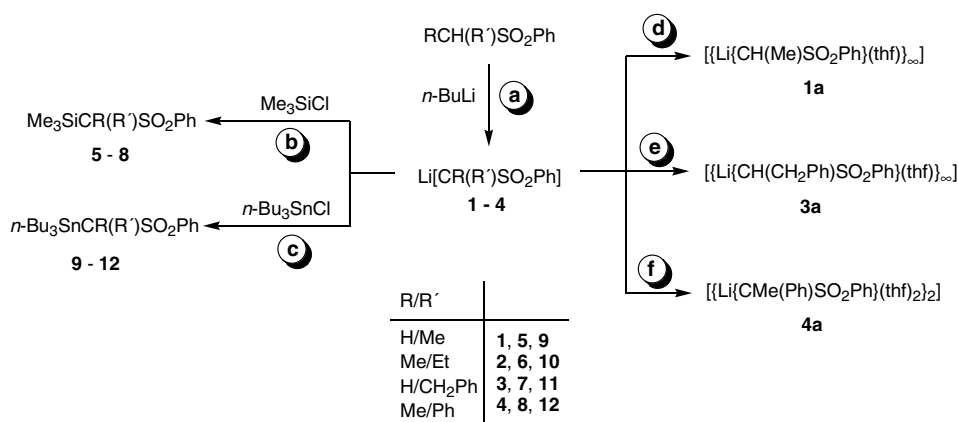
In the case of **1** ($\text{R}/\text{R}' = \text{H}/\text{Me}$), **3** ($\text{R}/\text{R}' = \text{H}/\text{CH}_2\text{Ph}$) and **4** ($\text{R}/\text{R}' = \text{Me}/\text{Ph}$) from thf/ n -hexane (**1**, **4**) and thf/ n -pentane (**3**) solutions, respectively, precipitated well shaped crystals (**1a**, **3a**, **4a**) that proved to be suitable for single-crystal X-ray diffraction measurements (Scheme 1, d–f). Compounds **1a** and **3a** were obtained by dissolution of the solvate-free compounds **1** and **3**, respectively, in thf and precipitation with n -hexane/ n -pentane. Analogously, crystals of **4a** were obtained, but those of better

Table 1
Selected chemical shifts of the lithiated sulfones $\text{Li}[\text{CR}(\text{R}')\text{SO}_2\text{Ph}]$ (**1–4**) in thf- d_8

	R/R'	$\alpha\text{-CRR}'$		$\alpha\text{-CHRR}'^a$	
		δ_{H}^b	δ_{C}	δ_{H}	δ_{C}
1	H/Me	1.70	39.2	3.11	50.5
2	Me/Et	–	47.8	2.91	61.5
3	H/CH ₂ Ph	2.17	44.9	3.32	57.4
4	Me/Ph	–	57.6	4.20	66.4

^a In $\text{HCR}(\text{R}')\text{SO}_2\text{Ph}$ for comparison.

^b For $\text{R} = \text{H}$.



Scheme 1.

quality crystallized directly from the reaction mixture $\text{PhCH}(\text{Me})\text{SO}_2\text{Ph}/n\text{-BuLi}$. In contrast to the powdery lithium compounds **1**, **3** and **4**, the complexes **1a** and **3a** crystallize with one molecule of thf per lithium and **4a** with two molecules of thf per lithium.

2.2.1. Solid state structure of $[\{\text{Li}\{\text{CH}(\text{Me})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty]$ (**1**)

Compound **1a** crystallizes in a 1D polymeric ladder-like structure which is shown in Fig. 1. Selected bond lengths and angles are given in Table 2. The smallest distances between non-hydrogen atoms between the strands (>3.1 Å) show that there are no unusual interstrand interactions. The strands extend along the crystallographic *a*-axis and are built up by eight-membered $\text{Li}_2\text{C}_2\text{S}_2\text{O}_2$ centrosymmetric rings. The marked feature of the structure of **1a** is a direct Li–C bonding interaction; the distance

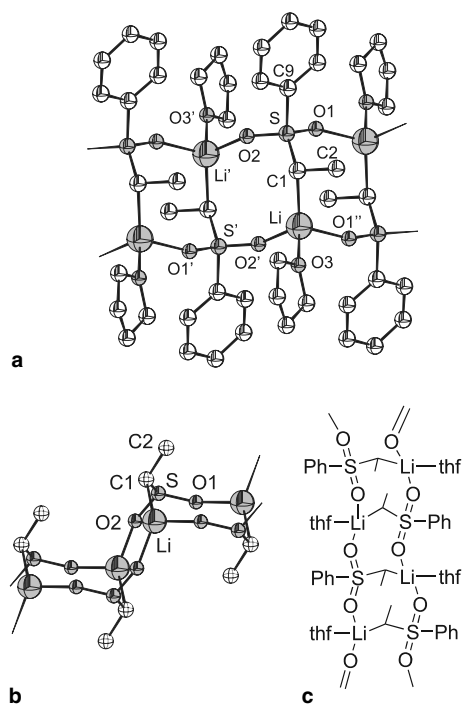


Fig. 1. $[\{\text{Li}\{\text{CH}(\text{Me})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty]$ (**1a**): Front (a) and side view (b) of the solid-state structure and structural formula (c). Hydrogen atoms were omitted for clarity and in the side view 'b' also the phenyl groups and thf ligands. From the disordered thf C atoms only the major occupied positions (71(1)%) are shown.

Table 2
Selected interatomic distances (Å) and angles (°) in $[\{\text{Li}\{\text{CH}(\text{Me})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty]$ (**1a**)

Li–C1	2.215(5)	Li–C1–C2	103.9(2)
Li–O1''	1.922(5)	Li–C1–S	111.4(2)
Li–O2'	1.903(5)	S–C1–C2	115.7(2)
Li–O3	2.023(5)	O1''–Li–C1	115.2(2)
C1–C2	1.503(4)	O2'–Li–C1	123.8(2)
C1–S	1.656(3)	O3–Li–C1	100.9(2)
C3–S	1.790(3)	O1''–Li–O2'	109.9(2)
S–O1	1.448(2)	O1–S–O2	115.5(1)
S–O2	1.449(2)		

between Li and C1 is 2.215(5) Å. The donor set of Li is completed by three oxygen atoms, one (O3) from the thf ligand and two (O1'', O2') from SO_2 groups of the neighboring $\text{Li}\{\text{CH}(\text{Me})\text{SO}_2\text{Ph}\}(\text{thf})$ entities. The angles around C1 (Li–C1–C2, Li–C1–S, S–C1–C2) are between 103.9(2)° and 115.7(2)°. Thus, the C1 atom is best described as sp^3 hybridized. The C1–S conformation was found to be staggered and the Li–C1 vector is directed along the acute bisector of the O1–S–O2 angle as exhibited by the two torsional angles O1–S–C1–Li $-61.2(2)^\circ$ and O2–S–C1–Li $68.5(2)^\circ$. Thus, **1a** may be stabilized by a negative hyperconjugation $n_{\text{C1}}-\sigma_{\text{SC3}}^*$ (torsional angle: C3–S–C1–Li $-176.5(2)^\circ$) between the anionic lone pair orbital at the C1 and the orbitals of the S–C3 backbone.

2.2.2. Solid state structure of $[\{\text{Li}\{\text{CH}(\text{CH}_2\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty]$ (**3a**)

The 1D polymeric solid state structure of $[\{\text{Li}\{\text{CH}(\text{CH}_2\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty]$ (**3a**) is shown in Fig. 2. Selected bond lengths and angles are given in Table 3. Along the crystallographic *b*-axis the crystal is threaded by strands built-up of alternating eight- and four-membered rings. There are no unusual interstrand interactions; the smallest distance between non-hydrogen atoms is >3.5 Å. The

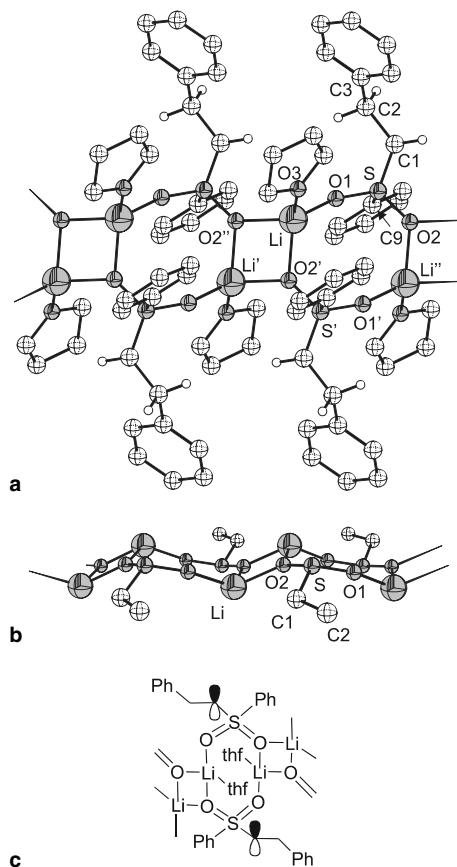


Fig. 2. $[\{\text{Li}\{\text{CH}(\text{CH}_2\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty]$ (**3a**): Front (a) and side view (b) of the solid-state structure and structural formula (c). In 'a' hydrogen atoms of the phenyl substituents and of the thf ligands were omitted for clarity. In the side view 'b' phenyl groups and thf ligands are not shown.

Table 3
Selected interatomic distances (Å) and angles (°) in $[\{\text{Li}\{\text{CH}(\text{CH}_2\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})\}_\infty]$ (**3a**)

Li–O1	1.883(4)	O1–Li–O2''	117.5(2)
Li–O2''	1.975(5)	O1–Li–O2'	119.6(2)
Li–O2'	1.982(4)	O1–Li–O3	106.9(2)
Li–O3	1.936(4)	O2'–Li–O2''	87.5(2)
Li···Li'	2.859(8)	Li–O2'–Li'	92.5(2)
C1–C2	1.515(4)	S–C1–C2	119.9(2)
C1–S	1.608(3)	C1–S–O1	112.9(1)
C9–S	1.812(2)	C1–S–O2	109.8(1)
S–O1	1.461(2)	O1–S–O2	114.8(1)
S–O2	1.480(2)		

strands exhibit crystallographically imposed inversion symmetry; the eight- and four-membered rings are centrosymmetric. In the $\text{Li}_2\text{S}_2\text{O}_4$ eight-membered rings the two lithium atoms are bridged by two $\text{O}_2\text{S}(\text{Ph})\text{CHCH}_2\text{Ph}$ groups. One oxygen atom (O2) of each of these SO_2 groups bridges two Li atoms (Li–O–Li) and builds up the Li_2O_2 four-membered rings. The Li–O1 bond is considerably shorter than the Li– μ -O2 bonds (1.883(4) versus 1.975(5)/1.982(4) Å). As expected, the S=O bond to the bridging oxygen atom is considerably longer than that to the non-bridging oxygen atom (1.480(2) versus 1.461(2) Å). Due to the inversion symmetry the Li_2O_2 rings are planar. The $\text{Li}_2\text{S}_2\text{O}_4$ rings exhibit approximately a chair conformation [9] with the Li/Li' and O2/O2' atoms in the plane. The coordination sphere of the lithium atoms is completed by coordination of one thf molecule, thus exhibiting a LiO_4 donor set. There is no Li–C bonding; the distance between Li and the carbanionic C1 atom amounts to 4.238(5) Å. In accordance with that, the S–C1–C2 angle is 119.9(2)° indicating that the C1 atom is best described as sp^2 hybridized.

2.2.3. Solid state structure of $[\{\text{Li}\{\text{CMe}(\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})_2\}_2]$ (**4a**)

Compound **4a** crystallizes in dimeric molecules $[\{\text{Li}\{\text{CMe}(\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})_2\}_2]$ having crystallographically imposed inversion symmetry. The unit cell contains two symmetrically independent dimers that are very similar in their structures. One of them is shown in Fig. 3, selected bond lengths and angles are given in Table 4. The central structural unit of the dimeric molecule is a centrosymmetric eight-membered $\text{Li}_2\text{S}_2\text{O}_4$ ring in which the two lithium atoms are bridged by two $\text{O}_2\text{S}(\text{Ph})\text{CMePh}$ groups. The $\text{Li}_2\text{S}_2\text{O}_4$ ring adopts a chair conformation with Li/Li' and O2/O2' in the plane. The coordination sphere of lithium is completed by two oxygen atoms of thf ligands. Again, the primary donor set of lithium consists of four oxygen atoms. There are no Li···C contacts; the distance of lithium to the carbanionic α -C atom (C1) is 3.93(1)/3.80(1) Å.¹ As expected, the carbanionic C1 atom is essentially planar (sum of angles: 358.0°/359.3°; distance of C1 from the C2,C3,S1 plane: 0.127(5)/0.074(5) Å) and the angles S1–C1–C2, S1–C1–C3,

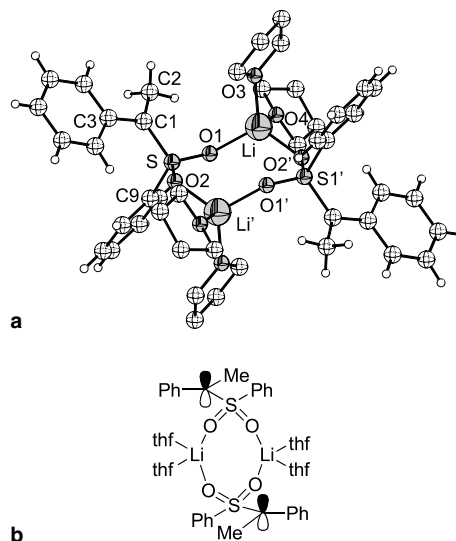


Fig. 3. $[\{\text{Li}\{\text{CMe}(\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})_2\}_2]$ (**4a**): Solid-state structure (a) and structural formula (b). Hydrogen atoms of the thf ligands were omitted for clarity.

Table 4
Selected interatomic distances (Å) and angles (°) in $[\{\text{Li}\{\text{CMe}(\text{Ph})\text{SO}_2\text{Ph}\}(\text{thf})_2\}_2]$ (**4a**)^a

Li–O1	1.890(8)/1.920(8)	O1–Li–O2'	114.8(4)/112.6(3)
Li–O2'	1.897(8)/1.950(9)	O3–Li–O4	106.3(4)/103.5(3)
Li–O3	1.949(8)/1.929(8)	O1–S–O2	115.6(2)/116.3(2)
Li–O4	1.928(9)/1.966(8)	C2–C1–C3	119.7(5)/119.6(4)
C1–S	1.670(5)/1.659(5)	S–C1–C2	115.0(4)/116.6(4)
C1–C2	1.503(7)/1.527(7)	S–C1–C3	123.3(3)/123.1(3)
C9–S	1.783(5)/1.791(4)		
S–O1	1.456(4)/1.469(3)		
S–O2	1.460(3)/1.464(3)		

^a The values of the two crystallographically independent molecules are separated by a slash.

and C2–C1–C3 range from 115.0(4)°/116.6(4)° to 123.3(3)°/123.1(3)°. Thus, the carbanionic C1 atom can be described as sp^2 hybridized with the lone electron pair perpendicular to the C1,C2,C3,S1 plane. Since this plane is coplanar with the plane of the phenyl group C3, ..., C8 (interplanar angle: 5.0(3)°/7.8(3)°), a conjugative interaction between the lone pair and the π^* -orbital of the phenyl ring may stabilize the carbanion, as was previously found for benzyl anions [10]. In accordance with this, the C1–C3 bond is relatively short (1.446(7)/1.448(7) Å) compared to $=\text{C}-\text{C}_{\text{ar}}$ (conjugated) bonds (median 1.470, lower/upper quartile 1.463/1.480, $n = 37$, n – number of observations) [11]. Furthermore, the lone electron pair is approximately periplanar to the S–Ph bond thus allowing a stabilizing hyperconjugative $n_{\text{C1}}-\sigma_{\text{SPh}}^*$ interaction. This is typical for α -sulfonyl carbanions [4,12–14].

2.3. Computational results

Quantum chemical calculations on the DFT level of theory of $\text{Li}[\text{CH}(\text{Me})\text{SO}_2\text{Ph}]$ (**13**) have been performed to gain

¹ Here and the following the values for the two symmetrically independent molecules are separated by a slash.

further insight into the unusual [LiO₃C] coordination mode of the lithiated sulfone **1a**. Geometry optimizations without any symmetry restrictions led to two different equilibrium structures for **13**. One structure (**13a**) exhibits a Li coordination at the anionic carbon atom and at one oxygen atom of the sulfonyl group (coordination mode: κ^2C,O). In the other structure (**13b**) the lithium atom was found to be coordinated through two sulfonyl oxygen atoms (coordination mode: κ^2O,O'). To complete the ligand sphere of Li, geometry optimizations without any symmetry restrictions of the solvated compound Li[CH(Me)SO₂Ph]·2Me₂O (**13**·2Me₂O) were also performed. Even for **13**·2Me₂O two equilibrium structures were found showing an analogous coordination of the lithium atom as described before with two additional coordinated Me₂O molecules. Thus, in both compounds Li adopts a tetrahedral coordination with three O atoms and one C atom (**13a**·2Me₂O) and with four O atoms (**13b**·2Me₂O), respectively. The molecular structures of these two compounds are shown in Fig. 4. Molecular structures of **13a** and **13b** are not shown; they are essentially the same as **13a**·2Me₂O/**13b**·2Me₂O but without the two Me₂O molecules. Selected geometrical parameters for all four lithiated sulfones are given in Table 5.

Coordination of a sulfonyl oxygen atom to lithium gives rise to an elongation of the S–O bond (1.512–1.526 Å versus 1.474/1.483 Å). As expected, these bonds are longer in the compounds **13a/13b** (C.N.(Li) = 2) than in **13a**·2Me₂O/**13b**·2Me₂O (C.N.(Li) = 4): 1.526–1.530 Å versus 1.512–1.516 Å. As expected from Gutmann's bond length

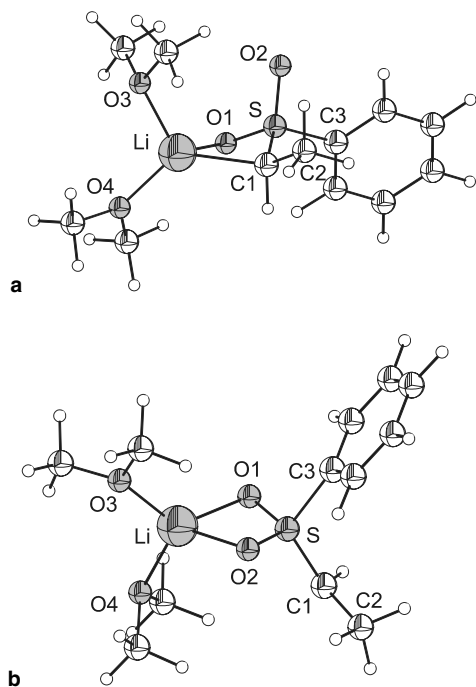


Fig. 4. Calculated structures of Li[CH(Me)SO₂Ph]·2Me₂O along with the numbering schemes. (a) **13a**·2Me₂O. (b) **13b**·2Me₂O. The structures of **13a** and **13b** are essentially the same but without coordinated Me₂O; their numbering schemes are analogous.

Table 5

Calculated distances (Å) and angles (°) for lithiated sulfones Li[CH(Me)SO₂Ph] (coordination mode: κ^2C,O (**13a**); κ^2O,O' (**13b**)) and their dimethyl ether adducts Li[CH(Me)SO₂Ph]·2Me₂O **13a**·2Me₂O and **13b**·2Me₂O, respectively

	13a	13a ·2Me ₂ O	13b	13b ·2Me ₂ O
Li–O1	1.855	1.982	1.888	2.012
Li–O2	(3.290)	(3.249)	1.885	2.013
Li–C1	2.109	2.259	(3.528)	(3.588)
S–C1	1.737	1.712	1.641	1.657
S–O1	1.526	1.515	1.526	1.512
S–O2	1.474	1.483	1.530	1.516
S–C3	1.815	1.822	1.832	1.832
S–C1–C2	116.1	116.9	120.2	119.0
O1–S–O2	117.1	117.0	107.1	109.7
O1–S–C1	102.3	103.8	111.6	111.2
O2–S–C1	111.4	110.8	112.8	112.0
O1–Li–O2			81.3	75.9
O1–Li–C1	79.6	73.4		
Li–O3/Li–O4		1.977/1.953		1.932/1.962
O3–Li–O4		108.4		112.3

rules [15], the Li–O bonds are longer in **13a**·2Me₂O/**13b**·2Me₂O than in **13a/13b** (1.982–2.013 Å versus 1.855–1.888 Å). The same holds for the Li–C distances (2.259 Å in **13a**·2Me₂O versus 2.109 Å in **13a**). Furthermore, the coordination of the carbanionic center to lithium gives rise to a substantial elongation of the S–C1 bond (1.737/1.712 Å versus 1.641/1.657 Å). Although the coordination modes of Li in **1a** (experimental values taken from the solid-state structure), where Li is coordinated to the anionic C atom and to three O atoms (from coordinated thf and *intermolecularly* from two sulfonyl O atoms), and in **13a**·2Me₂O (calculated values in the gas phase), where Li is coordinated to the anionic C atom and to three O atoms (from two coordinated Me₂O and *intramolecularly* from one sulfonyl O atom), are different, the Li–C distances (2.259 Å in **13a**·2Me₂O; 2.215(5) Å in **1a**) agree well. The calculated value for the S–C1 bond in **13a**·2Me₂O (1.712 Å) was found to be slightly longer than that in **1a** (1.656(3) Å).

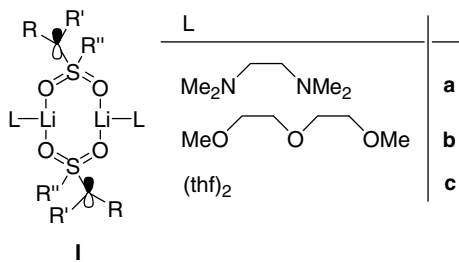
In both structures with Li–C bonds (**13a** and **13a**·2Me₂O) the anionic C atom is strongly pyramidalized (sum of angles at C1: 334.7°/337.6°). The pyramidalization of the C atom in the two compounds with exclusively Li–O contacts, **13b** and **13b**·2Me₂O, was found to be less (sum of angles at C1: 351.6°/347.4°). In all four structures there is a staggered C_α–S conformation. In **13b** and **13b**·2Me₂O the lone pair at the C atom is *gauche* to both oxygen atoms. Thus, a negative hyperconjugation (n_C–σ_{SPh}^{*}) between the anionic lone pair at C_α and the orbitals of the S–Ph bond seems to be of major importance for the carbanion stabilization [16–18]. In **13a** and **13a**·2Me₂O the torsional angles C3–S–C1–Li (–134.9°/–143.7°) point to reduced negative hyperconjugation. Accordingly, the C3–S bonds in **13a/13a**·2Me₂O are shorter (1.815/1.822 Å) than in **13b/13b**·2Me₂O (1.832/1.832 Å).

The compounds where the Li is bound via C and O to the deprotonated sulfone (**13a** and **13a**·2Me₂O) are

energetically more stable than those where the Li is bound through two sulfonyl O atoms (**13b** and **13b** · 2Me₂O). As expected, the energy difference is larger for the compounds where Li has a coordination number 2 ($\Delta E(\mathbf{13a}/\mathbf{13b}) = 5.7$ kcal/mol and 5.0 kcal/mol ZPE corrected) than for the compounds where Li is tetracoordinated ($\Delta E(\mathbf{13a} \cdot 2\text{Me}_2\text{O}/\mathbf{13b} \cdot 2\text{Me}_2\text{O}) = 2.8$ kcal/mol and 2.5 kcal/mol ZPE corrected). Quantum chemical calculations of Li[CH₂SO₂Me] gave an analogous result. The structure in which the Li is associated with one O atom and the anionic C atom was found to be energetically more stable than the structure in which the Li is associated with two O atoms [17,19].

2.4. Conclusion

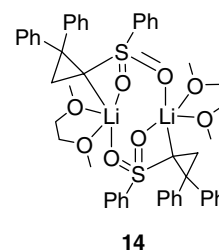
α -Lithiated sulfones Li[CR(R')SO₂R''] (**I**) have been found to crystallize typically as dimers in the solid state without the formation of Li–C bonds. Thus, with tmeda [5,20,21], diglyme [12,22], and thf [6] as co-ligands eight-membered Li₂S₂O₄ rings were formed having strong Li–O bonds. In these compounds Li exhibits LiO₂N₂ (formula **1a**), LiO₅ (formula **1b**) and LiO₄ (formula **1c**) primary donor sets. The strongly binding tridentate pmdta coligand gave rise to the formation of a monomeric compound where the Li is bound only to one oxygen atom of the sulfonyl group (Li donor set: LiON₃) [13].



In this work, we succeeded to obtain the solvate-free lithiated sulfones Li[CR(R')SO₂Ph] (**1–4**) and by crystallization from thf/*n*-hexane or thf/*n*-pentane the tetrahydrofuran adducts in well-shaped crystals (see Scheme 1, d–f). Compound **4a** (R/R' = Me/Ph) crystallizes with two molecules of thf and is a dimeric type **1c** compound. The less-solvated compounds **1a** and **3a** (one molecule thf per Li) exhibited 1D polymeric structures that are unprecedented so far. As in **4a**, the structural motif in **3a** consists of Li₂S₂O₄ eight-membered rings with lithium in an LiO₄ environment. The loss of thf is compensated for by the coordination of an oxygen atom from a neighboring Li₂S₂O₄ ring.

The marked structural feature of compound **1a** is the Li–C bond. Thus, the solid-state structure of **1a** is formally built-up from (thf)Li–CH(Me)SO₂Ph in which the coordination sphere of lithium is completed (LiO₃C) by oxygen coordination from neighboring units. The only other lithiated sulfone having a Li–C bond is the dimeric cyclopropyl

derivative **14** that has the typical Li₂S₂O₄ ring with an additional Li–C bond. These Li–C bonds are considerably longer than that in **1a** (2.44(1) versus 2.215(5) Å) [23]. Furthermore, in the hexameric structure of the dilithiated sulfone Li₂[C(SiMe₃)SO₂Ph] (**15**) [(**15**)₆ · Li₂O · (thf)₁₀] Li–C distances between 2.18 and 3.08 Å were found [24]. In general, the Li–C distance in **1a** (2.215(5) Å) is in the range of Li–C_{sp³} distances in “terminally bonded” organolithium compounds [25] as shown by the comparison with the sulfanyl derivatives [{Li(CH₂SPh)(tmeda)}₂] (2.131(4) Å) [7] and [Li(CH₂SPh)(pmdta)] (pmdta = *N,N,N',N'',N''*-pentamethyldiethylenetriamine) (2.146(5)/2.20(1) Å) [26].



The Li–C1 coordination does not give rise to an unusual length of the C_α–S bond as a comparison of the C1–S bond in **1a** (1.656(3) Å) with those of **3a** and **4a** (1.608(3)–1.670(5) Å) exhibits. Regardless of whether the lithium atom is coordinated to sulfonyl oxygen atoms (**3a**, **4a**) or additionally to the α -carbon atom (**1a**) the bonds between sulfur and the α -carbon atoms are significantly shortened (1.608(3)–1.670(5) Å) compared to S–C bonds in non-lithiated alkyl phenyl sulfones (median: 1.778 Å; lower/upper quartile: 1.764/1.790 Å; *n* = 94 [11]). Such bond shortening is also observed in other lithiated sulfones (1.608(6)–1.683(2) Å [5,6,12,13,20–22]) and is mostly due to electrostatic effects (the attraction between the negatively charged anionic C atom and the positively charged S atom) [14]. Furthermore, in **1a**, **3a**, and **4a** the S–O bonds are elongated (1.448(2)–1.480(2) Å) compared with those in non-lithiated sulfones (median: 1.437 Å; lower/upper quartile: 1.431/1.442 Å; *n* = 316 [11]). This can be discussed in terms of the electrostatic effect of the carbanion neighbored by the S atom [14] and the Li coordination to the O atoms.

Overall, the structures of lithiated sulfones presented in this work are a further confirmation that tetrahydrofuran adducts of functionalized organolithium compounds exhibit a much greater structural diversity than those with tmeda or other chelating coligands.

3. Experimental

3.1. General considerations

All reactions and manipulations were carried out under purified argon using standard Schlenk techniques except the manipulations of organotin and organosilicon compounds. *n*-Pentane, *n*-hexane and thf-*d*₈ were dried with

LiAlH₄ and thf was distilled from sodium benzophenone ketyl. NMR spectra were recorded on Varian Gemini 200, Gemini 2000, and Unity 500 spectrometers using the protio impurities and the ¹³C resonances of the deuterated solvents as references for ¹H and ¹³C NMR spectroscopy, respectively. δ(¹¹⁹Sn) is relative to external SnMe₄ in C₆D₆. The preparative centrifugal thin layer chromatography was made by using a Chromatotron (Harrison Research).

3.2. General procedure for metalation of RCH(R')SO₂Ph (R/R' = H/Me, Me/Et, H/CH₂Ph, Me/Ph) and subsequent reaction with Me₃SiCl/n-Bu₃SnCl

At -78 °C to a stirred solution of RCH(R')SO₂Ph (10.0 mmol) in thf (15 ml) a solution of *n*-BuLi in *n*-hexane (10.0 mmol, 1.5 M) was added dropwise. After stirring for 15 min at -78 °C the mixture was warmed to room temperature and stirred for 2 h. Me₃SiCl (10.0 mmol) or *n*-Bu₃SnCl (10.0 mmol) was added at -78 °C by a syringe, and the mixture was stirred for 18 h at room temperature. The reaction mixture was hydrolyzed with distilled water (20 ml) and extracted with ether (2 × 30 ml). The combined organic layers were dried with Na₂SO₄. After the solvents were removed in vacuo, the residue was purified as described below.

3.2.1. Me₃SiCH(Me)SO₂Ph (5)

Purification by preparative centrifugal thin layer chromatography using *n*-pentane/diethyl ether for elution. Yield: 2.30 g (95%). Anal. Calc. for C₁₁H₁₈SO₂Si (242.41): C, 54.50; H, 7.48; S, 13.23. Found: C, 55.08; H, 7.41; S, 13.10%. ¹H NMR (400 MHz, CDCl₃): δ 0.23 (s, 9H, Si(CH₃)₃), 1.09 (d, ³J_{H,H} = 7.47 Hz, 3H, CH₃), 2.60 (q, ³J_{H,H} = 7.26 Hz, 1H, CH), 7.44–7.47/7.78–7.80 (m/m, 4H, *o*-H/*m*-H, Ph), 7.48–7.52 (m, 1H, *p*-H, Ph). ¹³C NMR (100 MHz, CDCl₃): δ -1.5 (s, Si(CH₃)₃), 11.5 (s, CH₃), 50.5 (s, CH), 127.7/128.7 (s/s, *o*-C/*m*-C), 132.6 (s, *p*-C), 140.0 (s, *i*-C).

3.2.2. Me₃SiCMe(Et)SO₂Ph (6)

Purification by preparative centrifugal thin layer chromatography using *n*-pentane/diethyl ether for elution. Yield: 2.43 g (90%). Anal. Calc. for C₁₃H₂₂SO₂Si (270.46): C, 57.73; H, 8.20; S, 11.86. Found: C, 58.05; H, 8.20; S, 11.71%. ¹H NMR (400 MHz, CDCl₃): δ 0.26 (s, 9H, Si(CH₃)₃), 0.86 (t, ³J_{H,H} = 7.58 Hz, 3H, CH₂CH₃), 1.17 (s, 3H, CCH₃), 1.39/1.71 (m/m, J_{H,H} = 7.5 Hz/7.5 Hz, 1H/1H, CH₂CH₃), 7.43–7.48/7.73–7.76 (m/m, 4H, *o*-H/*m*-H, Ph), 7.51–7.56 (m, 1H, *p*-H, Ph). ¹³C NMR (100 MHz, CDCl₃): δ -0.5 (s, Si(CH₃)₃), 10.5 (s, CH₂CH₃), 18.5 (s, CCH₃), 27.9 (s, CH₂CH₃), 57.2 (s, Me₃SiC), 128.5/129.9 (s/s, *o*-C/*m*-C), 132.9 (s, *p*-C), 137.2 (s, *i*-C).

3.2.3. Me₃SiCH(CH₂Ph)SO₂Ph (7)

Purification by recrystallization from isopropanol. Yield: 2.90 g (91%). Anal. Calc. for C₁₇H₂₂SO₂Si (318.51): C, 64.11; H, 6.96; S, 10.07. Found: C, 64.43; H, 7.17; S, 10.52%. ¹H NMR (200 MHz, CDCl₃): δ 0.26 (s, 9H,

Si(CH₃)₃), 2.97–3.00 (m, 2H, CHCH₂), 3.08–3.14 (m, 1H, CHCH₂), 6.72–6.77/7.02–7.05/7.32–7.47/7.69–7.74 (m/m/m, 10H, *o*-H/*m*-H/*p*-H, Ph). ¹³C NMR (50 MHz, CDCl₃): δ -0.8 (s, Si(CH₃)₃), 32.3 (s, CHCH₂), 57.4 (s, CHCH₂), 126.3 (s, *p*-C Ph), 127.8/128.1/128.3/128.8 (s/s/s/s, *o*-C/*m*-C, Ph + SO₂Ph), 132.7 (s, *p*-C, SO₂Ph), 138.5/141.1 (s/s, *i*-C, Ph + SO₂Ph).

3.2.4. Me₃SiCMe(Ph)SO₂Ph (8)

Purification by recrystallization from diethyl ether. Yield: 2.90 g (91%). Anal. Calc. for C₁₇H₂₂SO₂Si (318.51): C, 64.11; H, 6.96; S, 10.07. Found: C, 63.96; H, 6.75; S, 10.36%. ¹H NMR (400 MHz, CDCl₃): δ 0.27 (s, 9H, Si(CH₃)₃), 1.61 (s, 3H, CCH₃), 7.20–7.26/7.38–7.45 (m/m, 10H, *o*-H/*m*-H/*p*-H, 2 × Ph). ¹³C NMR (100 MHz, CDCl₃): δ -0.8 (s, Si(CH₃)₃), 18.1 (s, CCH₃), 61.6 (s, SiCCH₃(Ph)), 127.2 (s, *p*-C, Ph), 127.8/127.9/128.3/129.2 (s/s/s/s, *o*-C/*m*-C, Ph + SO₂Ph), 132.6 (s, *p*-C, SO₂Ph), 136.1/136.9 (s/s, *i*-C, Ph + SO₂Ph).

3.2.5. *n*-Bu₃SnCH(Me)SO₂Ph (9)

Purification by preparative centrifugal thin layer chromatography using *n*-pentane/diethyl ether for elution. Yield: 3.90 g (85%). Anal. Calc. for C₂₀H₃₆SO₂Sn (459.27): C, 52.30; H, 7.90; S, 6.98. Found: C, 52.96; H, 7.84; S, 7.33%. ¹H NMR (400 MHz, CDCl₃): δ 0.90 (t, 9H, δ-CH₃, Bu), 1.14–1.19 (m, 6H, α-CH₂, Bu), 1.31–1.38 (m, 6H, γ-CH₂, Bu), 1.52–1.59 (m, 6H, β-CH₂, Bu), 1.25 (d, ³J_{H,H} = 7.26 Hz, 3H, Bu₃SnCH(CH₃)), 2.83 (q, ³J_{H,H} = 7.26 Hz, 1H, Bu₃SnCH(Me)), 7.46–7.56/7.80–7.82 (m/m, 5H, Ph). ¹³C NMR (100 MHz, CDCl₃): δ 13.7 (s, C4, Bu), 27.3 (s + d, ³J_{Sn,C} = 62.6 Hz, C3, Bu), 28.9 (s + d, ²J_{Sn,C} = 19.6 Hz, C2, Bu), 11.0 (s + d, ¹J_{Sn,C} = 329.2 Hz, C1, Bu), 12.9 (s, Bu₃SnCH(CH₃)), 48.0 (s + d, ¹J_{Sn,C} = 136.9 Hz, Bu₃SnCH(Me)), 127.7/128.7 (s/s, *o*-C/*m*-C), 132.3 (s, *p*-C), 139.9 (s, *i*-C). ¹¹⁹Sn NMR (186 MHz, CDCl₃): δ 5.6.

3.2.6. *n*-Bu₃SnCMe(Et)SO₂Ph (10)

Purification by preparative centrifugal thin layer chromatography using *n*-pentane/diethyl ether for elution. Yield: 3.40 g (70%). Anal. Calc. for C₂₂H₄₀SO₂Sn (487.33): C, 54.22; H, 8.27; S, 6.58. Found: C, 54.64; H, 8.38; S, 6.85%. ¹H NMR (500 MHz, CDCl₃): δ 0.89 (t, 9H, δ-CH₃, Bu), 1.11–1.21/1.24–1.42/1.49–1.62/1.82–2.00 (m/m/m/m, 26H, CH₂, Bu + Me + Et), 7.41–7.57/7.69–7.75 (m/m, 5H, Ph). ¹³C NMR (100 MHz, CDCl₃): δ 13.6 (s, C4, Bu), 27.4 (s + d, ³J_{Sn,C} = 67.0 Hz, C3, Bu), 28.9 (s + d, ²J_{Sn,C} = 18.4 Hz, C2, Bu), 12.1 (s + d, ¹J_{Sn,C} = 325.6 Hz, C1, Bu), 12.0 (s, CH₂CH₃), 19.4 (s, CCH₃), 28.7 (s, CH₂CH₃), 62.7 (s + d, ¹J_{Sn,C} = 178.7 Hz, Bu₃SnCMe(Et)), 128.3/129.5 (s/s, *o*-C/*m*-C), 132.4 (s, *p*-C), 136.1 (s, *i*-C). ¹¹⁹Sn NMR (186 MHz, CDCl₃): δ 12.1.

3.2.7. *n*-Bu₃SnCH(CH₂Ph)SO₂Ph (11)

Purification by preparative centrifugal thin layer chromatography using *n*-pentane/diethyl ether for elution.

Yield: 3.20 g (60%). Anal. Calc. for $C_{26}H_{40}SO_2Sn$ (535.37): C, 58.33; H, 7.53; S, 5.99. Found: C, 58.53; H, 7.45; S, 5.85%. 1H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, 9H, δ - CH_3 , Bu), 0.99–1.13 (m, 6H, α - CH_2 , Bu), 1.26–1.33 (m, 6H, γ - CH_2 , Bu), 1.41–1.54 (m, 6H, β - CH_2 , Bu), 2.98–3.06 (m, 2H, $CHCH_2$), 3.28–3.31 (m, 1H, $CHCH_2$), 6.85–6.87/7.05–7.12/7.38–7.41/7.45–7.48/7.76–7.78 (m/m/m/m/m, 10H, *o*-H/*m*-H/*p*-H, $2 \times Ph$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.6 (s, C4, Bu), 27.2 (s + d, $^3J_{Sn,C} = 66.7$ Hz, C3, Bu), 28.7 (s + d, $^2J_{Sn,C} = 19.3$ Hz, C2, Bu), 11.5 (s + d, $^1J_{Sn,C} = 336.9$ Hz, C1, Bu), 33.8 (s, $CHCH_2Ph$), 55.0 (s + d, $^1J_{Sn,C} = 128.4$ Hz, $Bu_3SnCH(CH_2Ph)$), 126.5 (s, *p*-C, Ph), 127.6/128.1/128.4/128.7 (s/s/s/s, *o*-C/*m*-C, Ph + SO_2Ph), 132.3 (s, *p*-C, SO_2Ph), 138.3/140.7 (s/s, *i*-C, Ph + SO_2Ph). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ 3.4.

3.3. Synthesis of $Li[CH(Me)SO_2Ph]$ (1),

$Li[CMe(Et)SO_2Ph]$ (2) and $Li[CH(CH_2Ph)SO_2Ph]$ (3)

At room temperature to a stirred solution of *n*-BuLi in *n*-hexane (10.0 mmol, 0.375 M) $RCH(R')SO_2Ph$ ($R/R' = H/Me$, Me/Et , H/CH_2Ph) (10.0 mmol) was added dropwise. Stirring the reaction mixture for 30 min resulted in precipitation of **1**, **2**, and **3**, respectively, as yellow powders, which were filtered off, washed with *n*-pentane (2×10 ml) and dried in vacuo. **Compound 1**: Yield: 1.76 g (100%). 1H NMR (200 MHz, *thf-d*₈): δ 1.39 (d, $^3J_{H,H} = 5.81$ Hz, 3H, CH_3), 1.70 (broad, 1H, CH), 7.19–7.29/7.71–7.74 (m, 5H, Ph). ^{13}C NMR (50 MHz, *thf-d*₈): δ 11.8 (s, CH_3), 39.2 (s, CH), 126.2/128.4 (s/s, *p*-C/*m*-C/*o*-C, Ph). **Compound 2**: Yield: 1.92 g (94%). 1H NMR (400 MHz, *thf-d*₈): δ 0.93 (t, $^3J_{H,H} = 7.24$ Hz, 3H, CH_2CH_3), 1.62 (broad, 3H, CH_3), 2.04 (broad, 2H, CH_2CH_3), 7.12 (broad, 1H, *p*-H, Ph), 7.23/7.62 (broad/broad, 4H, *o*-H/*m*-H, Ph). ^{13}C NMR (100 MHz, *thf-d*₈): δ 15.2/16.2 (s/s, $2 \times CH_3$), 26.7 (s, CH_2CH_3), 47.8 (s, $CMe(Et)$), 127.2 (s, *p*-C), 125.3/128.2 (s/s, *o*-C/*m*-C), 151.4 (s, *i*-C). **Compound 3**: Yield: 2.51 g (100%). 1H NMR (400 MHz, *thf-d*₈): δ 2.17 (broad, 1H, $CHCH_2$), 3.38 (broad, 2H, $CHCH_2$), 6.90–7.42/7.85–7.86 (m/m, 10H, Ph). ^{13}C NMR (100 MHz, *thf-d*₈): δ 33.9 (s, $CHCH_2$), 44.9 (s, $CHCH_2$), 125.0 (s, *p*-C, Ph), 125.8/128.1/128.9/129.0 (s/s/s/s, *o*-C/*m*-C/*p*-C, Ph + SO_2Ph), 147.4/154.1 (s/s, *i*-C, Ph + SO_2Ph).

3.4. Synthesis of $Li[CMe(Ph)SO_2Ph]$ (4)

At 0 °C to a stirred suspension of $PhCH(Me)SO_2Ph$ (10.0 mmol, 2.46 g) in toluene (40 ml) was added dropwise a solution of *n*-BuLi in *n*-hexane (10.0 mmol, 1.5 M). Stirring for 2 h at room temperature and addition of *n*-hexane (20 ml) resulted in precipitation of **4** as a yellow powder, which was filtered off, washed with *n*-pentane (2×10 ml) and dried in vacuo. Yield: 2.25 g (89%). 1H NMR (400 MHz, *thf-d*₈): δ 2.10 (s, 3H, $CCH_3(Ph)$), 6.32–6.36 (m, 1H, *p*-CH, Ph), 6.85–6.89/7.08–7.10/7.20–7.25/7.72–7.75 (m/m/m/m, 9H, Ph + SO_2Ph). ^{13}C NMR (100 MHz,

*thf-d*₈): δ 16.3 (s, $CCH_3(Ph)$), 57.6 (s, $CCH_3(Ph)$), 115.0 (s, *p*-C, Ph) 119.7 (s, *p*-C, SO_2Ph) 125.7/127.3/128.5/129.1 (s/s/s/s, *o*-C/*m*-C, Ph + SO_2Ph), 145.3 (s, *i*-C, Ph), 150.8 (s, *i*-C, SO_2Ph).

3.5. Synthesis of $n-Bu_3SnCMe(Ph)SO_2Ph$ (12)

At room temperature, to a stirred solution of **4** in toluene/*n*-hexane prepared as described above, $n-Bu_3SnCl$ (10.0 mmol) was added by a syringe. Then, the reaction mixture was stirred for 18 h at room temperature. Afterwards, water (20 ml) was added. The phases were separated and the aqueous phase was extracted with diethyl ether (2×30 ml). The combined organic phases were dried (Na_2SO_4) and after the removal of the solvents in vacuo volatile impurities were removed by heating the residue up to 200 °C at 0.01 Torr. Yield: 2.60 g (49%). Anal. Calc. for $C_{26}H_{40}SO_2Sn$ (535.37): C, 58.33; H, 7.53; S, 5.99. Found: C, 59.01; H, 7.80; S, 5.83%. 1H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, 9H, δ - CH_3 , Bu), 1.10–1.17 (m, 6H, α - CH_2 , Bu), 1.22–1.31 (m, 6H, γ - CH_2 , Bu), 1.40–1.49 (m, 6H, β - CH_2 , Bu), 1.68 (s + d, $^3J_{Sn,H} = 39.0$ Hz, 3H, CH_3), 7.11–7.26/7.28–7.30/7.34–7.40/7.49–7.52 (m/m/m/m, 10H, *o*-H/*m*-H/*p*-H, Ph + SO_2Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5 (s, C4, Bu), 27.2 (s + d, $^3J_{Sn,C} = 66.7$ Hz, C3, Bu), 28.7 (s + d, $^2J_{Sn,C} = 18.4$ Hz, C2, Bu), 12.8 (s + d, $^1J_{Sn,C} = 323.4$ Hz, C1, Bu), 18.9 (s, CH_3), 64.2 (s + d, $^1J_{Sn,C} = 154.5$ Hz, $Bu_3SnCCH_3(Ph)$), 126.6 (s, *p*-C, Ph), 127.8/127.9/128.1/128.9 (s/s/s/s, *o*-C/*m*-C, Ph + SO_2Ph), 132.2 (s, *p*-C, SO_2Ph), 136.1/137.6 (s/s, *i*-C, Ph + SO_2Ph). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ 29.2.

3.6. Growing of single-crystals of **1a**, **2a**, and **4a**

3.6.1. $[Li\{CH(Me)SO_2Ph\}(thf)_\infty]$ (1a)

At room temperature $Li[CH(Me)SO_2Ph]$ (**1**) (10.0 mmol, 1.76 g), prepared as described above, was dissolved in *thf* (10 ml). Heating for 5 min to 50 °C resulted in a clear orange solution. Cooling to room temperature and addition of *n*-hexane (5 ml) resulted in crystallization of $[Li\{CH(Me)SO_2Ph\}(thf)_\infty]$ (**1a**).

3.6.2. $[Li\{CH(CH_2Ph)SO_2Ph\}(thf)_\infty]$ (3a)

At room temperature $Li[CH(CH_2Ph)SO_2Ph]$ (**3**) (10.0 mmol, 2.52 g), prepared as described above, was dissolved in *thf* (20 ml). Addition of *n*-pentane (30 ml) resulted in crystallization of $[Li\{CH(CH_2Ph)SO_2Ph\}(thf)_\infty]$ (**3a**).

3.6.3. $[Li\{CMe(Ph)SO_2Ph\}(thf)_2]_2$ (4a)

At 0 °C to a stirred suspension $PhCH(Me)SO_2Ph$ (10.0 mmol, 2.46 g) in *thf* (40 ml) was added dropwise a solution of *n*-BuLi in *n*-hexane (10.0 mmol, 1.5 M). Stirring for 30 min at room temperature resulted in a clear brownish-orange solution. Addition of *n*-pentane (10 ml) and cooling to –45 °C resulted in crystallization of $[Li\{CMe(Ph)SO_2Ph\}(thf)_2]_2$ (**4a**) within some days.

Table 6
Crystallographic and data collection parameters for complexes **1a**, **3a**, and **4a**

Compound	1a	3a	4a
Empirical formula	C ₁₂ H ₁₇ LiO ₃ S	C ₁₈ H ₂₁ LiO ₃ S	C ₂₂ H ₂₉ LiO ₄ S
<i>M_r</i>	248.26	324.35	396.45
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	5.499(1)	13.775(5)	9.966(2)
<i>b</i> (Å)	20.358(4)	5.5726(8)	13.795(4)
<i>c</i> (Å)	12.392(5)	23.069(6)	17.121(5)
α (°)			93.48(3)
β (°)	95.16(4)	102.55(4)	103.14(3)
γ (°)			107.40(3)
<i>V</i> (Å ³)	1381.6(8)	1728.6(8)	2166(1)
<i>Z</i>	4	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.194	1.246	1.216
μ (Mo K α) (mm ⁻¹)	0.226	0.197	0.173
<i>F</i> (000)	528	688	848
θ Range (°)	2.59–25.00	2.60–26.08	2.12–25.00
Number of reflections collected	14 661	11 269	9420
Number of reflections observed [<i>I</i> > 2 σ (<i>I</i>)]	1562	2104	3292
Number of independent reflections (<i>R</i> _{int})	2444 (0.1184)	3249 (0.0632)	6507 (0.0656)
Data/restraints/parameters	2444/0/172	3249/0/208	6507/0/505
Goodness-of-fit on <i>F</i> ²	0.957	0.955	0.901
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0537, 0.1288	0.0484, 0.1172	0.0646, 0.1589
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0902, 0.1455	0.0790, 0.1290	0.1339, 0.2014
Largest difference in peak and hole (e Å ⁻³)	0.281 and -0.322	0.293 and -0.298	0.313 and -0.435

3.7. X-ray structure determinations

Crystals of **1a**, **3a**, and **4a** suitable for X-ray diffraction measurements were obtained as described above. Intensity data were collected on a STOE IPDS diffractometer at 220(2) K (**3a**, **4a**) and 268(2) K (**1a**), respectively, using graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 6. Absorption corrections were applied numerically (*T*_{min}/*T*_{max}: 0.90/1.00, **1a**; 0.96/0.98, **3a**; 0.92/0.98, **4a**). The structures were solved by direct methods with SHELXS-97 and refined using full-matrix least-squares routines against *F*² with SHELXL-97 [27]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined isotropically with fixed displacement parameters (riding model). In **1a** the C atoms of the thf molecule are disordered over two positions with occupancies of 71(1)% and 29(1)%; the C atoms of the minor occupied positions were isotropically refined.

3.8. Computational details

All DFT calculations were carried out by the GAUSSIAN-03 program package [28] using the hybrid functional B3LYP [29] and the basis 6-311+G(d,p) for all atoms. All systems have been fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations.

4. Supplementary material

CIF's have been deposited in the Cambridge Crystallographic Data Centre, with the numbers CCDC-296930 (**1a**), CCDC-296931 (**3a**), and CCDC-296932 (**4a**).

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank Merck (Darmstadt) for gifts of chemicals.

References

- [1] (a) G.L. Edwards, in: A.R. Katritzky, O. Meth-Cohn, C.W. Rees (Eds.), *Comprehensive Organic Functional Group Transformations*, vol. 1, Elsevier, Oxford, 1995, pp. 105–169; (b) N.W.A. Geraghty, in: A.R. Katritzky, O. Meth-Cohn, C.W. Rees (Eds.), *Comprehensive Organic Functional Groups Transformations*, vol. 4, Elsevier, Oxford, 1995, pp. 41–93.
- [2] P. Beak, D.B. Reitz, *Chem. Rev.* 78 (1978) 275–316.
- [3] X.-M. Zhang, F.G. Bordwell, M. van der Puy, H.E. Fried, *J. Org. Chem.* 58 (1993) 3060–3066.
- [4] G. Boche, *Angew. Chem.* 101 (1989) 286–306.
- [5] H.-J. Gais, G. Hellmann, H. Günther, F. Lopez, H.J. Lindner, S. Braun, *Angew. Chem.* 101 (1989) 1061–1063.
- [6] H.-J. Gais, G. Hellmann, H.J. Lindner, *Angew. Chem.* 102 (1990) 96–99.
- [7] R. Amstutz, T. Laube, W.B. Schweizer, D. Seebach, J.D. Dunitz, *Helv. Chim. Acta* 67 (1984) 224–236.
- [8] F. Becke, F.W. Heinemann, D. Steinborn, *Organometallics* 16 (1997) 2736–2739.
- [9] R. Bucourt, *Top. Stereochem.* 8 (1974) 159–224.
- [10] (a) A.E. Dorigo, Y. Li, K.N. Houk, *J. Am. Chem. Soc.* 111 (1989) 6942–6948;

- (b) A.R. Campanelli, A. Domenicano, F. Ramondo, *J. Phys. Chem. A* 107 (2003) 6429–6440.
- [11] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. II* (1987) S1–S19.
- [12] H.J. Gais, M. Van Gumpel, G. Raabe, J. Müller, S. Braun, H.J. Lindner, S. Rohs, J. Runsink, *Eur. J. Org. Chem.* (1999) 1627–1651.
- [13] H.-J. Gais, M. van Gumpel, M. Schleusner, G. Raabe, J. Runsink, C. Vermeeren, *Eur. J. Org. Chem.* (2001) 4275–4303.
- [14] G. Boche, J.C.W. Lohrenz, J. Ciolowski, W. Koch, in: S. Patai, Z. Rapoport (Eds.), *The Chemistry of Functional Groups, Supplement S, The Chemistry of Sulphur-Containing Functional Groups*, Wiley, Chichester, 1993, pp. 339–362.
- [15] V. Gutmann, G. Resch, W. Linert, *Coord. Chem. Rev.* 43 (1982) 133–164.
- [16] G. Raabe, H.-J. Gais, J. Fleischhauer, *J. Am. Chem. Soc.* 118 (1996) 4622–4630.
- [17] R. Koch, E. Anders, *J. Org. Chem.* 59 (1994) 4529–4534.
- [18] K.W. Henderson, A.R. Kennedy, D.J. MacDougall, D. Shanks, *Organometallics* 21 (2002) 606–616.
- [19] D.A. Bors, A. Streitwieser Jr., *J. Am. Chem. Soc.* 108 (1986) 1397–1404.
- [20] G. Boche, M. Marsch, K. Harms, G.M. Sheldrick, *Angew. Chem.* 97 (1985) 577–578.
- [21] J. Müller, M. Neuburger, M. Zehnder, *Helv. Chim. Acta* 78 (1995) 615–618.
- [22] H.-J. Gais, J. Vollhardt, G. Hellmann, H. Paulus, H.J. Lindner, *Tetrahedron Lett.* 29 (1988) 1259–1262.
- [23] W. Hollstein, K. Harms, M. Marsch, G. Boche, *Angew. Chem.* 100 (1988) 868–869.
- [24] H.-J. Gais, J. Vollhardt, H. Günther, D. Moskau, H.J. Lindner, S. Braun, *J. Am. Chem. Soc.* 110 (1988) 978–980.
- [25] W.N. Setzer, P. von Ragué Schleyer, *Adv. Organomet. Chem.* 24 (1985) 353–451.
- [26] T. Ruffer, C. Bruhn, A.H. Maulitz, D. Ströhl, D. Steinborn, *Organometallics* 19 (2000) 2829–2831.
- [27] G.M. Sheldrick, *SHELXS-97, SHELXL-97: Programs for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, 1990/1997.
- [28] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.R. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *GAUSSIAN-03, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.
- [29] (a) A.D. Becke, *Phys. Rev. A* 38 (1988) 3098–3100;
(b) A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648–5652;
(c) C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785–789;
(d) P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.* 98 (1994) 11623–11627.