Alkali metal derivatives of sulfinimidamides. Preparation and crystal structures

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Abstract

A series of compounds has been prepared in which the NH proton of the sulfiniminamines $Me_3SiN=S(R)-NHR'$ (R = Ph (mainly) or ^tBu, $R' = {}^tBu$ or $SiMe_3$) is replaced by Li, Na, K, Rb, or Cs. The compounds form a series of reagents of increasing reactivity which could be used, for example, to introduce chelating ligands into transition metal complexes. The structures of the compounds have been determined by X-ray diffraction. When there is a phenyl substituent on the sulfur atom, the metal derivatives are isomorphic dimers, involving three fused four-membered rings in a step-shaped structure. The higher the atomic number of the metal, the stronger is the η-coordination of the phenyl group to the metal. With a t-butyl group on the sulfur atom the structures of the lithium derivatives $[(Me_3SiN=S(^tBu)-NR')Li]_2$ are different for $R' = SiMe_3$ and ^tBu. For the former the step-shaped structure is still present, but the latter forms an eight-membered ring. Although these ^tBu derivatives are synthesized in diethyl ether, their lithium atoms are not coordinated by donor molecules, in contrast to those in the phenyl-substituted species.
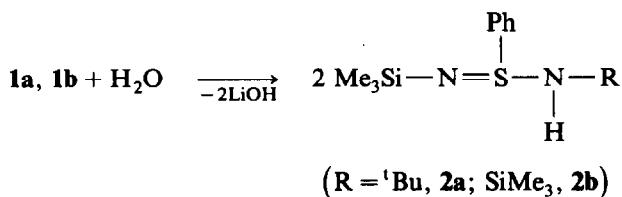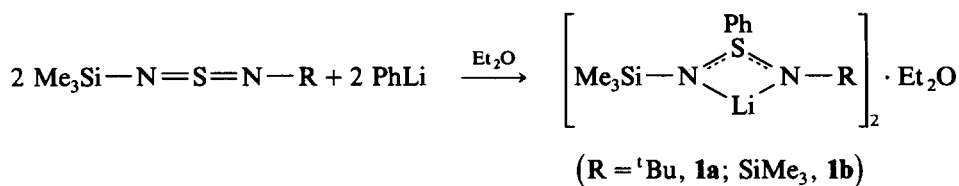
Introduction

The first sulphur diimide $S(NSiMe_3)_2$ was obtained by Wannagat und Kuchertz [1] in 1962, reacting a bis(trimethylsilyl)substituted alkali metal amide with SCl_2. Scherer and Schmitt described a synthesis of N,N,N'-tris(trimethylsilyl)(methyl) sulfiniminamine in 1969; they treated methyllithium with sulphurdiimide then added trimethylchlorosilane, to obtain $Me_3SiN=S(Me)N(SiMe_3)_2$ [2]. The reactivity and structure of lithiumorganylsulfinimidamides were first discussed in 1976 [3]. Lithium derivatives are accessible via metal exchange reactions, and sulfinimidamide anions are of interest as ligands in transition metal chemistry [4]. By variation of the substituents on nitrogen, anions of various bulks can be made [5].

Our aim is to prepare (and structurally characterize) "tailor-made" alkali metal organylsulfinimidamides in order to enable reaction with even less reactive transition metal halides.

Results and discussion

The sulphur diimides $Me_3SiN=S=NR$ react with phenyllithium in diethylether at $-60°C$. The products **1a** and **1b** are dimers, containing only one coordinated ether

$$2\ Me_3Si\!-\!N\!=\!S\!=\!N\!-\!R + 2\ PhLi \xrightarrow{Et_2O} \left[Me_3Si\!-\!N\underset{Li}{\overset{\overset{\displaystyle Ph}{\overset{|}{S}}}{<}}N\!-\!R \right]_2 \cdot Et_2O$$

$$\left(R = {}^tBu,\ \mathbf{1a};\ SiMe_3,\ \mathbf{1b} \right)$$

$$\mathbf{1a, 1b} + H_2O \xrightarrow[-2LiOH]{} 2\ Me_3Si\!-\!N\!=\!\underset{\underset{H}{|}}{\overset{\overset{Ph}{|}}{S}}\!-\!N\!-\!R$$

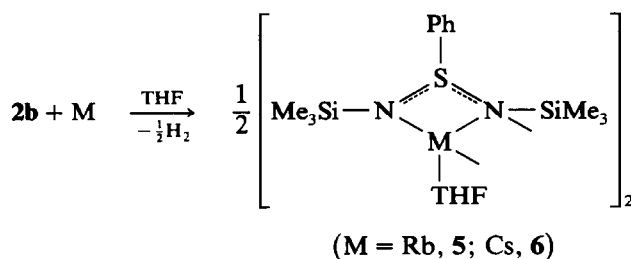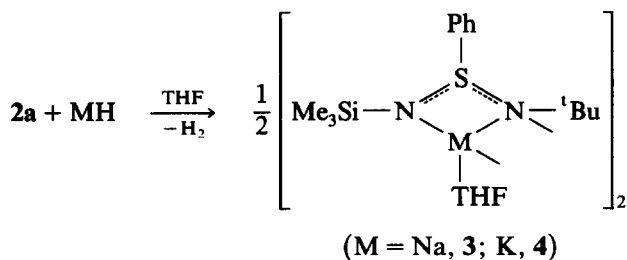$$\left(R = {}^tBu,\ \mathbf{2a};\ SiMe_3,\ \mathbf{2b} \right)$$

Scheme 1

molecule according to NMR-spectroscopic investigations. In addition, the lithium atoms appear to be in magnetically different environments [9].
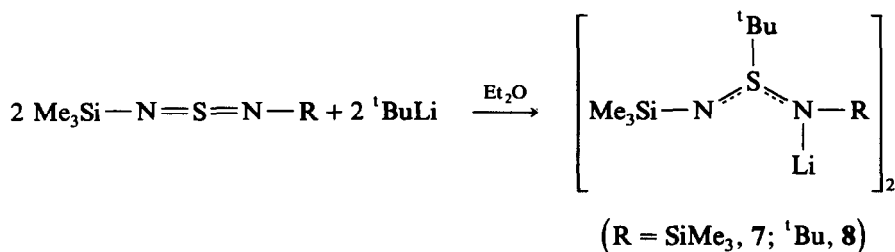
After hydrolysis [7] the phenylsulfiniminamines **2a** and **2b** can be obtained as white crystalline solids in moderate yields.

To make the sodium and potassium derivatives, the *N*-trimethylsilyl-*N'*-tert-butyl-*S*-phenylsulfiniminamine **2a** was treated with sodium or potassium hydride. The products **3** and **4** are dimers which are coordinated by one THF molecule per monomer. Treatment of the *N*,*N'*-bis(trimethylsilyl)-*S*-phenylsulfiniminamine (**2b**) with rubidium and caesium gives the corresponding alkali metal derivatives **5** and **6**.

The rubidium and caesium *N*,*N'*-bis(trimethylsilyl)-*S*-phenylsulfinimidamides **5** and **6** are also dimers with one THF molecule per monomer. A different structural type was obtained by the reaction of a sulphur diimide with tert-butyl lithium.

$$\mathbf{2a} + MH \xrightarrow[-H_2]{THF} \frac{1}{2}\left[Me_3Si\!-\!N\underset{\underset{THF}{\overset{|}{M}}}{\overset{\overset{\overset{Ph}{|}}{S}}{<}}N\!-\!{}^tBu \right]_2$$

$$(M = Na,\ \mathbf{3};\ K,\ \mathbf{4})$$

$$\mathbf{2b} + M \xrightarrow[-\frac{1}{2}H_2]{THF} \frac{1}{2}\left[Me_3Si\!-\!N\underset{\underset{THF}{\overset{|}{M}}}{\overset{\overset{\overset{Ph}{|}}{S}}{<}}N\!-\!SiMe_3 \right]_2$$

$$(M = Rb,\ \mathbf{5};\ Cs,\ \mathbf{6})$$

Scheme 2

$$2\ \mathrm{Me_3Si-N{=}S{=}N-R} + 2\ {}^{t}\mathrm{BuLi} \xrightarrow{\mathrm{Et_2O}}
\left[\mathrm{Me_3Si-N} \underset{\underset{\overset{|}{\mathrm{Li}}}{\diagdown}}{\overset{\overset{{}^{t}\mathrm{Bu}}{\overset{|}{\mathrm{S}}}}{\diagup}} \mathrm{N-R} \right]_2$$

$$\left(\mathrm{R = SiMe_3,\ 7;\ {}^{t}Bu,\ 8} \right)$$

Scheme 3

Although the reaction was carried out in diethyl ether, like the preparation of **1a** and **1b**, no coordinated ether was present in the product.

Crystal structure of 2a

The *N*-trimethylsilyl-*N'*-tert-butyl-*S*-phenylsulfiniminamine (**2a**) is a monomer in the solid state (Fig. 1). Table 1 presents the crystallographic data, Table 2 selected bond lengths and angles, and Table 3 the fractional coordinates.

The two sulphur–nitrogen bonds differ by 9.7 pm. The N2 nitrogen atom makes a single bond to the sulphur atom and is additionally bonded to a tert-butyl group and a hydrogen atom, the position of which was determined from a difference-Fourier-synthesis. The N2 atom clearly shows a pyramidal environment, and is 31.5 pm above the plane defined by the neighbouring atoms. The distance of 157.0(1) pm between S1 and N1 does not quite correspond to the length of a double bond.

The value of the torsion angle N1–S1–C1–C6 (31.5°) shows that the plane of the phenyl ring is almost perpendicular to the bisector of the plane defined by the sulphur and the nitrogen atoms. The angle N1–S1–C1 is 7.7° greater than the angle N2–S1–C1, i.e. the nitrogen atom with the shorter bond to the sulphur atom defines the greater N–S–C angle of the two.
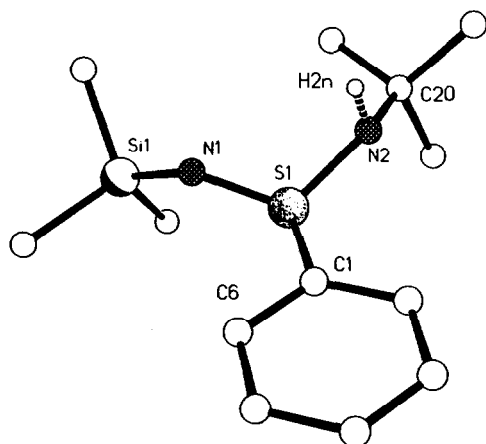

Fig. 1. Crystal structure of **2a**.

Table 1

Crystallographic data for **2a**, **3–8**

	2a	3	4	5	6	7	8
Empirical formula	$C_{13}H_{24}N_2SiS$	$C_{17}H_{31}N_2ONaSiS_2$	$[C_{17}H_{31}N_2OKSiS_2]$	$[C_{16}H_{31}N_2OSi_2SRb]_2$	$[C_{16}H_{31}N_2OSi_2SCs]_2$	$[C_{10}H_{27}LiN_2Si_2S]_2$	$[C_{11}H_{27}LiN_2SiS]_2$
Formula weight	268.5	362.6	378.7	441.1	488.6	270.5	254.4
Data collection at T (°C)	−120	−120	−120	−120	−60	−80	−120
Crystal dimensions (mm)	0.4×0.5×0.7	0.5×0.5×0.6	0.3×0.5×0.6	0.2×0.2×0.7	0.4×0.7×0.8	0.6×0.7×0.8	0.4×0.7×0.8
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (pm)	997.1(1)	962.8(3)	1044.5(1)	1012.7(2)	1012.7(2)	891.1(2)	864.7(4)
b (pm)	1104.1(2)	1048.6(2)	996.2(1)	1066.2(2)	1072.6(2)	1810.1(3)	1769.6(6)
c (pm)	1442.4(1)	2141.7(4)	2113.1(3)	1104.7(2)	2190.3(7)	1827.6(4)	1811.2(7)
α (°)	90	80.85(2)	90	102.70(1)	90	62.15(1)	118.47(2)
β (°)	94.63(1)	84.82(2)	102.63(1)	98.30(1)	92.28(2)	89.13(1)	90.25(3)
γ (°)	90	78.27(2)	90	95.54(1)	90	89.27(1)	90.01(3)
Cell volume (nm³)	1.583	2.086	2.146	1.141	2.377	2.606	2.436
Formula units per cell Z	4	2	2	1	2	3	3
Calculated density ρ_{calc} (Mg m⁻³)	1.127	1.154	1.172	1.284	1.365	1.034	1.041
Absorption coefficient μ (mm⁻¹)	0.25	0.23	0.40	2.31	1.73	0.30	0.24

F(000)	584	784	816	460	992	888	840
Measured 2θ-range (°)	8–55	8–45	8–50	8–50	8–60	8–45	8–45
Number of measured reflections	3105	5712	4326	4096	7921	7856	7605
Number of unique reflections	2689	5426	3761	3980	6908	6768	6320
Number of observed reflections	2366	4514	2955	3256	5063	5796	5207
$F > p\sigma(F)$; $p =$	3	3	3	3	3	3	3
R	0.0319	0.0425	0.0518	0.0422	0.0489	0.0412	0.0450
wR	0.0397	0.0491	0.0600	0.0443	0.0571	0.0495	0.0507
Goodness of fit	1.9318	1.4714	1.4400	1.7806	1.7481	1.8366	1.5796
Weighting factor g	0.00015	0.00050	0.00080	0.00020	0.00040	0.00030	0.00040
Refined parameters	154	426	208	235	208	435	439
Data-to-parameter ratio	15.4:1	10.6:1	14.2:1	13.9:1	24.3:1	13.3:1	11.9:1
Largest maximum (e^- nm^{-3} × 10^2)	2.4	3.6	4.6	6.0	8.3	3.2	3.6
Largest minimum (e^- nm^{-3} × 10^2)	2.0	3.7	3.4	5.2	5.5	2.4	2.6
Absorption correction	–	–	–	semi-empirical	semi-empirical	–	–

Table 2

Selected bond lengths (pm) and angles (°) for **2a, 3–6**

	2a	3 [a]	4	5	6
M1	–	Na	K	Rb	Cs
R	^{t}Bu	^{t}Bu	^{t}Bu	SiMe$_3$	SiMe$_3$
M1–N1	–	239.9(3)	275.2(3)	287.7(4)	304.5(3)
M1–N2	–	263.2(3)	288.0(2)	308.3(3)	325.0(3)
M1–N2a	–	240.9(3)	283.4(3)	292.2(2)	318.7(3)
M1–O1	–	235.0(2)	271.6(3)	291.6(3)	310.1(5)
S1–N1	157.0(1)	160.7(3)	160.1(3)	158.9(4)	158.7(3)
S1–N2	166.7(1)	162.3(3)	161.7(3)	161.5(3)	160.9(3)
S1–C1	179.9(2)	181.0(3)	180.5(3)	180.7(3)	180.9(4)
M1–cent.	–	386.3	369.8	369.9	355.1
N1–S1–N2	113.5(1)	110.7(1)	110.4(1)	110.4(2)	108.3(2)
N1–S1–C1	105.0(1)	103.1(1)	103.5(1)	102.7(2)	103.3(2)
N2–S1–C1	97.3(1)	98.5(1)	99.3(1)	99.4(1)	99.7(2)
C1–P$_{NSN}$ [b]	111.2	109.4	110.4	109.7	110.0
M–Ph–P$_{Ph}$ [c]	–	49.1	57.7	61.0	77.6
P$_{NSNM}$–P$_{NMNM}$ [d]	–	133.3	123.9	122.6	115.1
N1–S1–C1–C6	31.5	16.2	11.2	6.3	−8.6

[a] Average values of two independent molecules; esd's reflect the extreme values. [b] Angle of the S1–C1 vectors to the plane defined by N1–S1–N2. [c] Angle of the vectors M1–phenyl centre to the plane of the phenyl ring. [d] Angle between the four-membered ring units M1–N2–S1–N2 and M1–N2–M1a–N2a.

Crystal structures of the alkali metal derivatives 3 (Na), 4 (K), 5 (Rb), and 6 (Cs)

The structures are depicted in Figs. 2–5. Relevant crystallographic data are given in Table 1, selected bond lengths and angles in Table 2, and fractional coordinates in Tables 4–7.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (pm$^2 \times 10^{-1}$) for **2a**

	x	y	z	U_{eq} [a]
S(1)	5493(1)	3482(1)	6138(1)	24(1)
N(1)	6283(1)	4713(1)	6175(1)	26(1)
C(1)	6295(2)	2570(2)	5309(1)	23(1)
C(2)	7658(2)	2739(2)	5235(1)	29(1)
C(3)	8338(2)	1963(2)	4678(1)	36(1)
C(4)	7669(2)	1032(2)	4204(1)	36(1)
C(5)	6310(2)	870(2)	4281(1)	36(1)
C(6)	5617(2)	1632(2)	4836(1)	30(1)
Si(1)	6849(1)	5377(1)	7214(1)	28(1)
C(11)	6108(2)	6924(2)	7250(1)	45(1)
C(12)	8720(2)	5523(2)	7263(1)	39(1)
C(13)	6411(2)	4513(2)	8264(1)	42(1)
N(2)	3983(1)	3565(1)	5555(1)	26(1)
C(20)	2793(2)	3708(2)	6115(1)	31(1)
C(21)	2829(2)	4896(2)	6655(1)	37(1)
C(22)	1579(2)	3696(2)	5405(2)	50(1)
C(23)	2749(2)	2633(2)	6777(2)	49(1)

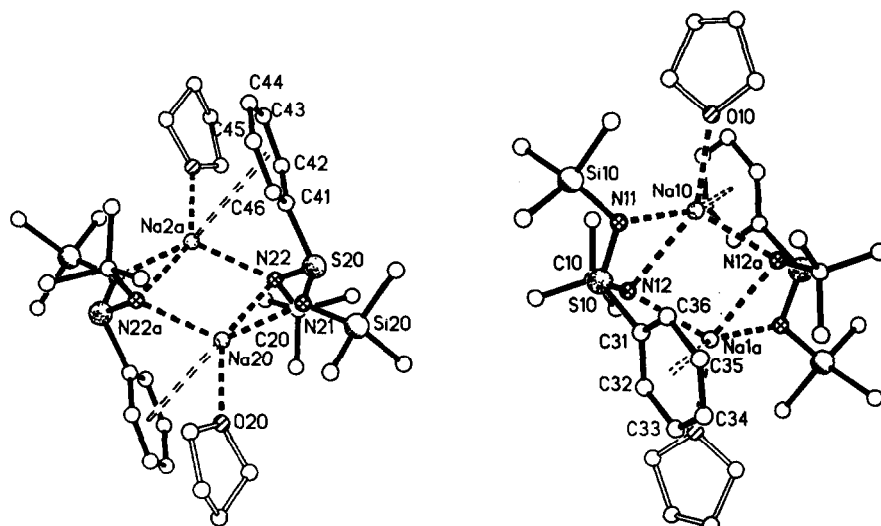[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fig. 2. Crystal structure of 3. In the Discussion the chemically-equivalent atoms S10 and S20 are referred to as S1, N11 and N21 as N1, etc.

Like the alkali metal derivatives investigated by Veith et al. [10,11] and sodium (ditert-butylfluorosilyl)tert-butylamide [12], the alkali metal sulfinimidamides described here have a step-shaped structure (Fig. 2). Unlike lithium(ditert-butylfluoro-
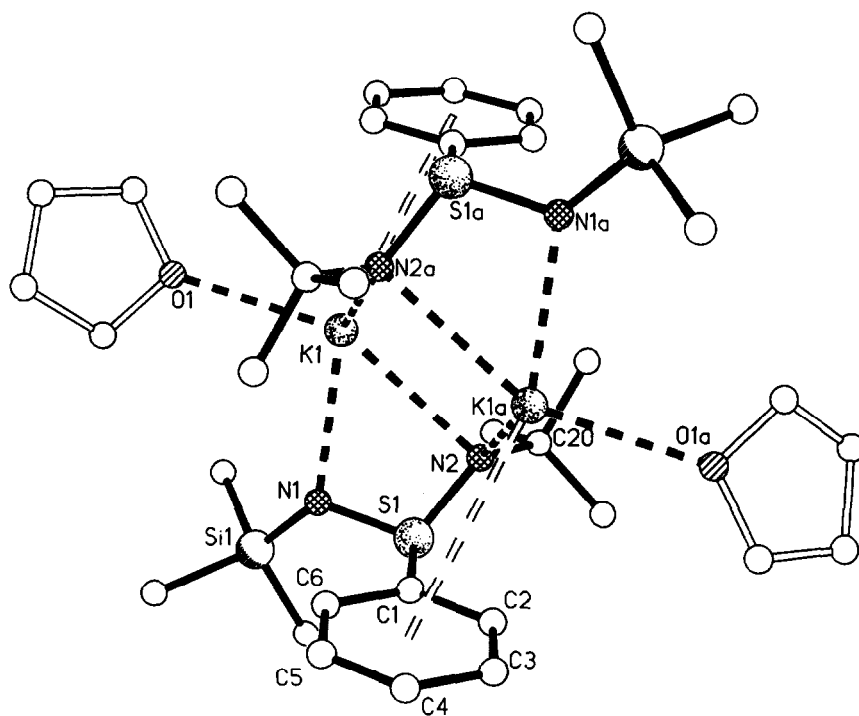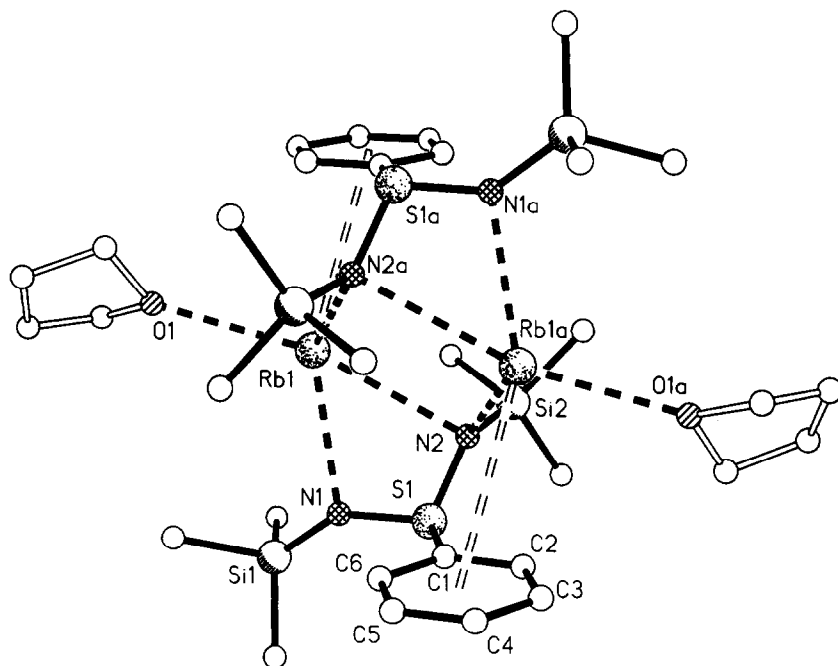

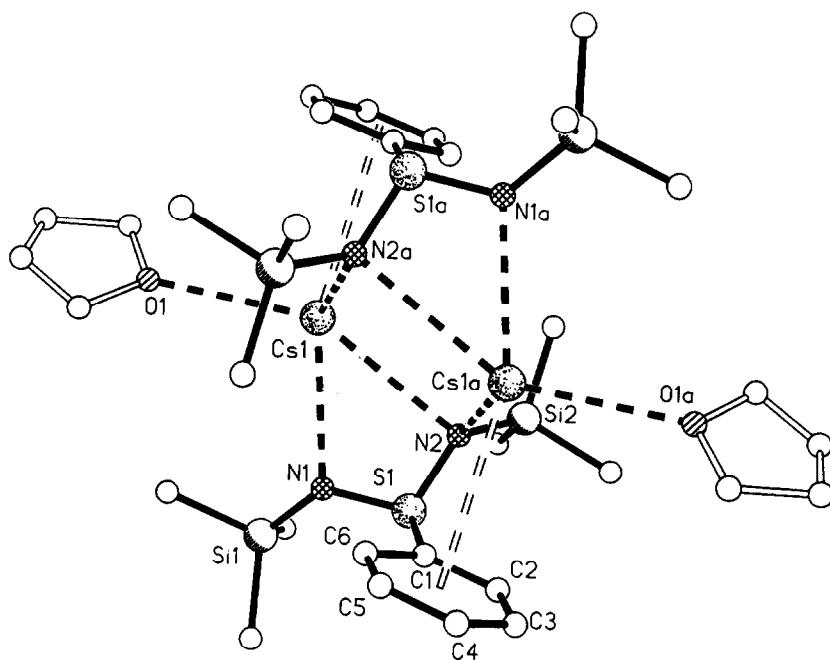Fig. 3. Crystal structure of 4.

Fig. 4. Crystal structure of **5**.

Fig. 5. Crystal structure of **6**.

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for **3**

	x	y	z	U_{eq} [a]
S(10)	4306(1)	3713(1)	9002(1)	26(1)
C(31)	3412(3)	2887(3)	9679(1)	27(1)
C(32)	4138(3)	1791(3)	10050(1)	33(1)
C(33)	3429(3)	1136(3)	10549(1)	39(1)
C(34)	1997(3)	1564(3)	10681(1)	42(1)
C(35)	1266(3)	2642(3)	10309(1)	39(1)
C(36)	1968(3)	3306(3)	9803(1)	33(1)
N(11)	3199(2)	5071(2)	8829(1)	29(1)
Si(10)	2444(1)	5403(1)	8114(1)	25(1)
C(11)	3685(3)	5855(3)	7436(1)	42(1)
C(12)	1750(3)	3987(3)	7909(2)	45(1)
C(13)	934(3)	6806(3)	8168(2)	41(1)
N(12)	5634(2)	3953(2)	9358(1)	26(1)
C(10)	6956(3)	4027(3)	8936(1)	38(1)
C(14)	8170(3)	3736(3)	9382(2)	44(1)
C(15)	6901(3)	5420(3)	8569(2)	51(1)
C(16)	7268(3)	3020(4)	8473(2)	53(1)
Na(10)	4097(1)	6275(1)	9521(1)	31(1)
O(10)	3049(2)	8439(2)	9084(2)	45(1)
C(51)	1943(4)	9411(3)	9311(2)	51(1)
C(52)	1632(4)	10500(4)	8765(2)	71(2)
C(53)	3068(6)	10398(5)	8380(3)	64(2)
C(53')	2360(22)	10023(15)	8209(7)	77(11)
C(54)	2384(4)	9944(3)	8458(2)	52(2)
S(20)	8976(1)	1614(1)	5975(1)	28(1)
C(41)	8132(3)	2719(3)	5320(1)	28(1)
C(42)	8836(3)	3653(3)	4973(1)	35(1)
C(43)	8148(4)	4559(3)	4501(2)	46(1)
C(44)	6774(4)	4534(3)	4376(2)	51(1)
C(45)	6082(3)	3609(3)	4724(2)	49(1)
C(46)	6749(3)	2704(3)	5199(1)	38(1)
N(21)	7964(2)	553(2)	6157(1)	32(1)
Si(20)	7007(1)	532(1)	6866(1)	31(1)
C(21)	5989(4)	-809(3)	6951(2)	55(1)
C(22)	8118(4)	212(4)	7555(2)	62(2)
C(23)	5743(4)	2097(3)	6934(2)	49(1)
N(22)	10426(2)	991(2)	5598(1)	28(1)
C(20)	11748(2)	578(2)	5992(1)	33(1)
C(24)	13026(3)	545(4)	5509(2)	59(1)
C(25)	11787(4)	-843(3)	6360(2)	58(1)
C(26)	11811(4)	1526(4)	6467(2)	59(1)
Na(20)	9264(1)	-1042(1)	5534(1)	31(1)
O(20)	8625(2)	-2943(2)	6106(1)	37(1)
C(61)	7454(3)	-3409(3)	5908(2)	41(1)
C(62)	7190(4)	-4545(3)	6397(2)	53(1)
C(63)	8597(4)	-5024(3)	6688(2)	57(1)
C(64)	9133(3)	-3756(3)	6675(2)	44(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

silyl)tert-butylamide [13,14], which has a butterfly-shaped structure, the four-membered MNSN rings fused to the central M_2N_2 four-membered ring are above and below the plane of the central ring unit. The only monomeric derivatives known to

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (pm$^2 \times 10^{-1}$) for **4**

	x	y	z	U_{eq} [a]
K(1)	3163(1)	5452(1)	4694(1)	36(1)
S(1)	4130(1)	4817(1)	6306(1)	30(1)
C(1)	5600(3)	5812(3)	6545(1)	29(1)
C(2)	6786(3)	5175(3)	6795(1)	36(1)
C(3)	7919(3)	5928(4)	7010(2)	42(1)
C(4)	7867(3)	7319(4)	6977(2)	44(1)
C(5)	6690(4)	7938(3)	6737(2)	47(1)
C(6)	5552(3)	7200(3)	6522(2)	40(1)
N(1)	3050(2)	5884(3)	5967(1)	35(1)
Si(1)	1822(1)	6361(1)	6330(1)	46(1)
C(11)	190(3)	6047(4)	5781(2)	54(1)
C(12)	1832(4)	5493(7)	7109(2)	98(2)
C(13)	1936(5)	8185(5)	6499(3)	108(3)
N(2)	4566(2)	3877(2)	5766(1)	30(1)
C(20)	4092(3)	2454(3)	5775(1)	30(1)
C(21)	4789(5)	1715(4)	6389(2)	75(2)
C(22)	2631(4)	2330(4)	5718(3)	75(2)
C(23)	4459(6)	1779(4)	5194(3)	87(2)
O(1)	1504(3)	7421(3)	4128(2)	78(1)
C(7)	1369(5)	8564(5)	4506(2)	80(2)
C(8)	1170(7)	9696(5)	4075(2)	108(3)
C(9)	639(7)	9119(5)	3418(2)	105(3)
C(10)	849(5)	7698(5)	3478(2)	80(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

data are those of rhodium and palladium [15]. The derivatives **3–6** described here are all isostructural. At the centre of the M_2N_2 four-membered ring in each structure there is a centre of inversion. All the metals are coordinated by three nitrogen atoms and one THF molecule.

The distance between N1 and the metal is the shortest of the three metal–nitrogen distances since N1 is coordinated to one metal atom only. The N2 nitrogen atom is coordinated to two metal atoms, which results in longer nitrogen–metal distances. The shorter N2–metal distance is that to the symmetry equivalent M1a atom, whereas the distance between M1 and N2 is the longest metal–nitrogen distance in the dimeric structure. The average metal–nitrogen distance is 248.0 pm in **3**, 282.2 pm in **4**, 296.1 pm in **5**, and 316.1 pm in **6**. The difference in the metal–nitrogen distances between **3** and **4** is 34.2 pm, between **4** and **5** 13.9 pm, and between **5** and **6** 20.0 pm. These differences correspond to the differences in the radii of the metals (Na/K: 40 pm; K/Rb: 15 pm; Rb/Cs: 20 pm) [16], and are also reflected in the metal–oxygen distances to the coordinated THF molecule. The nitrogen–sulphur distances in the anion are not as different as in structure **2a**. The same features as in structure **2a** are observed for the N–S–C angle, the shorter S–N bond being associated with the larger angle.

One important feature of these structures is that the metals are four-coordinate in all cases, with a gap in the coordination sphere of the metal filled by the π-electron system of the phenyl substituent. The distance between metal and centre of the phenyl ring decreases on going from the sodium derivative **3** (386.3 pm) to the

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (pm$^2 \times 10^{-1}$) for **5**

	x	y	z	U_{eq} [a]
Rb(1)	5522(1)	3430(1)	5826(1)	58(1)
S(1)	5377(1)	3123(1)	2511(1)	55(1)
C(1)	6332(3)	4582(3)	2352(3)	39(1)
C(2)	5708(4)	5342(3)	1637(3)	55(1)
C(3)	6413(4)	6449(4)	1481(4)	68(2)
C(4)	7742(4)	6788(3)	2022(4)	68(2)
C(5)	8375(3)	6034(4)	2725(4)	60(1)
C(6)	7663(3)	4911(3)	2879(3)	48(1)
N(1)	6408(3)	2605(3)	3452(4)	80(2)
Si(1)	7200(2)	1283(2)	3342(2)	39(1)
Si(1′)	6549(2)	945(2)	2596(2)	37(1)
C(11)	6055(5)	−101(4)	3490(5)	91(2)
C(12)	8091(5)	961(5)	2063(6)	130(3)
C(13)	8575(7)	1369(8)	4698(7)	69(3)
C(13′)	5575(11)	110(8)	1017(7)	81(4)
N(2)	4234(3)	3759(2)	3229(3)	48(1)
Si(2)	2632(1)	2965(1)	2911(1)	47(1)
C(21)	2090(4)	2037(4)	1240(4)	67(2)
C(22)	2390(4)	1802(3)	3930(4)	64(2)
C(23)	1478(3)	4199(3)	3297(4)	58(1)
O(1)	7228(3)	2937(3)	7987(3)	91(1)
C(7)	7516(9)	1662(8)	8203(10)	71(4)
C(7′)	7975(10)	1893(9)	7557(9)	70(4)
C(8)	8795(5)	1814(4)	8839(5)	78(2)
C(9)	8996(5)	3206(4)	9619(5)	85(2)
C(10)	7723(5)	3680(5)	9217(4)	84(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

caesium derivative **6** (355.1 pm) by 31.2 pm. This fall in the strength of the weak metal–ring interaction [16,17], is caused by three structural factors:

(a) Of the M–N distances the M1–N2a distance increases more than the average, which enables the metal to move from the *ipso*-carbon atom to the ring centre.

(b) The angle between the normals of the N_2M_2 and the MNSN planes narrows increasingly on going from **3** to **6**. This allows the phenyl ring in **6** to lie closer to the metal than in **3**, although the angle between the S1–C1 bond and the plane NSN defined by N1–S1–N2 remains constant.

(c) The torsion angle N1–S1–C1–C6 shows that the phenyl ring turns towards the metal. The vector between the ring centre and metal forms and angle of 49.1° to the phenyl ring plane in **3**, compared with 77.6° in **6**, i.e. shows that this vector moves towards perpendicularity.

In addition to these steric effects there is also a significant electronic effect. The interaction of alkali metal cations with π-electron systems increases with increasing atomic number [16,18*].

Replacement of the t-butyl substituent at the N2 nitrogen atom by a trimethyl-silyl groups has no significant influence on the structure, but replacement of the

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* Reference number with asterisk indicates a note in the list of references.

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for **6**

	x	y	z	U_{eq} [a]
Cs(1)	5505(1)	3293(1)	5540(1)	53(1)
S(1)	5091(1)	3137(1)	3809(1)	47(1)
C(1)	5826(4)	4496(4)	347092)	52(1)
C(2)	5127(6)	5133(5)	3014(2)	72(2)
C(3)	5657(8)	6230(6)	2778(3)	91(2)
C(4)	6851(9)	6672(6)	2990(3)	101(3)
C(5)	7534(7)	6025(6)	3444(3)	92(2)
C(6)	7045(5)	4929(5)	3680(2)	68(2)
N(1)	6245(3)	2612(3)	4248(2)	51(1)
Si(1)	7042(1)	1258(1)	4084(1)	59(1)
C(11)	7912(8)	1301(7)	3344(3)	114(3)
C(12)	5938(7)	−125(5)	4047(4)	115(3)
C(13)	8331(7)	1041(7)	4705(3)	100(3)
N(2)	4020(3)	3807(3)	4222(2)	46(1)
Si(2)	2409(1)	3379(1)	4139(1)	62(1)
C(21)	1556(8)	3979(17)	4755(6)	291(9)
C(22)	2139(10)	1723(7)	4020(10)	276(13)
C(23)	1601(9)	4106(16)	3459(6)	243(8)
O(1)	7690(5)	2039(6)	6361(3)	126(2)
C(7)	9081(8)	2099(13)	6331(4)	158(5)
C(8)	9608(8)	1752(9)	6883(4)	133(4)
C(9)	9657(8)	973(8)	7179(4)	112(3)
C(10)	7384(7)	1399(8)	6873(4)	108(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

phenyl group bonded to the sulphur atom by a t-butyl group has a marked structural effect.

Crystal structures of the lithium derivatives 7 and 8

The structures of **7** and **8** are shown in Figs. 6 and 7. Again crystallographic data are given in Table 1, and selected bond lengths and angles in Table 8. Tables 9 and 10 list the fractional coordinates.

Although the presence of one diethyl ether molecule is observed in the ^{1}H NMR spectra of **1a** and **1b**, solid lithium derivatives **7** and **8** contain no coordinated ether even though the syntheses were performed in this solvent (Figs. 6 and 7).

Compound **7**, with two trimethylsilyl groups bonded to the nitrogen atoms, still has the step-shaped structure of the other alkali metal derivatives **3–6** (Table 8), although the distance between Li1 and N2 is rather long compared to other lithium–nitrogen bond lengths.

The distance across the ring is 43 pm longer than the other two lithium–nitrogen distances. In **8** the corresponding distance is 89 pm longer (279.6 pm). For this reason we prefer to describe the structure of **8** as involving an eight-membered ring than being step-shaped. In this case the metal is clearly coordinated by only two nitrogen atoms. This difference must be ascribed to the difference in the electronic properties of the substituents at the nitrogen atom, since they have almost the same bulk.
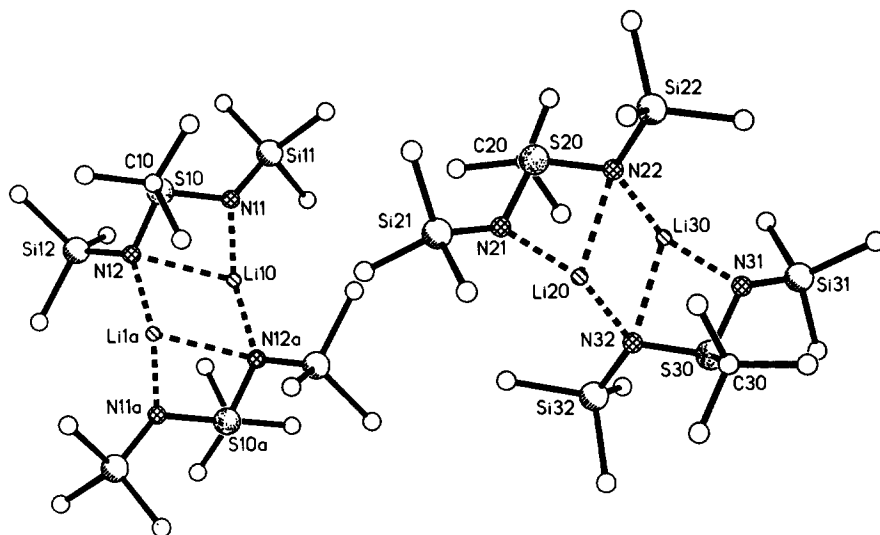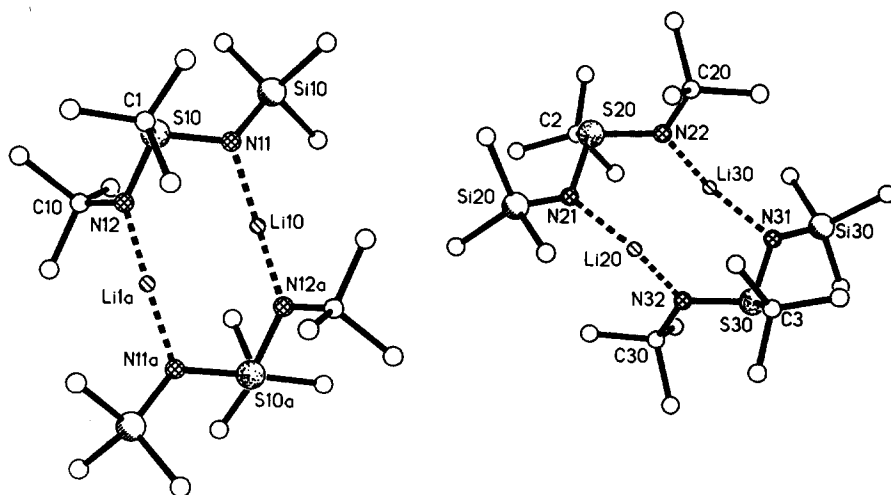
Fig. 6. Crystal structure of 7. In the Discussion the chemically-equivalent atoms S10 and S20 are referred to S1, N11 and N2, as N1, etc.

In the case of R = SiMe$_3$ (7), the Li1–N2a bond length is 196.5 pm, while in **8** (R = ^{t}Bu) it is only 191.2 pm. A trimethylsilyl group bonded to the nitrogen atom is less electron releasing than the tert-butyl group, and so the metal seeks to form an interaction with a third nitrogen atom across the eight-membered ring. This view is supported by the fact that there are two signals for the SiMe$_3$ groups in the ^{1}H and ^{13}C NMR spectra. One of them is ascribed to the quarternary nitrogen atom, the other to the trigonally-coordinated nitrogen atom. The S–N distances are not

Fig. 7. Crystal structure of **8**. In the Discussion the chemically-equivalent atoms S10 and S20 are referred to S1, N11 and N21 as N1, etc.

Table 8

Selected bond lengths (pm) and angles (°) for **7** and **8**

	7 [a]	**8** [a]
Li1–N1	191.6(7)	190.4(7)
Li1–N2a	196.5(6)	191.2(7)
Li1–N2	237.4(8)	(279.6) [b]
S1–N1	160.5(3)	160.3(3)
S1–N2	162.4(3)	162.5(3)
S1–C1	185.4(3)	186.5(3)
N1–Li1–N2a	140.6(4)	149.1(4)
N1–S1–N2	105.7(1)	107.1(1)
N1–S1–C1	104.1(1)	104.1(1)
N2–S1–C1	103.4(1)	102.0(2)
C1–P$_{NSN}$ [c]	113.5	112.4
P$_{NSNM}$–P$_{NMNM}$ [d]	137.5	

[a] Average values of three independent molecules; esd's reflect the extreme values. [b] Non-bonded distance. [c] Angle between the S1–C1 vector and the plane defined by N1–S1–N2. [d] Angle between the four-membered ring units M1–N1–S1–N2 and M1–N2–M1a–N2a.

significantly different, but for steric reasons the S–C bonds are 4pm longer than those in compounds **2a–6** (see Tables 2 and 8). For the same reason the angle between the S–C bond and the NSN plane is 3° larger than those in **2a–6**.

Because of the very bulky substituents, which surround the lithium atoms like a basket, there are short Li–H distances (240–270 pm). The lithium atoms are sterically so well protected that no ether molecule can coordinate to it.

Experimental section

All experiments were carried out under dry argon with strict exclusion of air and moisture. Mass spectra: Varian CH5-spectrometer. ^{1}H, ^{7}Li, ^{13}C, ^{133}Cs NMR: 10% solutions in C$_7$D$_8$ (**2a**, **2b**: CDCl$_3$; **7**: C$_6$D$_6$), ^{29}Si-NMR: 20% solutions in CDCl$_3$ (**7**: C$_6$D$_6$); TMS, LiCl, CsF external, Bruker AM 250 (^{1}H-NMR of **2a**: WP 80 SY).

2a, 2b: A solution of 0.1 mol of R–N=S=N–SiMe$_3$ (**2a**: R = ^{t}C$_4$H$_9$, **2b**: R = SiMe$_3$) in 50 ml of hexane is cooled to −60°C and 0.1 mol of C$_6$H$_5$Li (2 M solution in Et$_2$O/cyclohexane) is added. The mixture is refluxed for 2 h. The lithium derivate (**1a, 1b**) formed is hydrolysed with 0.1 mol of H$_2$O, LiOH is filtered off, the solvent evaporated off and the residue recrystallized from hexane.

3, 4: A solution of 0.01 mol of **2a** in 20 ml of hexane is added to a suspension of 0.011 mol NaH (**3**) or KH (**4**) in 0.04 mol of THF and 30 ml hexane. The mixture is refluxed for 5 h and the excess of hydride then removed by filtration. The product is isolated and then recrystallized from hexane.

5, 6: A solution of an equimolar amount of **2b** (0.012 mol for the preparation of **5**, 0.0075 mol for **6**) in 20 ml of hexane is added dropwise to a suspension of 1 g Rb (**5**) or Cs (**6**) in 30 ml of hexane/THF. The mixture is refluxed for 5 h then filtered through a glass frit. The product is isolated and then recrystallized from the reaction solution.

Table 9

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (pm$^2 \times 10^{-1}$) for **7**

	x	y	z	U_{eq} [a]
S(10)	4332(1)	6293(1)	−1517(1)	34(1)
C(10)	2290(3)	6366(2)	−1363(2)	52(1)
C(17)	1969(4)	7294(2)	−1657(2)	82(2)
C(18)	1864(3)	5838(2)	−456(2)	69(2)
C(19)	1520(3)	6076(2)	−1912(2)	86(2)
N(11)	5075(2)	6606(1)	−919(1)	38(1)
Si(11)	6228(1)	7459(1)	−1266(1)	46(1)
C(11)	7903(3)	7087(2)	−586(2)	72(2)
C(12)	6856(5)	7844(2)	−2358(2)	102(2)
C(13)	5338(4)	8321(2)	−1125(3)	93(2)
N(12)	4649(2)	5293(1)	−1092(1)	36(1)
Si(12)	5533(1)	4977(1)	−1752(1)	45(1)
C(14)	4603(4)	5379(2)	−2777(2)	82(2)
C(15)	7520(3)	5320(2)	−1949(2)	70(2)
C(16)	5457(4)	3812(2)	−1239(2)	67(2)
Li(10)	5772(7)	5567(3)	−49(4)	79(3)
S(20)	664(1)	8739(1)	1667(1)	32(1)
C(20)	2695(3)	8759(2)	1417(2)	42(1)
C(27)	3103(3)	9674(2)	910(2)	77(2)
C(28)	3618(3)	8345(2)	2196(2)	59(1)
C(29)	2867(4)	8288(2)	917(2)	74(2)
N(21)	258(2)	7761(1)	2131(1)	40(1)
Si(21)	−1142(1)	7323(1)	1831(1)	46(1)
C(21)	−371(5)	6508(2)	1585(3)	107(3)
C(22)	−2476(4)	6821(2)	2733(2)	90(2)
C(23)	−2229(3)	8092(2)	940(2)	50(1)
N(22)	617(2)	9039(1)	2376(1)	35(1)
Si(22)	−615(1)	9860(1)	2172(1)	40(1)
C(24)	−299(4)	10767(2)	1126(2)	67(2)
C(25)	−297(4)	10230(2)	2951(2)	72(2)
C(26)	−2601(3)	9535(2)	2223(2)	66(2)
Li(20)	125(6)	7602(3)	3243(3)	68(3)
S(30)	1338(1)	7433(1)	4963(1)	40(1)
C(30)	−681(3)	7396(2)	5238(2)	53(1)
C(38)	−1116(4)	6477(2)	5688(2)	83(2)
C(39)	−804(4)	7793(3)	5806(2)	88(2)
N(31)	1715(2)	8413(1)	4498(1)	43(1)
Si(31)	3050(1)	8879(1)	4809(1)	54(1)
C(31)	4189(4)	8135(2)	5693(2)	93(2)
C(32)	4348(4)	9441(2)	3906(2)	93(2)
C(33)	2200(5)	9675(3)	5056(3)	122(4)
N(32)	1359(2)	7145(1)	4243(1)	38(1)
Si(32)	2547(1)	6303(1)	4451(1)	48(1)
C(34)	2333(4)	5999(2)	3616(2)	74(2)
C(35)	4543(3)	6573(2)	4507(2)	74(2)
C(36)	2096(4)	5359(2)	5446(2)	75(2)
Li(30)	1816(6)	8562(3)	3388(3)	66(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 10

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for **8**

S(10)	10495(1)	6276(1)	6617(1)	34(1)
C(1)	12626(3)	6365(2)	6540(2)	43(1)
C(17)	12950(4)	7295(2)	6779(2)	63(2)
C(18)	13166(3)	5763(2)	5656(2)	64(2)
C(19)	13342(3)	6135(2)	7171(2)	60(2)
N(11)	9800(3)	6573(1)	5973(1)	41(1)
Si(10)	8644(1)	7437(1)	6291(1)	38(1)
C(11)	7052(4)	7085(2)	5545(2)	62(2)
C(12)	7866(5)	7843(2)	7349(2)	84(2)
C(13)	9631(4)	8317(2)	6219(3)	80(2)
N(12)	10241(3)	5240(1)	6195(1)	41(1)
C(10)	9257(2)	4978(1)	6702(1)	41(1)
C(14)	9952(4)	5277(2)	7636(2)	60(2)
C(15)	7541(4)	5315(2)	6823(2)	55(2)
C(16)	9239(4)	3961(2)	6254(2)	62(2)
Li(10)	9238(7)	5634(4)	4910(4)	72(3)
S(20)	4577(1)	8761(1)	3334(1)	34(1)
C(2)	2488(3)	8771(2)	4597(2)	40(1)
C(27)	2123(4)	9693(2)	4234(2)	57(2)
C(28)	1473(3)	8472(2)	2817(2)	61(2)
C(29)	2328(4)	8181(2)	3981(2)	62(2)
N(21)	4989(3)	7760(1)	2794(1)	40(1)
Si(20)	6384(1)	7301(1)	3101(1)	35(1)
C(21)	5537(4)	6432(2)	3233(3)	69(2)
C(22)	7767(5)	6825(2)	2254(2)	72(2)
C(23)	7388(4)	8034(2)	4052(2)	57(2)
N(22)	4523(3)	9155(2)	2686(1)	42(1)
C(20)	5737(2)	9842(1)	2856(1)	44(1)
C(24)	5445(4)	10685(2)	3777(2)	60(2)
C(25)	5515(5)	10166(2)	2198(2)	71(2)
C(26)	7445(4)	9545(2)	2864(2)	59(2)
Li(20)	4821(7)	7404(5)	1630(4)	75(3)
S(30)	3553(1)	7370(1)	−16(1)	39(1)
C(3)	5651(3)	7337(2)	−268(2)	46(1)
C(37)	6631(3)	7707(2)	528(2)	59(2)
C(38)	6044(4)	6401(2)	−830(2)	66(2)
C(39)	5830(4)	7849(2)	−729(2)	67(2)
N(31)	3180(3)	8375(2)	514(1)	43(1)
Si(30)	1875(1)	8882(1)	213(1)	42(1)
C(31)	659(4)	8173(2)	−679(2)	76(2)
C(32)	627(5)	9497(3)	1121(3)	92(2)
C(33)	2814(5)	9665(3)	−14(4)	116(4)
N(32)	3553(3)	6989(2)	639(1)	45(1)
C(30)	2375(2)	6296(1)	449(1)	47(1)
C(34)	2509(5)	5998(2)	1136(2)	71(2)
C(35)	641(4)	6602(2)	439(2)	61(2)
C(36)	2640(5)	5453(2)	−444(2)	71(2)
Li(30)	3266(7)	8732(5)	1685(3)	76(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

7, 8: A solution of 0.01 mol of $^tC_4H_9Li$ (1.5 M solution in pentane) in 0.04 mol Et_2O is added at $-60\,^\circ C$ to a solution of 0.01 mol of $R-N=S=N-SiMe_3$ (**7**: $R = SiMe_3$, **8**: $R = {}^tC_4H_9$) in 50 ml of pentane. The mixture is refluxed for 1 h. The mixture is set aside for 4 days during which crystals of **7** or **8** separate.

N-*Trimethylsilyl*-N′-*tert-butyl-S-phenyl-sulfiniminamine (2a)*

M.p. 84–86 °C. Yield 14.77 g (55.1%). MS: m/z (%) = 268(18) $[M]^+$, FI-method: m/z (%) = 268(100) $[M]^+$. ^{1}H NMR: $\delta = 0.19$ (s, SiMe$_3$); 1.36 (s, $^tC_4H_9$); 7.35–7.80 (m, C_5H_5). ^{13}C NMR: $\delta = 1.90$ (Si(CH$_3$)$_3$); 30.86, (C(CH$_3$)$_3$); 53.76 (C(CH$_3$)$_3$); 126.06, 128.26, 129.59, 148.03 (C_6H_5). ^{29}Si NMR: $\delta = 0.56$ (SiMe$_3$).

N,N′-*Bis-trimethylsilyl-S-phenyl-sulfiniminamine (2b)*

M.p. 92–94 °C. Yield 12.95 g (45.6%). MS: m/z (%) = 284(24) $[M]^+$, FI-method: m/z (%) = 284(100) $[M]^+$. ^{1}H NMR: $\delta = 0.23$ (s, SiMe$_3$); 7.35–7.71 (m, C_6H_5). ^{13}C NMR: $\delta = 1.63$ (Si(CH$_3$)$_3$); 125.71, 128.67, 129.83, 150.68 (C_6H_5). ^{29}Si NMR: $\delta = 5.01$ (SiMe$_3$).

Bis(sodium-N-*trimethylsilyl*-N′-*tert-butyl-S-phenylsulfinimidamide-tetrahydrofuran) (3)*

Yield 3.26 g (90%). ^{1}H NMR: $\delta = 0.24$ (s, SiMe$_3$); 1.22 (s, $^tC_4H_9$); 1.27 (t, O(CH$_2$)$_2$(CH_2)$_2$); 3.55 (t, O(CH_2)$_2$(CH$_2$)$_2$); 7.16–7.84 (m, C_6H_5); ^{13}C NMR: $\delta = 1.35$, 2.69 (Si(CH$_3$)$_3$); 29.00 (O(CH$_2$)$_2$(CH_2)$_2$); 30.80 (C(CH$_3$)$_3$); 53.64 (C(CH$_3$)$_3$); 67.50 (O(CH_2)$_2$(CH$_2$)$_2$); 126.53, 128.32, 137.45, 149.53 (C_6H_5).

Bis(potassium-N-*trimethylsilyl*-N′-*tert-butyl-S-phenylsulfinimidamide-tetrahydrofuran) (4)*

Yield 3.40 g (90%). ^{1}H NMR: $\delta = 0.29$ (s, SiMe$_3$); 1.22 (s, $^tC_4H_9$); 1.43 (t, O(CH$_2$)$_2$(CH_2)$_2$); 3.54 (t, O(CH_2)$_2$(CH$_2$)$_2$); 6.97–7.75 (m, C_6H_5). ^{13}C NMR: $\delta = 2.92$ (Si(CH$_3$)$_3$); 25.80 (O(CH$_2$)$_2$(CH_2)$_2$); 32.03 (C(CH$_3$)$_3$); 53.59 (C(CH$_3$)$_3$); 67.73 (O(CH_2)$_2$(CH$_2$)$_2$); 126.22, 137.47 (C_6H_5).

Bis(rubidium-N,N′-*bis(trimethylsilyl)-S-phenyl-sulfinimidamidetetrahydrofuran) (5)*

Yield 3.22 g (61%). ^{1}H NMR: $\delta = 0.16$ (s, SiMe$_3$); 1.44 (t, (O(CH$_2$)$_2$(CH_2)$_2$); 3.51 (t, O(CH_2)$_2$(CH$_2$)$_2$); 7.19–7.76 (m, C_6H_5). ^{13}C NMR: $\delta = 3.38$ (Si(CH$_3$)$_3$); 25.78 (O(CH$_2$)$_2$(CH_2)$_2$); 67.72 (O(CH_2)$_2$(CH$_2$)$_2$); 127.82, 129.23, 137.47, 159.33 (C_6H_5).

Bis(caesium-N,N′-*bis(trimethylsilyl)-S-phenyl-sulfinimidamidetetrahydrofuran) (6)*

Yield 2.34 g (64%) ^{1}H NMR: $\delta = 0.21$ (s, SiMe$_3$); 1.46 (t, O(CH$_2$)$_2$(CH_2)$_2$); 3.51 (t, O(CH_2)$_2$(CH$_2$)$_2$); 7.19–7.80 (m, C_6H_5). ^{13}C NMR: $\delta = 3.43$ (Si(CH$_3$)$_3$); 25.93, (O(CH$_2$)$_2$(CH_2)$_2$); 67.89 (O(CH_2)$_2$(CH$_2$)$_2$); 125.67, 127.84, 137.72, 158.90 (C_6H_5). ^{133}Cs-NMR: $\delta = 156.12$.

Bis(lithium-N,N′-*bis(trimethylsilyl)-S-tert-butylsulfinimidamide) (7)*

Yield 2.30 g (85%). ^{1}H NMR: δ NMR: $\delta = 0.26$ (s), 0.27 (s) (SiMe$_3$); 1.01 (s, S$^tC_4H_9$). ^{7}Li NMR: $\delta = 1.59$. ^{13}C NMR: $\delta = 2.60$, 2.97 (Si(CH$_3$)$_3$); 22.78, 23.25 (S–C(CH$_3$)$_3$); ca. 36 (m, S–C(CH$_3$)$_3$.

*Bis(lithium-*N*-trimethylsilyl-*N*′-tert-butyl-*S*-tert-butylsulfinimidamide) (8)*

Yield 2.26 g (89%). ^{1}H NMR: $\delta = 0.23$ (s, SiMe$_3$); 1.06 (s), 1.07 (s) (S^{t}C$_4$H$_9$); 1.24 (s), 1.25 (s) (N^{t}C$_4$H$_9$). ^{7}Li NMR: $\delta = 1.87$. ^{13}C NMR: $\delta = 3.29$ (Si(CH$_3$)$_3$); 24.48, 24.56 (S–C(CH$_3$)$_3$); 33.50, 33.81 (N–C(CH$_3$)$_3$); 34.98 (S–C(CH$_3$)$_3$); 54.14 N–C(CH$_3$)$_3$). The appearance of two signals for the tert-butyl groups reflect the disorder found in the crystal structure.

*X-Ray crystal structure determinations of **2a**, **3–8***

The structures of **2a**, **3–8** were measured on a Stoe-Siemens-AED four-circle diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 71.069$ pm) at $-120\,^\circ$C for **2a**, **3–5**, and **8**; for **6** ($-60\,^\circ$C) and **7** ($-80\,^\circ$C) data had to be collected at higher temperatures because of phase transitions at lower temperatures. The structures of **2a**, **3**, **4**, **7** and **8** were solved by direct methods [19] and those of **5** and **6** by Patterson methods. All structures were refined by full-matrix least-squares, with all non-hydrogen atoms anisotropic. The hydrogen atoms were found by difference Fourier synthesis and refined with a riding model. Chemically equivalent hydrogen atoms were refined with the same isotropic displacement parameters. For **5** and **6**, a semi-empirical absorption correction was applied. Disorder involving tert-butyl and trimethylsilyl groups in **3** and **8** was treated with a refinement of the site occupation factors of the silicon and carbon atoms at the relevant positions. In **5** a trimethylsilyl group, and in **3** and **5** a THF-molecule, were disordered. In both cases, the site occupation of the disordered atoms was refined. In all cases a weighting scheme with $w^{-1} = \sigma^2(F) + gF^2$ was used. The factor g for each structure can be found in Table 1. Crystallographic data are found in Table 1, and fractional coordinates and equivalent isotropic displacement parameters in Tables 3–7, 9 and 10.

Acknowledgements

References and notes

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18 In contrast to the $[Ph_3C]^- Li^+$- and $[Ph_3C]^- Na^+$-derivatives, the alkali metal in the structure of $[Ph_3C]^- K^+$ determined by us, in collaboration with D. Hoffmann and P.v.R. Schleyer, is situated almost exactly above the centre of a phenyl ring.

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20 Further details of the crystal structure analyses can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany by quoting the deposit number CSD-55091, the authors, and the publication.