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Dimeric cyclic bis(amino)stannylenes and -plumbylenes – a multinuclear magnetic resonance study

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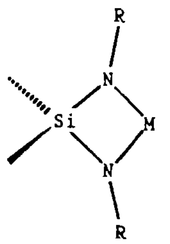
Abstract

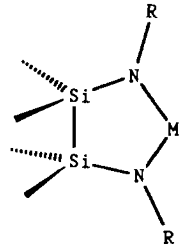
1,3-Dialkyl-4,4,5,5-tetramethyl-1,3,4,5,2λ^2-diazadisilastannolidines (**3**) and -plumbolidines (**4**) (alkyl = ^{t}Bu (**a**), ^{i}Pr (**b**), Et (**c**)) and 5,5-dimethyl-1-trimethylsilyl-3-(R)-1,3,2λ^2-diazastannolidines (**5**) and -plumbolidines (**6**) (R = Me_3Si (**a**), ^{i}Pr (**b**)) have been prepared. In the case of **3b**, **4b**, **3c** and **4c** monomer–dimer equilibria exist at room temperature and above. At low temperature (**3c**, **4c**) the mechanism (ring slippage) of the intramolecular rearrangement was established by dynamic ^{1}H and ^{13}C NMR. The heterocycles **5** and **6** are dimers in which the nitrogen atoms linked to less bulky substituents prefer selectively the bridging positions. The exchange reaction between $(\mathbf{6b})_2$ and $(\mathbf{1b})_2$ (dimeric 1.3-diisopropyl-2,2-dimethyl-1,3,2,4λ^2-diazasilastannetidine) leads preferably to dimers each built from two five- or from two four-membered rings rather than to dimers built from a five- and a four-membered ring. Natural abundance ^{15}N NMR has served to characterize some dimers. All compounds were characterized by ^{1}H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb NMR data. Some of these measurements are severely hampered owing to dynamic processes.

Introduction

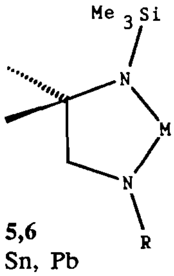
Cyclic bis(amino)stannylenes and -plumbylenes are monomers or dimers depending on the bulkiness of the substituents at nitrogen [1–3]. In the case of the four-membered cyclic compounds **1a** [1a] and **2a** [1b], **1a** is strictly monomeric in solution, but a monomer or dimer in the solid state [2], whereas **2a** is weakly associated in solution [4]. Both **1b** [3] and **2b** are dimers in solution with a fluxional structure [5]. Recently, we have prepared similar five-membered heteroxycles **3** and **4** [6]. Both **3a** and **4a** are monomers in solution [4], but for **3b**, **c** and **4b**, **c** the monomer–dimer equilibrium is shifted towards the dimers if the steric requirement of the nitrogen-substituents is decreasing. It was of interest to find out whether these compounds have a similar fluxional structure [5] as observed for **1b** and **2b**. Such a structure is favoured if the substituents at the nitrogen atoms are alike. Therefore, we have prepared cyclic compounds of the type **5** and **6** with different substituents at the nitrogen atoms. In the case of dimerization, only the sterically less shielded nitrogen atom is expected to prefer the bridging position.



1,2
M = Sn, Pb
R = ^{t}Bu(a), ^{i}Pr(b)



3,4
Sn, Pb
^{t}Bu(a), ^{i}Pr(b), Et(c)



5,6
Sn, Pb
Me_3Si(a), ^{i}Pr(b)

The monomeric bis(amino)stannylenes and -plumbylenes are multifunctional compounds with great

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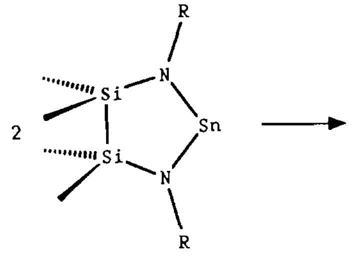
synthetic potential [6] and they show intriguing spectroscopic properties, in particular as far as multinuclear magnetic resonance is concerned [4, 7]. The dimers of **1** to **6** have attracted less attention so far. They are less easy to characterize than the monomers and, at least for M = Pb, they decompose readily in solution (benzene, toluene) at ambient temperature. Although the tin derivatives are somewhat more stable in solution, their dynamic properties often hamper a straightforward ^{1}H and ^{13}C NMR spectroscopic analysis. In this work we describe the synthesis and the dynamic behaviour of some derivatives of **3** to **6**. Together with ^{1}H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb NMR, ^{15}N NMR at natural abundance [8] has been used to characterize some dimers for the first time.

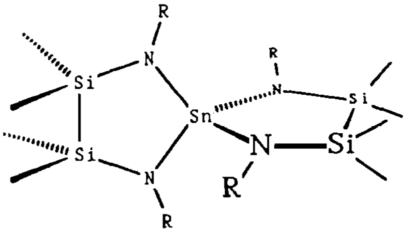
Results and discussion

Synthesis

All compounds were prepared by the reaction between the respective dilithiated amines and tin(II) and lead(II) chloride [1, 5, 6, 9]. The compounds are colourless (**3**, **5**) or yellowish (**4**, **6**) solids which can be stored at −10 °C in the dark for months. They are extremely sensitive towards air and moisture. The lead compounds (**4**, **6**) decompose rapidly (within several hours) in solution at ambient temperature. In the case of the tin compounds **3c** slow decomposition via redox processes in solution takes place (eqn. (1)), leading to tin and the spiro-tin(IV) derivative **7** which has been prepared independently by other methods [10].



3c



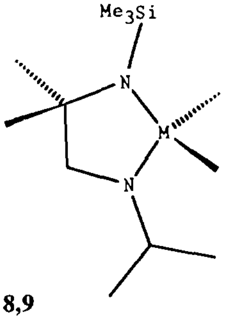
7

+ Sn (1)

The compounds **5b** and **6b** are dimeric [$(\mathbf{5b})_2$, $(\mathbf{6b})_2$] in solution at room temperature, as shown by the NMR spectra. However, they should exchange readily with other dimers. Previously, we have shown that a mixture of $(\mathbf{1b})_2$ and $(\mathbf{2b})_2$ readily equilibrates and contains the mixed dimer (**1b**/**2b**) [5]. In this context we have now studied the mixture of $(\mathbf{1b})_2$ and $(\mathbf{6b})_2$. This should reveal information on the preferred dimers in this system. Clearly, one would expect a complex mixture (see eqn. (2)) which may contain up to ten different dimers. Interestingly, the formation of dimers built by five- and four-membered rings (**6b**/**1b**), (**5b**/**1b**), (**6b**/**2b**) and (**5b**/**2b**) plays only a minor role in comparison to the combination of rings of the same size (**6b**/**5b**), $(\mathbf{5b})_2$, (**1b**/**2b**) and $(\mathbf{2b})_2$ (see also Figs. 1 and 2).

$$\begin{aligned}&(\mathbf{6b})_2 + (\mathbf{1b})_2 \rightleftharpoons\\ &\quad (\mathbf{6b}/\mathbf{1b}) + (\mathbf{5b}/\mathbf{1b}) + (\mathbf{6b}/\mathbf{2b}) + (\mathbf{5b}/\mathbf{2b})\\ &\quad + (\mathbf{6b}/\mathbf{5b}) + (\mathbf{5b})_2 + (\mathbf{1b}/\mathbf{2b}) + (\mathbf{2b})_2 \qquad (2)\end{aligned}$$

The heterocycles **8** and **9** were prepared to obtain some relevant NMR data for comparison with those of the dimers $(\mathbf{5})_2$ and $(\mathbf{6})_2$.



8,9
M = Sn, Pb

NMR spectra

^{1}H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb NMR data for **3**,**4** and **7** are given in Table 1, and Table 2 lists these parameters for **5**, **6**, **8** and **9**. Table 3 contains the ^{15}N NMR data for **3c**, **5**, **7**, **8** and **9**. The complete assignment of the low temperature ^{1}H, ^{13}C and ^{29}Si NMR spectra is difficult. In the case of the ^{1}H and ^{13}C NMR spectra of **3** and **4** the measurements had to be carried out in toluene (e.g. compounds **4** decompose rapidly in chlorinated hydrocarbons) at < −60 °C in order to slow down the various dynamic processes (*vide infra*). Under these conditions the solubility is much reduced and typical assignment procedures (such as two-dimensional ^{13}C/^{1}H heteronuclear shift correlations) would require a rather long time. The δ^{29}Si values for the different ^{29}Si nuclei in **3b**, **c** at −80 °C are very similar and no

TABLE 1. ^1H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb NMR data[a, b] of the monomeric and dimeric 1,3,4,5,2λ^2-diazadisilastannolidines (**3**) and -plumbolidines (**4**) and of the spiro-heterocyclic compound **7**

Compound	$\delta^{13}C$		$\delta^{29}Si$	$\delta^{119}Sn/\delta^{207}Pb$[d]
	MeSi[c]	NR		
3a				
25 °C	6.3[8.2]	57.7[25.5], 38.5[43.7]	−4.4[21.2]	759.0
δ^1H	0.36	1.38		
4a				
25 °C	9.3[<10]	57.5[22.4], 40.1[31.5]	7.3[27.1]	4900.0
δ^1H	0.38	1.33		
3b				
25 °C	2.1[9.0]	49.9[42.3], 32.4[39.9]	−2.6[76.6]	n.o.[e]
δ^1H	0.28	4.10[f], 1.30		
−75 °C	2.2(broad)	49.5(broad), 26.0 to 31.0(broad)	−2.2	210.0
δ^1H	0.44(broad)	4.05, 3.74(broad), 1.48, 1.30(broad)		
4b[g]				
25 °C	5.5	49.7, 32.2	8.1	n.o.
δ^1H	0.35	5.70, 1.27		
3c				
25 °C	1.6[<5]	41.8[80.8], 21.3[39.5]	2.0[20.5]	208.0[h]
δ^1H	0.34	3.35, 1.20		
−45 °C	3.3, 2.0, 1.3, −0.5	42.7, 41.4, 22.6, 20.2	1.8, 2.2	200.0
−60 °C δ^1H	0.33(s), 0.30(s), 0.24(s), 0.17(s)	3.6 to 3.0(multiplets), 1.16(t), 1.14(t)		
4c				
25 °C	3.5(broad)	41.2, 22.5	7.4	n.o.
δ^1H	0.29	4.08, 1.20		
−60 °C	5.9, 3.6, 3.0, −0.1	41.3, 40.6, 23.5, 21.2	7.8, 7.6	n.o.
δ^1H	0.52(s), 0.39(s), 0.22(s), 0.15(s)	4.4 to 3.7(multiplets), 1.47(t), 1.13(t)		
7				
25 °C	0.6[13.0]	40.7[4.0], 21.5[11.5]	−9.1[74.8]	−55.1
δ^1H	0.17	3.03[81.4], 1.17		

[a] In toluene-d_8 ($\approx$5 to 10%) in 5 mm (o.d.) tubes; δ values with respect to Me_4Si [^1H, $\delta^1H(C_6D_5CD_2H) = 2.03$; ^{13}C, $\delta^{13}C(C_6D_5CD_3) = 20.4$; ^{29}Si (external reference with $\Xi(^{29}Si) = 19867184$ Hz], Me_4Sn [^{119}Sn (external reference with $\Xi(^{119}Sn) = 37290665$ Hz)], Me_4Pb [^{207}Pb (external reference with $\Xi(^{207}Pb) = 20920597$ Hz)]. [b] Coupling constants $^nJ(^{119}SnX)$ or $^nJ(^{207}PbX)$ are given in square brackets. In all spectra the signal to noise ratio would have been sufficient to observe the respective ^{119}Sn or ^{207}Pb satellite signals; however frequently these satellite signals are too broad for detection as a result of the dynamic processes and because of fast relaxation of the ^{119}Sn or ^{207}Pb nucleus (see text and Figs 1 and 2). [c] For all $Me_2SiSiMe_2$ groups the $^1J(^{29}Si^{13}C)$ values are found in the range 45 ± 1.5 Hz. [d] The ^{207}Pb resonances for potential dimers were not observed, probably as a result of extreme exchange broadening (see text). [e] $\delta^{119}Sn = 708.0$ Hz at 105 °C. [f] $^3J(^{119}Sn^1H)$ 6.1 Hz. [g] All resonance signals are broad at room temperature and become even broader at lower temperature (25 to −70 °C). [h] $\delta^{119}Sn + 218$ (55 °C), $+253$ (80 °C).

assignment is given. However, ^{29}Si NMR spectra (conveniently recorded using the refocused INEPT pulse sequence [11]) are extremely useful for studying reaction solutions, even for complex mixtures (see Fig. 1, which corresponds to the exchange reaction in eqn. (2)).

The ^{119}Sn NMR spectra for all compounds, except of **3b**, could be readily obtained at ambient temperature. In the case of **3b** a ^{119}Sn resonance ($\delta^{119}Sn + 708.0$) in the typical range for monomers [4, 12] was observed at 105 °C in toluene, and a very broad resonance ($\delta^{119}Sn + 270.0$) typical of dimers, became observable at −80 °C. In the intermediate temperature range dynamic processes connected with the monomer–dimer equilibrium are fast and broaden the ^{119}Sn resonance over the range $\approx$400 ppm. For the same reason only a few ^{207}Pb resonances could be observed, considering the great difference of $\approx$2000 ppm for the $\delta^{207}Pb$ values for monomers and dimers. In the case of **6b** and also for the various products from the exchange reaction (eqn. (2)), where certain dimers are preferred, the ^{207}Pb resonances were readily detected. Then, of course ^{207}Pb NMR is a powerful tool in analyzing mixtures owing to the great sensitivity of ^{207}Pb nuclear shielding [13] to small structural changes (see Fig. 2).

TABLE 2. ^{1}H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb NMR data[a, b] of the dimeric 1,3,2λ^{2}-diazastannolidines (**5**) and -plumbolidines (**6**) and of two Sn(IV), Pb(IV) derivatives **8** and **9**, for comparison

Compound	N(1)SiMe$_3$	N(3)R	C(4)	C(5)	Me$_2$C(5)	$\delta^{29}Si$	$\delta^{119}Sn/\delta^{207}Pb$
5a[c]							
−50 °C	6.0	−0.3	60.4	66.5	37.8, 37.2	−2.0, 10.3[d] [28.8][<20]	262.0
$\delta^{1}H$	0.39[e]	0.31[e]	4.09, 2.36[f]		1.43, 1.18		
6a							
−40 °C	6.4	2.6	62.8	70.4	37.0, 34,6	−1.8, 6.5[d]	2980.0
$\delta^{1}H$	0.28[e]	-0.13[e]	4.83, 3.92[g]		1.54, 1,11		
5b							
25 °C	5.8[30.5]	55.2[27.2], 23.4[<5], 25.1[<5]	63.6[<5]	65.2[10.5]	37.2[6.0], 30.8[8.5]	−3.6[25.1]	243.0
$\delta^{1}H$	0.33	3.38, 1.08, 1.67	4.00, 2.47[h]		1.38, 1.23		
6b							
25 °C	6.1[36.0]	54.0[26.0], 24.7[<5], 25.3[<5]	66.5[19.0]	71.1[14.6]	37.1[10.0], 34.3[40.0]	−3.0[<10]	2966 (−22 °C)
$\delta^{1}H$	0.33	4.58, 0.89, 1.33	4.88, 3.72[i]		1.54, 1.30		
8[j]							
25 °C	5.0[7.4]	52.1[10.2], 25.8[19.7]	69.5[23.1]	59.1[5.1]	30.6[14.0]	1.7[37.4]	91.6
$\delta^{1}H$	0.11	3.19[58.0], 1.00	2.71[60.4]		1.28		
9[k]							
25 °C	5.5[14.2]	55.2[17.4], 26.5[50.1]	73.3[5.4]	60.7[12.0]	31.0[19.6]	−1.1[36.6]	312.7
$\delta^{1}H$	0.11	3.31[112.5], 1.03[3.8]	3.14[158.8]		1.35		

[a, b] See footnotes [a, b] in Table 1. [c] ^{13}C Resonances are still broad at −50 °C. [d] ^{29}Si assignment. [e] Assignment may be reversed. [f] $^{2}J(^{1}H^{1}H)$ 10.9 Hz. [g] $^{2}J(^{1}H^{1}H)$ 12.0 Hz. [h] $^{2}J(^{1}H^{1}H)$ 13.5 Hz. [i] $^{2}J(^{1}H^{1}H)$ 13.2 Hz. [j] $\delta^{13}C$(MeSn) 0.5 [419.1]; $\delta^{1}H$(MeSn) 0.33 [60.0] [k] $\delta^{13}C$(MePb) 15.3 [289.9]; $\delta^{1}H$(MePb) 1.03 [72.1].

TABLE 3. Some ^{15}N NMR data[a] of compounds **3**, **4**, **5**, **7**, **8** and **9**

Compound	M	$\delta^{15}N$ [$^{1}J(M^{15}N)$] (M = ^{119}Sn, ^{207}Pb)
3a (25 °C)[b]	Sn	-192.9[382.0]
4a (25 °C)[b]	Pb	-119.8[671.4]
3b (105 °C)	Sn	-210[$-$][b]
3c (25 °C)	Sn	-310.5[n.o.]
7 (25 °C)	Sn	-348.0[97.7]
5a (-20 °C)	Sn	-249.6[310.0](Sn*N*<), -315.2[n.o.](Sn*N*Sn)
5b (25 °C)[c]	Sn	-274.5[320.0](Sn*N*<), -309.4[169.0](Sn*N*Sn)
8 (25 °C)[d]	Sn	-329.6[17.2](Si*N*), -328.9[4.0](^{i}Pr*N*)
9 (25 °C)[e]	Pb	-310.5[190.2](Si*N*), -296.6[245.9](^{i}Pr*N*)

[a] In 10 mm (o.d.) tubes in C_6D_6 (*c*. 5 to 10%), except for **3b** and **5a** (in toluene-d_8); $\delta^{15}N$ values relative to external $MeNO_2$ (neat) with $\Xi(^{15}N) = 10136767$ Hz. [b] Ref. 4. [c] Assignment is based on the relative intensities of $^{117/119}Sn$ satellite signals for the Sn*N*Sn- and Sn*N*< fragments (see Fig. 3). [d] Assignment is based on the observation of $^{1}J(^{29}Si^{15}N) = 14.3$ Hz. [e] Assignment is based on the observation of $^{1}J(^{29}Si^{15}N) = 13.7$ Hz.

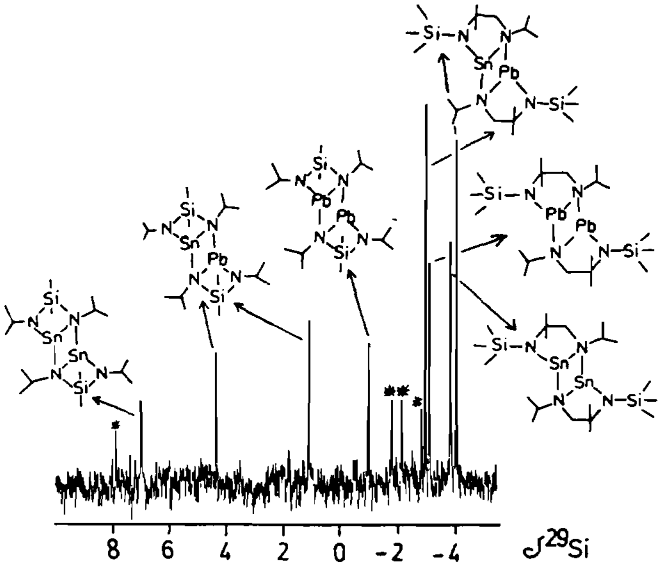


Fig. 1. 59.6 MHz ^{29}Si NMR spectrum (refocused INEPT pulse sequence with ^{1}H decoupling [11b, c, d], 10 min spectrometer time) of the equilibrated reaction mixture (eqn. (2)) of $(\mathbf{6b})_2$ and $(\mathbf{1b})_2$ (≈1:1) in toluene at -40 °C. The assignment is based on the $\delta^{29}Si$ data for $(\mathbf{1b})_2$, $(\mathbf{2b})_2$ and (**1b**/**2b**) [5], for $(\mathbf{5b})_2$ and $(\mathbf{6b})_2$. The remaining two intense signals must belong to (**5b**/**6b**). Additional weak signals, marked by asterisks, are believed to arise from dimers built by five- and four-membered rings.

Dynamic processes hamper the measurement of ^{15}N NMR spectra in natural abundance. Relaxating agents cannot be used, owing to the sensitivity of the compounds. Therefore, polarization transfer techniques [11] (based on small long range coupling constants $^{n}J(^{15}N^{1}H)$ ($n = 2$, 3, 4) are the only way to circumvent the unfavourable relaxation properties of the ^{15}N nuclei in these molecules. However, these methods may fail to give results since the transverse relaxation rates of the protons and of the ^{15}N nuclei are affected by the dynamic processes. Thus, it was possible for **3c** (where dynamic processes are rather fast at room temperature) to observe an averaged ^{15}N resonance. In the case of more strongly associated dimers such as **5**, there was a chance to obtain ^{15}N NMR spectra with a signal to noise ratio that allowed the observation of $^{119/117}Sn$ satellites in order to measure the coupling constants $^{1}J(^{119}Sn^{15}N)$ for the different nitrogen atoms in a dimer for the first time (see Fig. 3).

Both ^{15}N resonances are shifted to lower frequencies with respect to monomers. This can be attributed to the changes in the electronic structure at the tin atom and in particular, at the tetracoordinate nitrogen atom. Here, the $\delta^{15}N$ value is in the range known [14] for other ammonium-type nitrogen atoms. The coupling constant $|^{1}J(^{119}Sn^{15}N)|$ for the tetracoordinate nitrogen is significantly smaller than

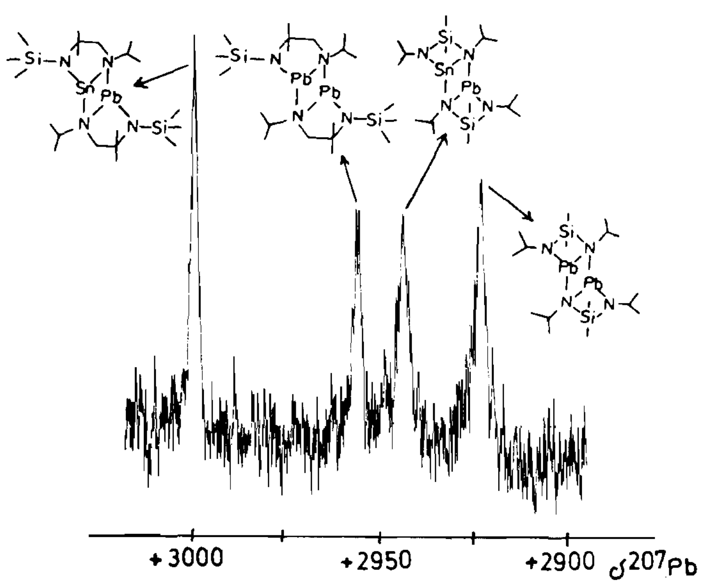


Fig. 2. 62.6 MHz ^{207}Pb{^{1}H} NMR spectrum (10 min spectrometer time) of the reaction mixture according to eqn. (2) in toluene at −40 °C. The assignment is based on the known δ^{207}Pb values for **(2b)**$_2$, **(1b/2b)** [5] and **(6b)**$_2$. Therefore, the remaining signal must belong to **(5b/6b)**. The information from the ^{207}Pb NMR spectrum is superior to that from ^{119}Sn NMR spectra since there is strong overlap in the region around $\delta^{119}\text{Sn} \approx -240$ which is typical of all ^{119}Sn resonances involved, cxcept of that for **(1b)**$_2$ [5].

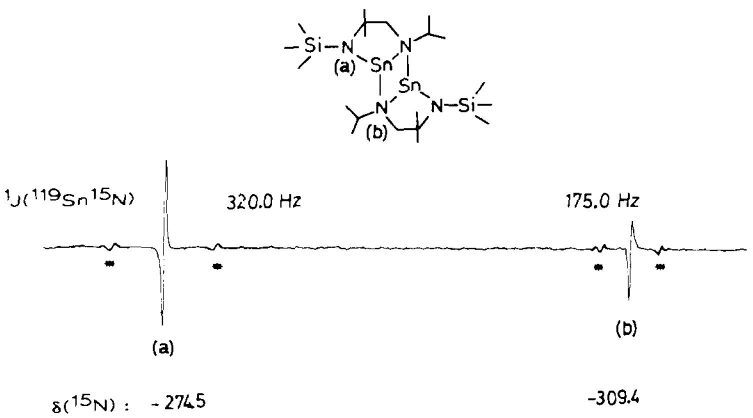


Fig. 3. 40.5 MHz ^{15}N NMR spectrum of **(5b)**$_2$ in toluene (c. 5%, 10 mm (o.d.) tube) at 25 °C. The basic INEPT pulse sequence [11a] proved most efficient assuming $^3J(^{15}\text{N}^1\text{H}) \approx 2.5$ Hz and a recycle delay of 3 s (the spectrum is the result of 3000 scans, ≈2.5 h spectrometer time). The basic INEPT pulse sequence allows ^{1}H relaxation during data acquisition, avoids the problem to select a suitable delay for refocusing [in particular for N(b)] prior to ^{1}H decoupling during data acquisition, and it does not depend critically on $T_2(^{119}\text{Sn})$. Of course, the disadvantage are the broadened out-of-phase singulets. The integral intensities of the $^{117/119}$Sn satellite signals for the N(a) and N(b) resonances correspond to the presence of one and two, respectively, tin atoms linked to the nitrogen atoms.

in comparable monomers. Assuming a negative sign for $^1J(^{119}\text{Sn}^{15}\text{N})$ in the monomers, which is supported by numerous arguments [15], this is the correct trend. The nitrogen lone electron pair as one source of negative contributions to $^1J(^{119}\text{Sn}^{15}\text{N})$ is no longer present in the case of the tetracoordinate nitrogen, whereas the influence of both the nitrogen and the tin lone electron pair have to be considered for the other $^1J(^{119}\text{Sn}^{15}\text{N})$ value.

Coupling constants between $^{117/119}$Sn or ^{207}Pb and other nuclei (such as ^{1}H, ^{13}C, ^{15}N, ^{29}Si) are useful for the assignment of particular resonance signals. However, many NMR measurements had to be carried out at low temperature, as a consequence of the dynamic situation, and the longitudinal relaxation (time constant T_1) of the heavy nuclei ^{119}Sn or ^{207}Pb becomes dominated by the chemical-shift-anisotropy (CSA) mechanism (T_1^{CSA}). This mechanism is very efficient at high field strength B_0 (B_0^2 dependence!) and low temperature, and may cause averaging of the scalar coupling [16]. A typical example is shown in Fig. 4 for ^{29}Si NMR spectra of **3a**.

In ^{119}Sn and ^{207}Pb NMR spectra two factors are responsible for the broad resonances which are usually observed for compounds of the type **1** to **6**. There is the partially relaxed scalar coupling $^1J(^{119}Sn^{14}N)$ and $^1J(^{207}Pb^{14}N)$, respectively. As found out from the ^{15}N NMR spectra (see Fig. 3 and ref. 4), these coupling constants may be in the order of several hundred Hz, which means that there is significant residual broadening even if the quadrupolar ^{14}N relaxation is very fast. Since $T_1^{CSA} \approx 7/6$ T_2^{CSA} [16], the CSA mechanism will also affect the linewidth of the ^{119}Sn or ^{207}Pb resonance signals, especially at low temperatures. This is demonstrated in Fig. 5, again for a simple case like **4a**. The temperature dependence of the linewidth of the ^{207}Pb resonance is typical of competing relaxation mechanisms. The quadrupolar ^{14}N relaxation rate is accelerated at lower temperature, leading eventually to 'decoupling' of the ^{14}N nucleus and therefore to negligible contributions from scalar relaxation of the second kind (T_2^{SC}) [16] to $T_2(^{207}Pb)$. On the other hand, the efficiency of the CSA mechanism for ^{207}Pb spin relaxation steadily increases with decreasing temperature. Thus, the linewidth of the ^{207}Pb resonance approaches a minimum between -40 to -60 °C and increases again at still lower temperatures.

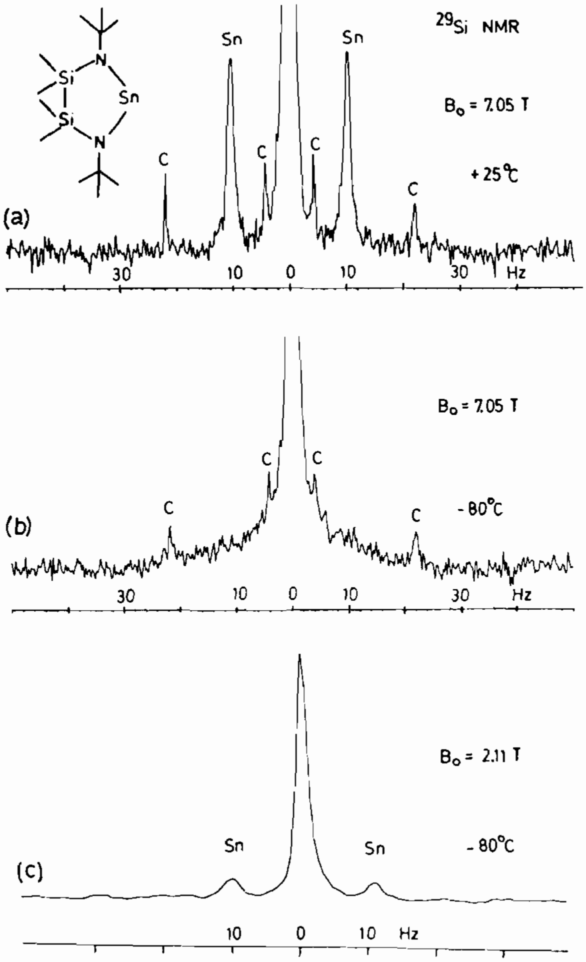


Fig. 4. Influence of chemical-shift-anisotropy (CSA) relaxation mechanism on the appearance of $^{117/119}$Sn satellite signals at high field strength and low temperature. ^{29}Si NMR spectra of **3a** (refocused INEPT pulse sequence with ^{1}H decoupling, 4 scans ($B_0 = 7.05$ T), 64 scans ($B_0 = 2.11$ T)), ≈15% in toluene-d_8, 10 mm (o.d.) tube at +25 to −80 °C. The satellites are marked by Sn ($^{117/119}$Sn) and C (^{13}C). (a) Spectrum at +25 °C; all satellites are clearly visible. (b) With decreasing temperature, the $^{117/119}$Sn satellites become broad (in contrast with the ^{13}C satellites) and vanish completely at −80 °C; the δ^{119}Sn value does not change appreciably in the same temperature range. (c) Under the same conditions (−80 °C) but at lower field strength ($B_0 = 2.11$ T), the $^{117/119}$Sn satellite signals are just slightly broader than the centre ^{29}Si resonance.

The dynamic processes in **3b, c** and **4b, c** are most easily explained considering Scheme 1 and the ^{1}H resonances (200 MHz) of the MeSi groups. For fast dissociation of the dimers into monomers, as a trivial case, one would expect a single ^{1}H(MeSi) resonance. This applies to **3b, c** and **4b, c** at room temperature and for **3b, 4b** down to −60 °C, until broadening, but no splitting of the ^{1}H(MeSi) resonance occurs. In contrast, the ^{1}H(MeSi) resonance of **3c** (Fig. 6) broadens significantly at −20 °C, and splits into two signals at −40 °C. These become again broader and, finally, there are four fairly sharp ^{1}H(MeSi) signals at −80 °C. The observation of four ^{1}H(MeSi) resonances is in accord with a rigid structure **A** or **A′** in Scheme 1. Two ^{1}H(MeSi) signals are correct for the fluxional structure of **A, A′** which rearrange into each other via **B**. The nitrogen and silicon atoms in **B** become equivalent but there are still two different sites for the MeSi groups. This proves that the intramolecular rearrangement cannot proceed via **C** since this structure would require the equivalence of all MeSi groups. Structure **C** can be ruled out also at higher temperatures taking into account the marked temperature dependence (at room temperature and above) of the ^{119}Sn resonance of **3b** and **3c** which then strongly supports monomer–dimer equilibria rather than intramolecular processes. Therefore, the compounds **3c** and **4c** behave analogous to **1b** and **2b** [5], suggesting that this type of fluxional character is of a more general nature.

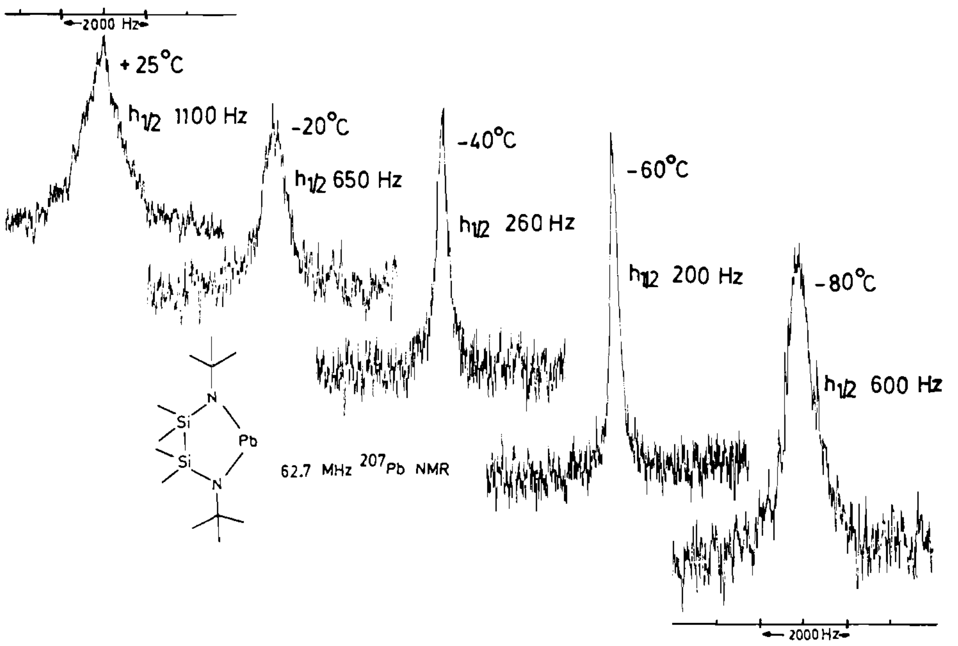


Fig. 5. Competition between the relaxation mechanism T_2^{SC} relaxation of the second kind owing to $^1J(^{207}Pb^{14}N)$) and T_2^{CSA} (owing to the large chemical shift anisotropy of the ^{207}Pb nuclei). A series of $^{207}Pb\{^1H\}$ NMR spectra, taken at various temperatures, of **4a**, ≈15% in toluene-d_8, 5 mm (o.d.) tube, is shown. The δ^{207}Pb value changes only by ≈30 ppm (proving the strictly monomeric character of **4a**), but the linewidths, $h_{1/2}$ (at half height) changes dramatically. The contribution of T_2^{SC} becomes less important at lower temperatures ('decoupling' of ^{14}N), in contrast with the increasing CSA contribution. Therefore, the values $h_{1/2}$ pass through a minimum (between −40 to −60 °C) and increase again at −80 °C.

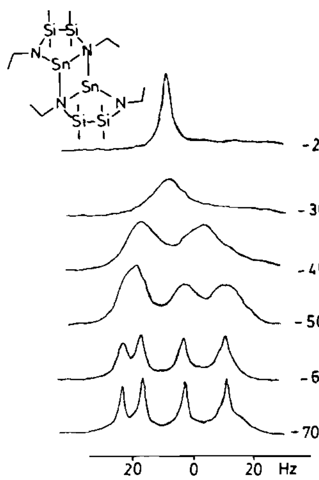


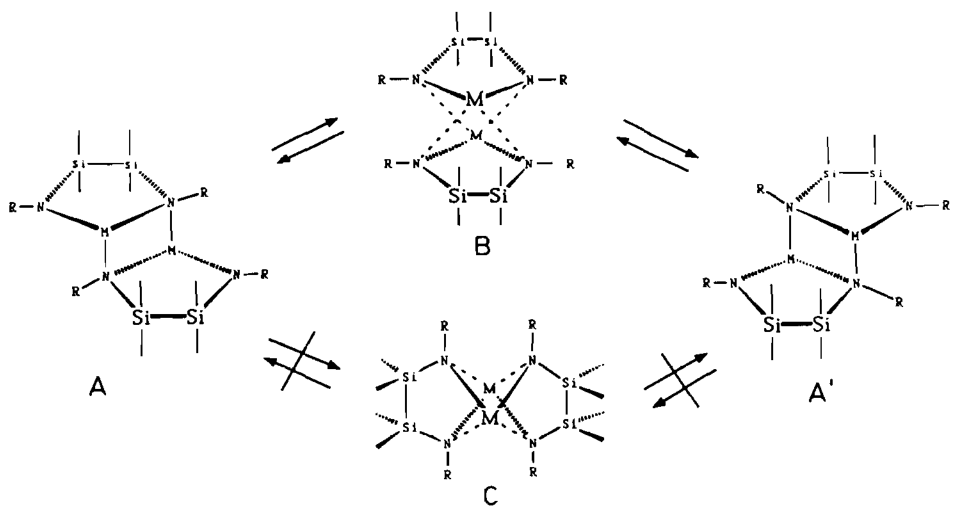
Fig. 6. 200 MHz ^{1}H NMR spectra of the MeSi groups of **3c** at various temperatures. The splitting of the ^{1}H resonances is in accord with the mechanism proposed in Scheme 1 for the intramolecular rearrangement.

Experimental

For all preparative work and handling of the products exclusion of air and traces of moisture was necessary. The starting materials were commercial products ($SnCl_2$, $PbCl_2$, Me_4Sn, Me_4Pb, $Cl–SiMe_2–SiMe_2–Cl$, $H_2N–CMe_2CH_2–NH_2$, $H_2N–CMe_2CH_2–NH–{}^iPr$, BuLi in hexane). From these compounds the educts (Me_2SnCl_2 [17], Me_2PbBr_2 [18], R–NH–$SiMe_2$–NH–R (R = ^{i}Pr, Et) [19], $Me_3Si–NH–CMe_2CH_2–NH–SiMe_3$ [20], $Me_3Si–NH–CMe_2CH_2–NH–{}^iPr$ [20]) were prepared following standard procedures. NMR measurements (see also Tables 1–3 and Figs. 1–6): Jeol FX90Q, Bruker AC 200, Bruker AC 300 and Bruker MSL 400. Mass spectra (EI, 80 eV): Varian MAT CH 7.

1,3-Dialkyl-4,4,5,5-tetramethyl-1,3,4,5,2λ²-diazadisilastannolidines (3) and -plumbolidines (4)

In a two-necked flask, under N_2 atmosphere, a freshly prepared suspension of 8 mmol of the dilithiated 1,2-bis(alkylamino)-tetramethyldisilane in 50 ml of ether/hexane (≈1:1) is stirred and cooled to −78 °C. After addition of solid $SnCl_2$ (1.5 g, 8.0 mmol) or $PbCl_2$ (2.22 g, 8.0 mmol) the yellow coloured mixture is warmed up to room temperature and stirred for 2 h. All solvents are removed *in vacuo*, 50 ml of hexane are added and the precipitate is filtered off and washed with hexane. After removing the hexane from the filtrate, the crude products are left in ≈40 to 90% yield. Further purification by



Scheme 1.

distillation is possible but the yield may be considerably reduced owing to extensive decomposition.

3b: b.p. 71 °C/1.33 torr; yield 49%; yellow solid; MS: 350 (M^+, 5%). *Anal.* Calc. for $C_{10}H_{26}N_2Si_2Sn$: C, 34.4; H, 7.5; N, 8.0. Found: C, 33.3; H, 7.7: N, 8.0%.

3c: b.p. 95 °C/0.13 torr; yield 47%; yellow solid; MS: 322 (M+, 3%).

4b: yield 54%; yellow solid; decomposes > 60 °C.

4c: yield 43%; yellow solid; decomposes > 60 °C.

*Dimeric 5,5-dimethyl-1-trimethylsilyl-3-(R)-1,3,2λ^2-diazastannolidines (**5**) and -plumbolidines (**6**)*

A solution of 10.0 mmol of the respective ethylenediamine (R = Me_3Si, ${}^iPr$) in 50 ml of toluene is treated with 20 mmol of BuLi (1.6 M in hexane) at 25 °C. The mixture is kept at reflux for 3 h. A suspension of the dilithiated ethylenediamine results which is ready for further reactions. Addition of 10 ml of THF to this suspension affords a clear solution which is then cooled to 0 °C. A solution of $SnCl_2$ (1.89 g, 10.0 mmol) in 20 ml of THF, or a suspension of $PbCl_2$ (2.78 g, 10.0 mmol) in 20 ml of THF, is added and the resulting mixture is stirred at room temperature for 3 h. The solvents are removed *in vacuo*, 50 ml of hexane are added and the insoluble material is filtered off. When the solvent is removed from the filtrate the products **5** and **6** are obtained as colourless to yellowish non-crystalline powders.

5a: yield 78%; m.p. 150–152 °C; light yellow solid.

5b: yield 65%; m.p. 148–150 °C; light yellow solid.

6a: yield 48%; m.p. 118–120; colourless solid.

6b: yield 45%; m.p. 125 °C, decomposes; colourless solid.

*3-Isopropyl-2,2,5,5-tetramethyl-1-trimethylsilyl-1,3,2-diazastannolidine (**8**) and -plumbolidine (**9**)*

The dilithiated ethylenediamine derivative (as described for **5**, **6**) (10.0 mmol) is cooled to −78 °C and a solution of Me_2SnCl_2 (2.20 g, 10 mmol) in 10 ml of ether, or a suspension of Me_2PbBr_2 (3.97 g, 10.0 mmol) in 10 ml of ether is added. After warming the reaction mixture to room temperature and heating to reflux for 3 h, insoluble material is filtered off. The solvents are removed from the filtrate *in vacuo* and fractional distillation of the residue gives 2.0 g (37%) of **8** as a colourless liquid, b.p. 58 °C/0.2 torr, or 2.3 g (52.5%) of **9** as a yellow liquid, b.p. 68 °C/0.1 torr.

Acknowledgments

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