Tetrakis(sulfurdiimido)silane, -germane and -stannane

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Two tetrakis(sulfurdiimido)silanes [$Si(NSNR)_4$ (R = ^{t}Bu **1a**, $SiMe_3$ **1b**)], two germanes [$Ge(NSNR)_4$ (R = ^{t}Bu **2a**, $SiMe_3$ **2b**)] and one stannane [$Sn(NSN^tBu)_4Sn$ **3a**] were prepared and characterised by ^1H, ^{13}C, ^{15}N, ^{29}Si and ^{119}Sn NMR spectroscopy in solution, and **3a** was also studied in the solid state by ^{119}Sn CP/MAS NMR. Whereas **1a**,**b** and **2a**,**b** are monomeric in solution, the ^{119}Sn NMR data suggest that **3a** is associated both in solution and in the solid state, and that the tin atoms are hexa-coordinated. The attempted stepwise synthesis of **1a** by using one, two, three or four equivalents of $K[(NSN)^tBu]$ led to mixtures of **1a** with $Cl_3Si(NSN^tBu)$ **4a**, $Cl_2Si(NSN^tBu)_2$ **5a**, and $ClSi(NSN^tBu)_3$ **6a**. Only one sulfurdiimido ligand of the silane **1a** reacted with hexachlorodisilane by oxidative addition and cleavage of the Si-Si bond to give the new heterobicyclic derivative **7a** which is held together by two different coordinative N-Si bonds.

Introduction

The chemistry of MX_4 compounds (M = Si, Ge, Sn) is well developed for various substitutents X such as halides, pseudohalides, chalcogenides, amides, or organyl groups [1, 2]. However, analogous derivatives of the type $M(NSNR)_4$ have not been reported as yet. Such compounds should be of interest with respect to their structural flexibility and their reactivity, since the M-N bonds [3] and the NSN cumulene systems [4] invite to carry out further transformations. Derivatives with two or three sulfurdiimido ligands linked to organosilicon, -germanium and -tin fragments have already been described [5, 6]. In the present paper, we report on the synthesis of tetrakis(sulfurdiimido)silicon (**1**), -germanium (**2**) and -tin (**3**) compounds and on their NMR spectroscopic characterisation.

Results and Discussion

Synthesis of the $M(NSNR)_4$ compounds

The reaction of four equivalents of the potassium salt $K[(NSN)R]$ (R = ^{t}Bu, $SiMe_3$) with the respective element tetrachloride leads directly to the corresponding tetrakis(sulfurdiimido) compound [eq. (1)]. Addition of 1,2-dimethoxyethane (DME) helps to improve the solubility of the potassium salts, $K[(NSN)R]$ (R = ^{t}Bu, $SiMe_3$), and thus accelerates the reaction. The products **1** - **3** are isolated as yellow to orange oils (**1b, 2a,b**) or orange solids (**1a**, m.p. 112°C; **3a**, m.p. 253°C). They are sensitive to moisture and readily soluble in toluene or chlorinated solvents.

$$4\ K[(NSN)R] + MCl_4 \xrightarrow[-78°C]{hexane/DME} M(NSNR)_4 + 4\ KCl \qquad (1)$$

M	Si	Ge	Sn
R = tBu	**1a**	**2a**	**3a**
R = $SiMe_3$	**1b**	**2b**	

$$x\ K[(NSN)tBu] + SiCl_4 \xrightarrow{hexane} \underset{\mathbf{4a}}{Cl_3Si(NSN^tBu)} + \underset{\mathbf{5a}}{Cl_2Si(NSNtBu)_2} + \underset{\mathbf{1a}}{Si(NSNtBu)_4} + \underset{\mathbf{6a}}{ClSi(NSNtBu)_3} \qquad (2)$$

	product distribution in (%)			
	4a	**5a**	**6a**	**1a**
x = 1	45.2	36.3	15.0	3.5
x = 2	33.3	42.0	19.4	5.3
x = 3		28.0	46.6	25.4
x = 4				100.0

Reactions of one, two or three equivalents of $K[(NSN)^tBu]$ with $SiCl_4$ lead to mixtures containing $Cl_3Si(NSN^tBu)$ (**4a**), $Cl_2Si(NSN^tBu)_2$ (**5a**), $ClSi(NSN^tBu)_3$ (**6a**) and $Si(NSN^tBu)_4$ (**1a**) [Eq. (2)]. This indicates that the reactivities of $SiCl_4$ and of substituted silanes such as $Cl_3Si(NSN^tBu)$ or $Cl_2Si(NSN^tBu)_2$ are comparable (equation (2)).

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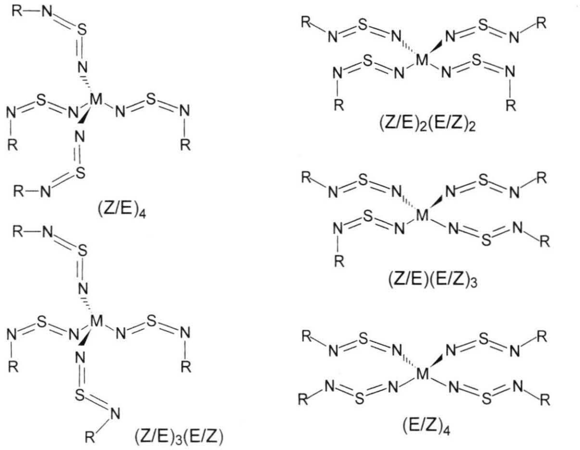
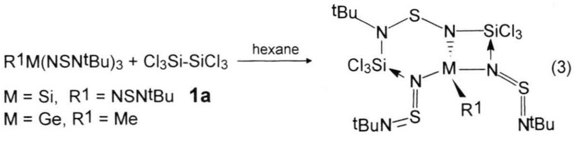
A prominent feature of many sulfur diimides is their fluxionality with respect to E/Z isomerisation. This is evident for alkyl groups as substituents [7-9] and also for numerous sulfur diimides bearing organometallic substituents [10-13]. For steric reasons, isomers with Z/Z configuration are unfavourable, in particular if a ^{t}Bu or a Me_3Si group is linked to one of the nitrogen atoms. This would leave fifteen configurational isomers for $M(NSNR)_4$ compounds, assuming rigid structures. If the E/E configuration is also excluded as unfavourable because of electron pair repulsion, five principal isomers remain, either with four times Z/E, four times E/Z, or Z/E and E/Z configurations as shown in Scheme 1. This situation corresponds closely to the findings for bis- and tris(sulfurdiimido) compounds [6].



Scheme 1. The five most likely configurations of tetrakis(sulfurdiimido)element compounds $M(NSNR)_4$ ($R = {}^tBu, SiMe_3$; M = Si, Ge, Sn); the first letter (E or Z) refers to the position of the substituent R.

Reaction of tetrakis(N-tert-butylsulfurdiimido)-silane with hexachlorodisilane

Treatment of tetrakis(N-*tert*-butylsulfurdiimido)silane **1a** with hexachlorodisilane [eq. (3)], either in an equimolar ratio or in excess, gave an orange oil which was characterised by ^{1}H, ^{13}C, ^{14}N, ^{15}N and ^{29}Si NMR in solution. For comparison, the analogous reaction was carried out with methyl-tris(N-*tert*-butylsulfurdiimido)germane. Apparently, only one of the sulfurdiimido groups reacts with Si_2Cl_6. The reaction proceeds by oxidative cleavage of the Si-Si bond, accompanied by reduction of sulfur (IV) to sulfur (II); this step of the reaction corresponds to previous findings for various sulfur diimides [6a, 14]. However, intramolecular coordination of nitrogen atoms of two different sulfurdiimido ligands to the $NSiCl_3$ groups prevents further reaction with Si_2Cl_6. The products are stable at room temperature for several days and can be stored at -20°C for longer periods without decomposition.



M = Si, R1 = NSNtBu **1a**
M = Ge, R1 = Me

M = Si, R1 = NSNtBu **7a**
M = Ge, R1 = Me **8a**

Reaction of tetrakis(N-tert-butylsulfurdiimido)-stannane with triethylborane

We have investigated the reactivity of tetrakis(N-*tert* -butylsulfurdiimido)-stannane **3a** towards triethylborane in order to compare with the analogous reactions of trimethyltin-substituted sulfur diimides $R'(NSN)SnMe_3$ ($R' = SnMe_3, {}^tBu, SiMe_3$). The latter have been transformed quantitatively into trimethylstannyl-amino(diethylborylamino)-sulfanes [15]. Although it cannot be excluded that the initial steps of the reaction of **3a** with Et_3B (1:4 or 1:8) are similar to that of $R'(NSN)SnMe_3$, decomposition becomes dominant in the case of **3a**. The identified decomposition products [eq. (4)] suggest that S-alkylation, followed by elimination of ethene, is favoured over rearrangement (migration of the stannyl fragment) and N-alkylation [15].

$$\underset{\mathbf{3a}\qquad x\,=\,4,\,8}{Sn(NSN^tBu)_4 + x\,BEt_3} \xrightarrow{\text{toluene/[D}_8\text{]toluene}} \text{decomposition into } Et_2BNH^tBu\ (\mathbf{9}),\ Et_3B\text{-}NH_2{}^tBu\ (\mathbf{10}), \text{ and unidentified products} \qquad (4)$$

NMR spectroscopic results

General

The NMR data of all new compounds are given in Tables I (**1-3**), II (**4-6**) and III (**7, 8**). It has been shown that ^{15}N NMR data of sulfur diimides [6,12,13] are particularly useful for the configu-

Table I. NMR data [a] of tetrakis(sulfurdiimido) compounds $M(NSNR)_4$ (**1a** - **3a**, **1b**, **2b**).

Compound	δ^1H ${}^tBu$; $SiMe_3$	$\delta^{13}C$ ${}^tBu$; $SiMe_3$	$\delta^{29}Si$ ($\delta^{119}Sn$)	$\delta^{15}N$ N^tBu / $NSiMe_3$	$\delta^{15}N$ NM	[b]
1a $Si(NSN^tBu)_4$ [c] $(Z/E)_4$	1.44	29.5/63.0	-74.7	-48.6	-84.8	**A, B**
2a $Ge(NSN^tBu)_4$ [d]	1.31	28.6/63.4		-48.0 (Z)	-71.3 (E)	**C**
	1.33	28.8/63.1		-49.6 (Z)	-72.6 (E)	
	1.36	28.7/62.8		-51.3 (Z)	-73.3 (E)	
	1.39	28.8/62.6		-53.6 (Z)	-73.6 (E)	
	0.89	31.0/62.2		+32.4 (E)	-150.1 (Z)	
	0.92	31.2/61.7		+36.9 (E)		
3a $Sn(NSN^tBu)_4$ [e]	1.54	29.9/60.6	(-624.0)	n.m.	n.m.	
	1.22	32.0/60.7				
		32.4/63.5				
1b $Si(NSNSiMe_3)_4$	0.20	0.8	-77.1	-60.7	-62.4	**A, B**
	(6.8)	(57.8)	+4.6			
2b $Ge(NSNSiMe_3)_4$	0.09	0.8	+5.2	-49.9	-72.4	**A, C**
	(6.4)					

[a] Measured at +27°C, in $[D_8]$toluene; coupling constants in Hz: ${}^1J({}^{29}Si{}^{13}C)$ and ${}^2J({}^{29}Si{}^1H)$ in parentheses; n.m. = not measured; [b] ${}^{15}N$ NMR methods : **A** = refocused INEPT pulse sequence with ${}^1H$ decoupling; **B** = ${}^1H$ inverse-gated decoupling; **C** = direct measurement, ${}^1H$ coupled; **D** = direct measurement, ${}^{15}N\{{}^1H\}$; [c] $\delta^{15}N(-40°C) = -49.6$ (N^tBu), -83.5 (NSi); ${}^{15}N$ NMR methods: **A**, **D**; [d] ${}^{15}N$ NMR spectrum recorded at -50°C; ${}^1H$ and ${}^{13}C$ NMR spectra recorded at -70°C; assignment of the proton and carbon resonances is based upon heteronuclear 2D ${}^{13}C/{}^1H$ shift correlations (${}^1J({}^{13}C{}^1H) = 145$ Hz, ${}^2J({}^{13}C{}^1H) = 5$ Hz); [e] Measured at -60°C; all ${}^1H$ and ${}^{13}C$ NMR signals are broad; $\delta^{119}Sn$ CP/MAS = -604.0.

rational assignment in solution. In this work, ${}^{15}N$ NMR spectra were recorded by using one of the following methods (i) ${}^1H$ inverse-gated decoupling for suppression of the NOE [16], (ii) direct measurement without ${}^1H$ decoupling and (iii) application of the refocused INEPT pulse sequence [17] with ${}^1H$ decoupling. The latter method (polarisation transfer based on ${}^3J({}^{15}N{}^1H) \sim 2.0$ - 2.5 Hz for $=N^tBu$ and 1.5 - 1.8 Hz for $=NSiMe_3$) aims for the selective detection of the $=N^tBu$ and $=NSiMe_3$ groups. Owing to typically long relaxation times $T_1({}^{15}N)$, the direct measurements required much spectrometer time and were not always successful.

${}^{15}N$ *NMR data*

The ${}^{15}N$ NMR data of **1a** clearly indicate that the $(Z/E)_4$ configuration (Scheme 1) is favoured. The ${}^{15}N(N^tBu)$ resonance (δ -48.6) appears in the typical range for sulfur diimide nitrogen atoms attached to a ${}^tBu$ group in Z position, and the $\delta^{15}N(NSi)$ value (-84.8) is characteristic for N atoms linked to a silyl substituent in E position (Fig. 1). However, although $(Z/E)_4$ appears to be the dominant configuration of **1a**, the fairly broad ${}^{15}N$ NMR signals ($h_{1/2} = 15$ Hz) at room temperature point towards dynamic processes. At lower temperature the ${}^{15}N$ NMR signals become sharp, but the chemical shifts do not change and no further signals appear.

In the case of the germanium derivative **2a**, it is evident from all NMR data that several isomers exist in solution. The $\delta^{15}N(N^tBu)$ values between -48.0 and -53.6 are in support of the Z positions of this groups and the $\delta^{15}N(NGe)$ values in the range of -71.3 to -73.6 are indicative of the E positions of these moieties. The ${}^{15}N$ NMR spectra suggest that four isomers with Z/E configuration are present in solution (Fig. 2). The four most likely isomers are $(Z/E)_4$, $(Z/E)_3(E/Z)$, $(Z/E)_2(E/Z)_2$ and $(Z/E)(E/Z)_3$ (Scheme 1). The signals of the E/Z parts of the isomers are still broad at -50°C and therefore not all resonances for the four isomers could be observed. It seems that the moieties with E/Z configuration are even less rigid than those with Z/E configuration. The same phenomenon was observed in the case of tris(sulfurdiimido)germanium compounds [6b].

The tetrakis(N-trimethylsilylsulfurdiimido)silicon and -germanium derivatives **1b** and **2b** possess a more fluxional character in solution than the corresponding N^tBu compounds **1a** and **2a**. The

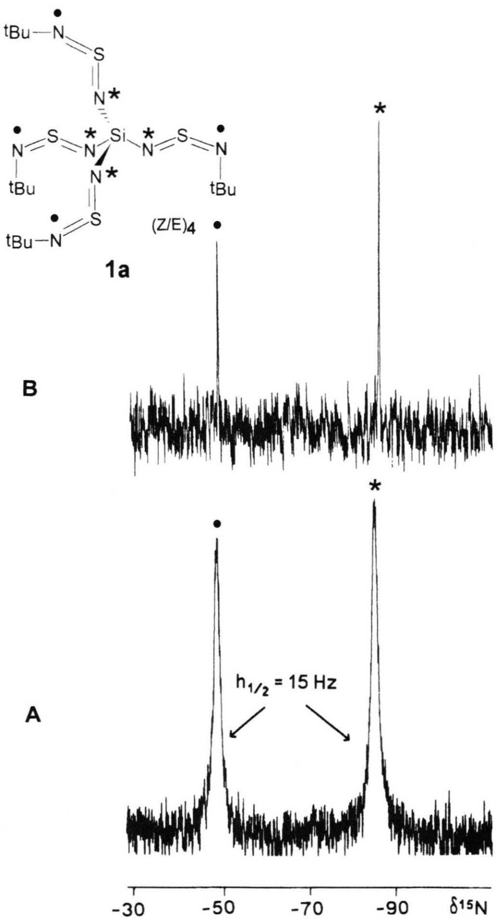


Fig. 1. **A**: 50.6 MHz $^{15}N\{^1H$ inverse-gated$\}$ NMR spectrum of $Si(NSN^tBu)_4$ (**1a**), measured in [D$_8$]toluene at 300K. Note the fairly broad resonance signals with $h_{1/2}$ = 15 Hz. **B**: 30.4 MHz $^{15}N\{^1H\}$ NMR spectrum of $Si(NSN^tBu)_4$ (**1a**), measured in [D$_8$]toluene at 233 K.

$\delta^{15}N(NSiMe_3)$ values of **1b** and **2b** are typical averaged values [12], indicating fast E/Z-Z/E isomerisation processes (Fig. 3).

^{29}*Si and* ^{119}*Sn NMR data*

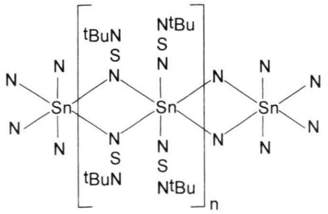
Comparing different sulfurdiimido compounds we have observed that the ^{29}Si nuclear shielding of the central silicon atom increases with an increasing number of sulfurdiimido groups [$Me_3Si(NSNSiMe_3)$: $\delta^{29}Si$ 1.6 [12a]; $Me_2Si(NSNSiMe_3)_2$: $\delta^{29}Si$ -16.2 [6a]; $MeSi(NSNSiMe_3)_3$: $\delta^{29}Si$ -44.5 [6b]; $Si(NSNSiMe_3)_4$ (**1b**): $\delta^{29}Si$ -77.1], which is the usual trend for the influence exerted by electronegative substituents. The same trend is found in the series $Cl_3Si(NSN^tBu)$ (**4a**, $\delta^{29}Si$ -38.7), $Cl_2Si(NSN^tBu)_2$ (**5a**, $\delta^{29}Si$ -53.3), $ClSi(NSN^tBu)_3$ (**6a**, $\delta^{29}Si$ -65.2) and $Si(NSN^tBu)_4$ (**1a**, $\delta^{29}Si$ -74.7) (Table II, Fig. 4). Furthermore there is a systematic shift of the $^{29}Si(SiMe_3)$ resonances towards lower frequencies when an increasing number of $NSNSiMe_3$ groups is attached to the central element [$Me_3M(NSNSiMe_3)$: $\delta^{29}Si$ 1.6 (M = Si), 0.1 (M = Ge) [12a]; $Me_2M(NSNSiMe_3)_2$: $\delta^{29}Si$ 2.8 (M = Si), 1.3 (M = Ge) [6a]; $MeM(NSNSiMe_3)_3$: $\delta^{29}Si$ 4.0 (M = Si), 2.8 (M = Ge) [6b]; $M(NSNSiMe_3)_4$: $\delta^{29}Si$ 4.6 (M = Si, **1b**), 5.2 (M = Ge, **2b**)].

Table II. NMR data[a] of compounds **4a** - **6a**.

Compound		δ^1H ^tBu	$\delta^{13}C$ ^tBu	$\delta^{29}Si$ SiCl
$Cl_3Si(NSN^tBu)$	**4a**	1.24	29.1/65.1	-38.7
$Cl_2Si(NSN^tBu)_2$	**5a**	1.32	29.3/64.2	-53.3
$ClSi(NSN^tBu)_3$	**6a**	1.38	29.4/63.5	-65.2

[a] Measured at +27°C, in C_6D_6.

According to the ^1H, ^{13}C and ^{119}Sn NMR spectra the structure of the tin derivative **3a** is still fluxional at -80°C. The $\delta^{119}Sn$ value (-624.0) of tetrakis(N-*tert*-butyl-sulfurdiimido)tin **3a** falls in the typical range for hexa-coordinated tin atoms [18]. The ^{119}Sn resonance is broad both at room temperature and at lower temperatures, possibly as a result of dynamic processes. It seems likely that the increase of the coordination number at the tin atom is caused by intermolecular association *via* the free electron pairs at the nitrogen atoms of the NSN system, analogous to bis- and tris(sulfurdiimido)tin compounds [6b]. The structure of **3a** in the solid state must be similar as in solution, since the solid-state ^{119}Sn CP/MAS NMR spectrum reveals an isotropic $\delta^{119}Sn$ value of -604.0, close to the value in solution (-624.0).



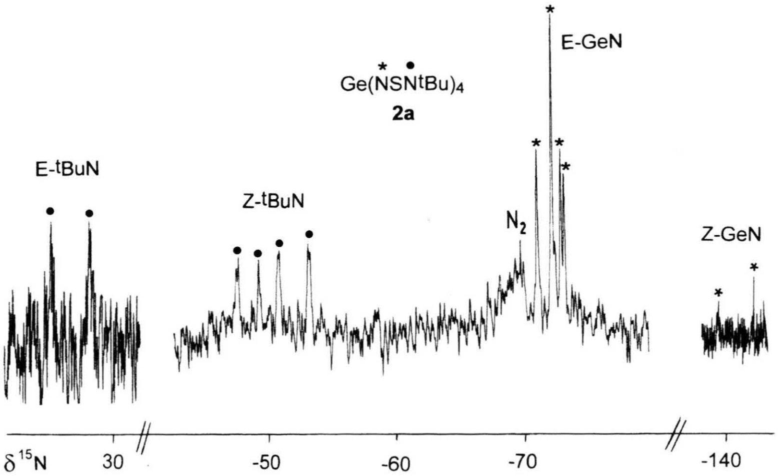


Fig 2. 30.4 MHz ^{15}N NMR spectrum (^{1}H coupled) of Ge(NSN^{t}Bu)$_4$ (**2a**), measured in [D$_8$]toluene at 223 K.

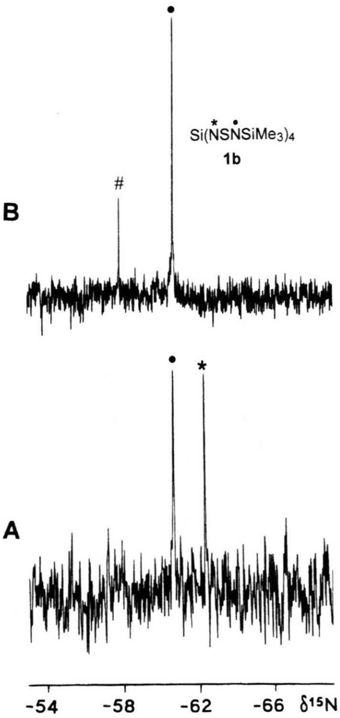


Fig. 3. 50.6 MHz ^{15}N NMR spectra of Si(NSNSiMe$_3$)$_4$ (**1b**), measured in [D$_8$]toluene at 300 K. **A**: ^{15}N{^{1}H inverse-gated}. **B**: Recorded by using the refocused INEPT pulse sequence with ^{1}H decoupling (for polarisation transfer, $^{3}J(^{15}N^{1}H)$ was assumed to be 1.8 Hz). The resonance of S(NSiMe$_3$)$_2$ is marked by **#**.

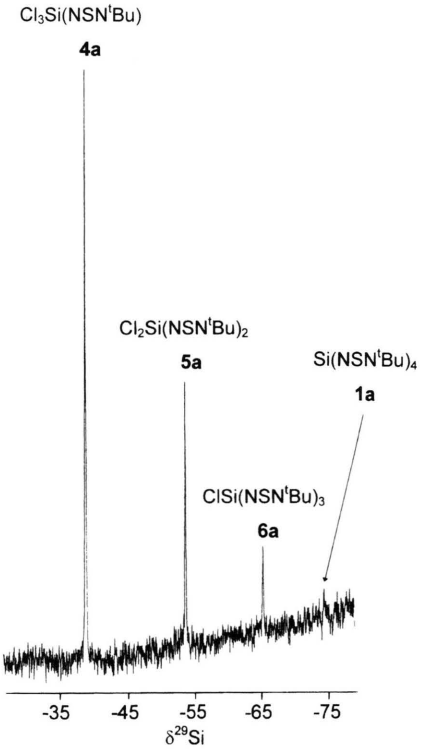
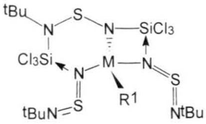


Fig. 4. 59.6 MHz ^{29}Si NMR spectrum (^{1}H coupled; C$_6$D$_6$ solution; 300K) of a mixture of Cl$_{4-n}$ Si(NSN^{t}Bu)$_n$ (n = 1-4), obtained from the 1:1 reaction of K[(NSN)^{t}Bu] with SiCl$_4$.

^{15}N and ^{29}Si NMR data of the heterocycles **7a** *and* **8a**

Two ^{29}Si NMR signals are observed for NSiCl$_3$ groups in **7a** and **8a** at rather low frequencies. It is therefore suggested that the silicon atoms are penta-coordinated due to an additional coordinative N-Si bond [6a]. The signal for the central Si atom in **7a** lies at fairly high frequency, when compared with **1a**. This ^{29}Si deshielding is caused by

Table III. NMR data[a] of the compounds **7a** and **8a**.



M = Si, R1 = NSNtBu **7a**
M = Ge, R1 = Me **8a**

Compound	δ^{13}C ^{t}Bu	MeGe	δ^{29}Si SiCl$_3$	Si	δ^{15}N =N^{t}Bu	=NM
7a [b]	29.6/63.9		-42.0	-26.2	-31.8	-67.0
	29.6/64.4		-45.1		-32.3	-97.0 (br)
	31.0/63.4				-35.2	
8a [c]	29.5/63.9	12.8	-42.6		-30.8	-96.6
	29.6/64.5		-45.1		-35.3	-98.5
	31.1/63.1					

[a] Measured at +27°C, in [D$_8$]toluene; ^{15}N NMR spectra were recorded at -50°C, direct measurement, ^{1}H coupled; br = broad; s = singulet; [b] δ^1H[corresponding δ^{13}C value]: 1.34 (s, 18H, ^{t}Bu) [29.6/64.4], 1.38 (s, 9H, ^{t}Bu) [29.6/63.9], 1.51 (s, 9H, ^{t}Bu) [31.0/63.4]; δ^{14}N: -25.0 (br, N^{t}Bu), -100.0 (br, NSi), region between -270.0 and -320.0 (br, NSiCl$_3$); [c] δ^1H[corresponding δ^{13}C value]: 1.18 (s, 3H, MeGe) [12.8], 1.33 (s, 9H, ^{t}Bu) [29.6/64.5], 1.36 (s, 9H, ^{t}Bu) [29.5/63.9], 1.39 (s, 9H, ^{t}Bu) [31.1/63.1]; δ^{14}N: -26.0 (br, N^{t}Bu), -101.0 (br, NGe), region between -270.0 and -320.0 (br, NSiCl$_3$).

the adjacent nitrogen atoms which are involved in donor-acceptor interactions [19], as proposed for the structure of **7a** (Table III, Fig. 5).

The ^{15}N NMR spectrum of **7a** (at -50°C) shows one signal at -67.0 ppm which is in the typical region for a =NSi group of an undisturbed sulfur diimide. In contrast the signals in the region between -32 and -35 ppm and the broad signal at -97.0 ppm are rather unusual for sulfurdiimido compounds. Obviously the untypical shifts are due to the coordinating =NSi groups. It seems likely that the resonances around -33 ppm belong to =N^{t}Bu and those at -97.0 ppm to =NSi groups. The signals of the coordinated NSiCl$_3$ groups were not observed. So far it is not possible to assign the configuration at the sulfur diimide systems of **7a** on the basis of the ^{15}N NMR data since no comparable compounds are available of which the molecular structure is known. In an analogous manner, the low temperature ^{15}N NMR spectrum of **8a** shows the two signals around -97 ppm (tentatively assigned to =NGe) and three resonances between -31 and -35 ppm (tentatively assigned to =N^{t}Bu). Again the resonances of the coordinated NSiCl$_3$ groups were not observed.

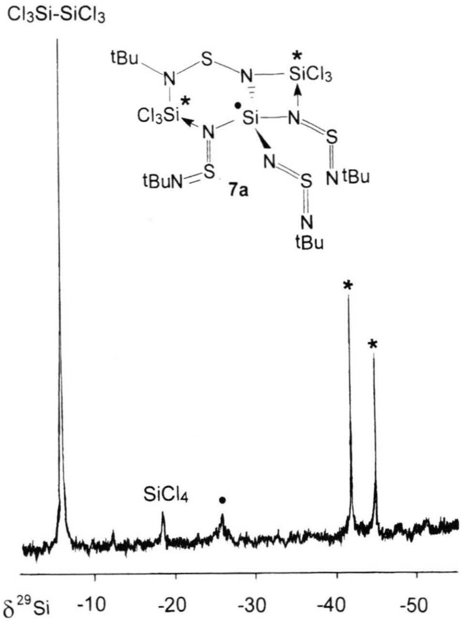


Fig. 5. 59.6 MHz ^{29}Si NMR spectrum (^{1}H coupled) of the heterocycle **7a**, measured in [D$_8$]toluene at 300K.

However, the ^{14}N NMR spectra of **7a** and **8a** show very broad signals in the region between δ -270 and -320 for these groups. Apparently both compounds are still involved in dynamic processes; thus it was not possible to detect any ^{15}N resonances at room temperature or to measure the ^{15}N NMR signals by polarisation transfer in order to assign definitely the signals of the =N^{t}Bu groups.

^{11}B and ^{14}N NMR data of the reaction mixture of **3a** *and BEt$_3$*

The ^{11}B NMR spectrum, recorded shortly after the mixture had reached room temperature, indicates the formation of a loose adduct of some kind between the sulfurdiimido compound and the borane (δ^{11}B *ca.* +62, depending on the amount of Et$_3$B present) in addition to decomposition reactions, leading *e.g.* to formation of Et$_2$BNH^{t}Bu (**9**) (δ^{14}N -250.0) and Et$_3$B-NH$_2{}^t$Bu (**10**) (δ^{14}N -335.0).

Experimental

All compounds were handled in an atmosphere of dry argon, and carefully dried solvents were used for all syntheses and the preparation of samples for NMR measurements. The potassium salts K[(NSN)R] (R = ^{t}Bu, SiMe$_3$) [5b] were prepared according to literature procedures. Triethylborane and hexachlorodisilane were commercial products and used without further purification. NMR instruments (all equipped with multinuclear units and variable-temperature control units) for liquid state measurements: JEOL FX 90Q (^{119}Sn NMR), Bruker ARX 250, Bruker AC 300 and Bruker AM 500 (^{1}H, ^{11}B, ^{13}C, ^{15}N, ^{29}Si, ^{119}Sn NMR). Chemical shifts are given with respect to Me_4Si [$\delta^{1}H$ (C_6D_5H) = 7.15, ($C_6D_5CD_2H$) = 2.03; $\delta^{13}C$ (C_6D_6) = 128.0, ($C_6D_5CD_3$) = 20.4; $\delta^{29}Si$ = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz], Et_2O-BF_3 [$\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 MHz], neat $MeNO_2$ [$\delta^{15}N$ = 0 for $\Xi(^{15}N)$ = 10.136767 MHz, and $\Xi(^{14}N)$ = 7.226455 MHz] and neat Me_4Sn [$\delta^{119}Sn$ = 0 for $\Xi(^{119}Sn)$ = 37.290665 MHz]. The mutual assignments of ^{1}H, ^{13}C and ^{15}N resonances to the different isomers were achieved by 2D^{13}C/^{1}H and 2D^{15}N/^{1}H heteronuclear shift correlations [based on $^{1}J(^{13}C^{1}H)$, $^{2}J(^{13}C^{1}H)$ and $^{3}J(^{15}N^{1}H)$]. A Bruker MSL 300 instrument (equipped with a multinuclear double-bearing probe head) served for the solid state 112 MHz ^{119}Sn CP/MAS NMR measurement; the sample was packed in an air-tight insert [20] fitting exactly into the commercial ZrO_2 rotor. The spectrum was run at two different spinning speeds for assignment of the isotropic δ value. Electron impact (EI) mass spectra (70 eV): Varian MAT CH 7 (EI-MS, 70 eV) with direct inlet.

Tetrakis(sulfurdiimido) compounds $M(NSNR)_4$ (M = Si, Ge, Sn; R = ^{t}Bu, **1a** *-* **3a***; M = Si, Ge; R = $SiMe_3$,* **1b**,**2b***). General procedure:*

A suspension of 6 mmol of the potassium sulfurdiimido salt, K[(NSN)R], in DME (30 ml) was added to the element tetrachloride (1.5 mmol) in hexane (20 ml) at -78°C. The mixture was stirred for 30 minutes at -78°C and then allowed to reach room temperature. After filtration the solvent was removed *in vacuo*, and the compounds were left as yellow to orange oils (**1b**, **2a,b**) or orange solids (**1a**, m.p. 112°C , **3a**, m.p. 253°C). In repeated experiments, yields were found to be 70-90% for the N-*tert*-butyl compounds and 30-70% for the N-trimethylsilyl compounds.

$Si(NSN^{t}Bu)_4$ (**1a**); $C_{16}H_{36}N_8S_4Si$; M = 496.862 g/mol; EI-MS: *m/z* (%) = 496 (1) [M^+], 439 (2) [M^+-57], 425 (78), 379 (81), 369 (60), 313 (60), 257 (100), 211 (70), 182 (20), 150 (15), 136 (23), 57 (1).

$Si(NSNSiMe_3)_4$ (**1b**); $C_{12}H_{36}N_8S_4Si_5$; M = 561.162 g/mol; EI-MS: *m/z* (%) = 545 (15), 459 (5.5), 339 (6), 294 (5.5), 278 (5), 73 (100).

Synthesis of $Cl_{4-n}Si(NSN^{t}Bu)_n$ (n = 1, **4a***; n = 2,* **5a***; n = 3,* **6a***)*

A suspension of the potassium salt $K[(NSN)^{t}Bu]$ (6 mmol) in hexane (50 ml) was added to silicon tetrachloride (6 mmol, 3 mmol or 2 mmol) in hexane (20 ml) at room temperature. The mixture was stirred for 4 h, and after filtering off insoluble material the solvent was removed in vacuo. In each case, a mixture of sulfur diimides was left as a yellow to orange oil.

Reactions of $R^{1}M(NSN^{t}Bu)_3$ with hexachlorodisilane: Synthesis of **7a** *and* **8a***. General procedure:*

A suspension of 2 mmol of $R^{1}M(NSN^{t}Bu)_3$ (M = Si, R^1 = $NSN^{t}Bu$, **1a**; M = Ge, R^1 = Me) in 40 ml of hexane was combined with a solution of 2 mmol or 8 mmol, respectively, of hexachlorodisilane in 30 ml of hexane at 0°C. The mixture was allowed to reach room temperature and then stirred for additional 24 h. Finally the solvent was removed in high vaccuum. **7a** was obtained as an orange, **8a** as a yellow oil.

Reaction of tetrakis(N-tert-butylsulfurdiimido)tin **3a** *with triethylborane (NMR tube)*

A solution of 1 mmol of **3a** in 2 ml of toluene/[D_8]toluene was combined with triethylborane (4 or 8 mmoles, respectively) at -78°C. The mixture was kept for 30 min at this temperature and then allowed to reach r. t. ^{119}Sn NMR showed that **3a** was no longer present, and ^{11}B NMR revealed the signals of decomposition products such as the aminoborane $Et_2BNH^{t}Bu$ (**9**). By trapping all volatile material, the aminoborane and Et_3B-$NH_2{}^{t}Bu$ (**10**) could be identified by their NMR data.

$Et_2BNH^{t}Bu$ (**9**): $\delta^{11}B$: 46.6 ($h_{1/2}$ = 110 Hz); $\delta^{14}N$: -250.0; $\delta^{13}C$([D_8]toluene, -50°C): 33.2, 52.1 (^{t}Bu), 13.1, 11.5 (br, CH_2), 10.4, 10.1 (CH_3).

Et_3B-$NH_2{}^{t}Bu$ (**10**): $\delta^{11}B$: -2.8 ($h_{1/2}$ = 183 Hz); $\delta^{14}N$: -335.0 (br); $\delta^{13}C$: 13.7 (br, CH_2), 10.1 (CH_3), 29.0/51.1 (^{t}Bu); $\delta^{1}H$: 0.40 (q, 7.7 Hz, CH_2), 0.99 (t, 7.7 Hz, CH_3), 1.24 (s, ^{t}Bu), 1.99 (br, NH_2); all spectra recorded at +27°C, in C_6D_6; br = broad; q = quadruplet; t = triplet; s = singulet.

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