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Multinucleus NMR characterization of new silylamines and their corresponding lithium silylamides

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Abstract

A series of linear silylamines R′Me$_2$Si–NMe–SiMe(R)–NHMe (R, R′ = Me, Vi or Ph) has been synthesized, as well as their corresponding lithium silylamides. They all have been analyzed by ^{1}H-, ^{13}C-, ^{29}Si-, ^{15}N- and ^{7}Li-NMR, in order to characterize the changes of electronic density in the molecules induced either by the silicon group or by the formation of the negative charge on the nitrogen atom. These changes give information about the nature of the [Si–N] or [Si–C] bonds. More particularly, a strong influence of the vinyl group on [–MeViSi–NHMe] has been observed, both in the silylamine and the corresponding silylamide. Indeed, in this case, the variations of the chemical shifts might be related to a 'delocalization' of the negative charge from nitrogen to silicon and the vinyl group. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silylamine; Lithium silylamide; NMR characterization

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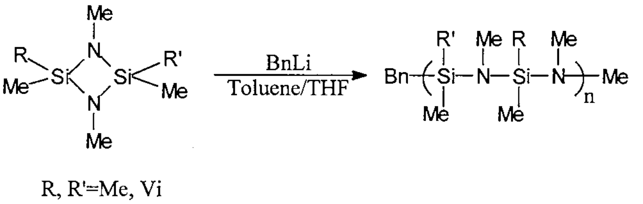
1. Introduction

We recently reported a comprehensive kinetic study on the polymerization of cyclodisilazanes [1,2] (Scheme 1), in toluene or THF/toluene, initiated by benzyl lithium. Under specific conditions, this polymerization can be controlled and considered as living. Although we have been able to show that the active center is a nitranion, its precise characterization was impossible on the growing chain, because of its too-low concentration in the reaction medium. Nevertheless, the silicon substituent R has been shown to have a strong effect on the kinetics of the polymerization [3]. Since a polymerization implies a step-reaction between the growing chain bearing the active center and the monomer, an interesting question is to locate the origin of the reactivity modification: by changing the silicon substituent, which one of the active center or the monomer reactivity is the most affected? An attractive solution to this problem was to modelize the active center, synthesizing organosilicon molecules with various groups on the silicon atom. These models could then be analyzed, mainly by NMR of the different nuclei. Therefore, this paper presents both the synthesis of new linear silylamines (**1**)–(**5**) and their corresponding nitranions (**1**$^-$)–(**5**$^-$) (Scheme 2), as well as their multinucleus NMR characterization.



Scheme 1. Polymerization of cyclodisilazanes.

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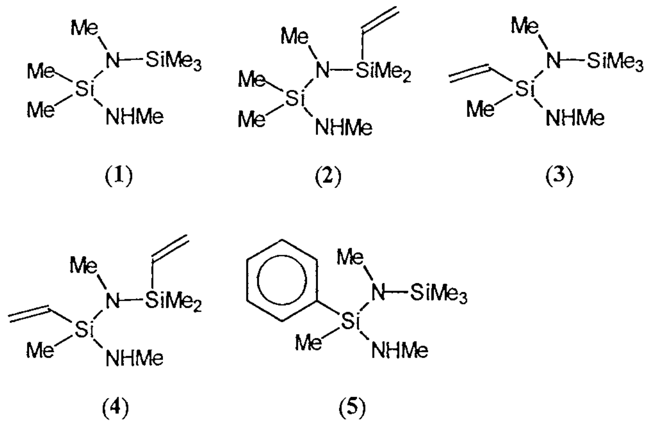


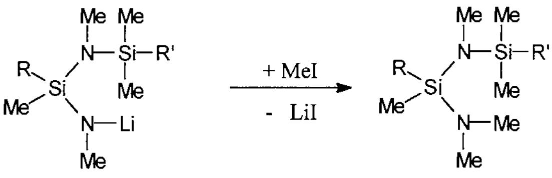
Scheme 2. Linear silylamines (1)–(5).

2. Results and discussion

The silylamines have been prepared in two steps (Scheme 3) according to the method used for the synthesis of cyclodisilazanes [4]. In a first step, methylamine is condensed with a dichlorosilane, forming a bis(methylamino)silane (7). After deprotonation of only one methylamine group by methyl lithium, the corresponding nitranion (7^-) is reacted with a chlorosilane, leading to the expected silylamine.

The nitranions (1^-)–(5^-) have been obtained by deprotonation of the corresponding silylamines by methyl lithium or butyl lithium. The stability of (1^-)–(5^-) has been checked, first by GC, following the evolution of the product of their reaction with methyliodide (Scheme 4), then by NMR, since some of the spectra have been repeated with a few months in-between. No evolution of these compounds has been detected in either cases.

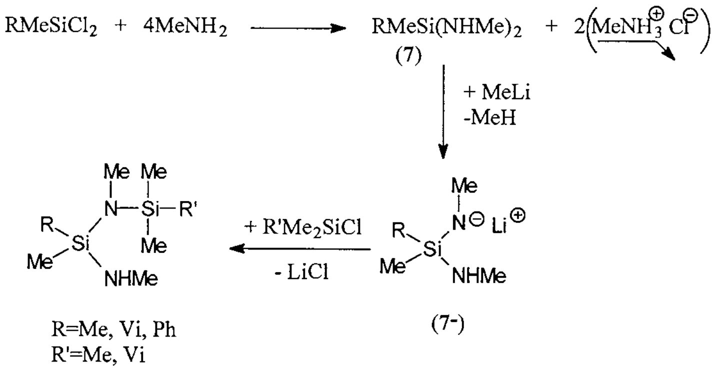
The NMR spectra have been recorded in two different solvents: toluene and a mixture of toluene/THF (50/50 vol./vol.), in order to modelize the two reaction media used for the polymerizations of cyclodisilazanes [1]. The results are presented in Tables 1–10. In most cases, the molecules behave similarly in both solvents, although the chemical shift variations between protonated silylamines and the corresponding nitranions are often enhanced in the presence of THF.



Scheme 4. Stability checks for (1^-)–(5^-).

Two different characteristics have to be analyzed: the effect of deprotonation for the same molecule (i.e **1** compared with **1**$^-$) and the effect of the silicon group substitution for the same type of molecules (i.e **3** or **5** compared with **1**). In the first part of this paper, we will examine the changes induced by the deprotonation itself and then, in the second part, we will briefly discuss the effect of substitution for the silylamines.

First, the analysis of the ^{1}H-NMR spectra (Tables 1 and 2) reveals the disappearing of the [N$\underline{H}$] signal upon deprotonation and the corresponding N-methyl signal changes from a doublet ($^3J = 6.5$ Hz) to a singlet that is shifted downfield. Among all proton signals, the ones close to the charge are of course the most modified, but it is also noteworthy that atoms even far away from the charge are influenced by its appearance. Compared with the silylamines (**1**)–(**5**), the *N*-methyl *t*-butylamine (**6**) undergoes the largest modification in the ^{1}H-NMR spectra, especially in THF/toluene, upon transformation in (**6**$^-$). This difference of behavior between silylamine and alkylamine can be explained by the specificity of the silicon-containing molecules. Indeed, it is well-known that silicon atoms can be involved in $(p \rightarrow d)_\pi$ interactions, particularly in silazanes or vinylsilanes [5,6]. For (**6**), the negative charge is well localized and has no possibility to 'delocalize'; for silylamines, the presence of the silicon atom enables this 'delocalization' through $(p \rightarrow d)_\pi$ interactions.



Scheme 3. Two step preparation of the silylamines.

Table 1
^{1}H-NMR chemical shifts of silylamines and silylamides in toluene-d8 at 20°C (in ppm relative to TMS)

	$\underline{\text{Me}}$–SiN$_2$ or $\underline{\text{CH}}_3$–C	$\underline{\text{Me}}$–Si–N	N$\underline{\text{H}}$Me	NH$\underline{\text{Me}}$ or NLi$\underline{\text{Me}}$	N$\underline{\text{Me}}$	$\underline{\text{CH}}$= or o-H	H(1) vinyl[a] or m-H	H(3) vinyl[a] or p-H
1	0.03	0.1	0.55	2.35	2.4			
1$^-$	0.35	0.36	—	3.03	2.72			
2	0.09	0.2		2.35	2.44	6.22	5.91	5.7
2$^-$	0.22	0.24	—	2.88	2.5	6.24	5.93	5.69
3	0.12	0.14	0.58	2.37	2.43	6.11	5.81	5.73
3$^-$	0.39	0.35		3.01	2.77	6.5	6.06	5.88
4	0.24	0.31		2.48	2.56	6.22 (extremity)	6.0	5.79
						6.32 (center)	6.03	5.85
4$^-$	0.3	0.22	—	2.84	2.5	6.32	5.92	5.68
							5.93	5.76
5	0.3	0.12		2.41	2.45	7.54	7.21	7.21
5$^-$	0.54	0.14	—	2.86	2.57	7.7	7.2–7.4	7.2–7.4
6	0.94		0.5–0.9	2.14				
6$^-$	0.8–1.6		—	2.22–2.8				

[a] H(1) is the hydrogen atom in the *cis* position with [CH=]. H(3) is in the *cis* position with the silicon atom.

Table 2
^{1}H-NMR chemical shifts of silylamines and silylamides in toluene-d8/THF-d8 at 20°C (in ppm relative to TMS)

	$\underline{\text{Me}}$–SiN$_2$ or $\underline{\text{CH}}_3$–C	$\underline{\text{Me}}$–Si–N	N$\underline{\text{H}}$Me	NH$\underline{\text{Me}}$ or NLi$\underline{\text{Me}}$	N$\underline{\text{Me}}$	$\underline{\text{CH}}$= or o-H	H(1) vinyl or m-H	H(3) vinyl or p-H
1	0.19	0.25	0.65	2.55	2.59			
1$^-$	0.15	0.24	—	2.92	2.69			
2	0.1	0.22	0.4–0.8	2.45	2.49	6.23	5.92	5.71
2$^-$	−0.03	0.13	—	2.75	2.51	6.18	5.8	5.62
3	0.22	0.23	0.68	2.55	2.59	6.21	6.02	5.84
3$^-$	0.24	0.27	—	2.96	2.73	6.44	5. 95	5.77
4	0.2	0.26	0.4–0.8	2.48	2.53	6.19 (extremity)	5.96	5.75
						6.28 (center)	5.98	5.81
4$^-$	0.25	0.25	—	2.0–3.2	2.0–3.2	5.2–6.5	5.2–6.5	5.2–6.5
5	0.26	0.07	0.7–0.9	2.44	2.44	7.51	7.19	7.19
5$^-$	0.26	0.04	—	2.76	2.64	7.54	7.17	7.17
6	0.94		0.58	2.17				
6$^-$	0.8–1.5		—	2.91				

In ^{13}C-NMR spectra (Tables 3 and 4), the same observations can also be made. The changes in [NH$\underline{\text{Me}}$] signals are of course more important than for [Si–N$\underline{\text{Me}}$–Si], which is further in the molecule. It is noteworthy that the vinyl group on the second silicon atom also exhibits some noticeable NMR shifts. Whereas the [MeNH–Si$\underline{\text{C}}$H=] signal in (**3**) and (**4**) is shifted downfield, the vinyl [=$\underline{\text{C}}$H$_2$] signal is the only one to be shifted upfield. Apparently, the charge on the nitrogen is then 'delocalized' and concentrated on the vinyl extremity [=CH$_2$]. As for the substitution of silicon atom with a phenyl group ((**5**) and (**5**$^-$)), the major change in the ^{13}C-NMR seems to be for the phenyl carbon next to the silicon, which is shifted downfield. Only a small effect is observed on the p-carbon atom, which is shifted upfield.

Contrary to all these results, ^{29}Si-NMR signals are shifted upfield (Tables 5 and 6). ^{29}Si-NMR chemical shift analysis is not as straightforward as ^{13}C or ^{1}H ones. Indeed, there is no simple relationship between the electroattracting (or electrodonating) character of a group and the ^{29}Si-NMR shift. For example, Filleux-Blanchard et al. have shown that the chemical shift of silicon decreases when a methyl group is substituted by a vinyl or a phenyl group [7]. This is explained by the reinforcement of the $(p \rightarrow d)_\pi$ interaction due to electroattracting groups.

Moreover, they have studied compounds with dialkylamino groups [R$_2$N–Si–] and they have observed a simultaneous increase in the electrodonating effect of the R group and the upfield shift of ^{29}Si-NMR signal. In the

Table 3
^{13}C-NMR chemical shifts of silylamines and silylamides in toluene-d8 at 20°C (in ppm relative to TMS)

	Me–SiN$_2$ or CH$_3$–C	Me–Si	NHMe or NLiMe	NMe	CH= or C$_{Ph}$–Si	=CH$_2$ or *o*-C	*m*-C	*p*-C
1	−0.5	1.2	27.6	30.5				
1$^-$	0.9	1.1	33.3	31				
2	0.31	0.33	28.4	31.5	141.7	131.6		
2$^-$	1.8	0.28	34.5	32.2	140. 9	132.5		
3	−2.0	1.2	27.7	30.7	139.1	131.9		
3$^-$	−1.2	1.3	33.0	30.8	143.6	128.1		
4	−1.26	0.3	28.5	31.6	141.5 (extremity) 139.7 (center)	131.7 (extremity) 132.8 (center)		
4$^-$	−1.14	0.12	34.1	32.1	141.4; 143.7	129.2; 132.3		
5	−0.7	1.9	28.8	31.8	140.4	135.1	128.6	130.0
5$^-$	1.8	1.8	34.3	32.4	142.7–143.8	134.9–135.2	129.0	129.0
6	29.6 (Me) 50.8 (C–N)		29.8					
6$^-$	31.9 (Me) 53.3 (C–N)		35.9					

Table 4
^{13}C-NMR chemical shifts of silylamines and silylamides in toluene-d8/THF-d8 at 20°C (in ppm relative to TMS)

	Me–SiN$_2$ or CH$_3$–C	Me–Si	NHMe or NLiMe	NMe	CH= or C$_{Ph}$–Si	=CH$_2$ or *o*-C	*m*-C	*p*-C
1	−0.7	0.9	27.4	30.3				
1$^-$	1.2	1.3	32. 8	30.3				
2	0.25	0.25	28.5	31.5	141.9	131.6		
2$^-$	2.7	1.2	34.4	32.1	143.7	131.0		
3	−2.2	1.0	27.6	30.5	139.1	131.6		
3$^-$	−0.7	1.3	32.8	30.3	144.9	127.6		
4	−1.4	0.7	28.6	31.9	141.9 (extremity) 140.3 (center)	132.1 (extremity) 133.2 (center)		
4$^-$	0.12	0.61	33.8	31.5	142.9; 145.7	128.7–130.5		
5	−0.7	1.91	28.9	31.8	140.7	135.2	128.7	130
5$^-$	1.34	2.01	34.0	31.7	147.2	135.1	128.1–128.7	128.1–128.7
6	29.4 (Me) 50.8 (C–N)		29.9					
6$^-$	32.1 (Me) 53.4 (C–N)		36.2					

mean time, a downfield shift of ^{15}N-NMR signal was recorded. This means that $(p \to d)_\pi$ interactions are maximum in this case.

In our case, almost all ^{29}Si-NMR signals are shifted upfield, implying that silicon environment is electron-enriched by the deprotonation process.

Also noteworthy is the important changes in the silylamide chemical shifts observed when toluene is replaced by toluene/THF mixture. In the presence of THF, the electronic density on silicon atoms is enhanced. Since we have shown that in apolar medium, silylamides are aggregated, whereas they are not in the presence of THF [1], it can be assumed that the THF molecules tend to dissociate more the ion pair, reinforcing the charge on the silylamide. This charge is then more 'delocalized' onto the silicon atoms.

An interesting comparison can be made at this point. Whereas all ^{29}Si-NMR signals are shifted upfield, the ^{13}C-NMR signal for *q*-carbon [C–N] of (**6**) is shifted downfield (Table 4), which indicates a decrease of the electronic density around the carbon. In this case, no $(p \to d)_\pi$ interaction is possible and the charge would remain localized on the nitrogen atom.

Almost all ^{15}N-NMR analyses of silylamides were impossible in pure toluene, probably because of the presence of aggregates (Tables 7 and 8). Since the ^{15}N-NMR is particularly difficult to observe, a multiplication of existing environments is really harmful. Usable ^{15}N-NMR spectrum was only obtained for (**3**$^-$). The chemical shift modifications are similar in pure toluene and in toluene/THF (when spectra could be obtained). Nevertheless, the interpretation of the spectra is rather complicated.

An upfield shift is observed for (**6**) and (**2**), which is expected for atoms which get richer in electrons, whereas in the case of (**1**) and (**3**), a downfield shift is observed. It is somewhat surprising that (**1**) and (**2**) do not behave the same way, since the groups on the silicon next to the charge are the same. According to the very weak signals observed in some cases (particularly in (**2**)), one can not exclude that some of the signals might not be correct or that only part of the nitrogen atoms were observed. Anyhow, the observed downfield shift for (**1**) and (**3**) could be explained by the delocalization of the nitrogen charge to the silicon and/or the vinyl group.

^{7}Li-NMR give hints about the aggregation pattern. Generally, the value of chemical shifts in toluene/THF is lower than in pure toluene (Tables 9 and 10). Since nitranionic species become less aggregated in polar medium, this result corroborates previous observations that δ_{Li} increases with aggregation [8–10]. Some examples in the literature show the possibility of separating the different signals assigned to the different aggregates by lowering the temperature [9]. In our case, this only broadened the lithium signal because of a strong increase of the solution viscosity (e.g. the half-height width changes from 23 Hz at ambient temperature to 93 Hz at 243 K for (**4**$^-$)) (Fig. 1).

Table 5
^{29}Si-NMR chemical shifts of silylamines and silylamides in toluene-d8 at 20°C (in ppm relative to TMS)

	N–$\underline{\text{Si}}$–N	$\underline{\text{Si}}$–N
1	−2.9	5.4
1$^-$		
2	−3.2	−2.6
2$^-$	−2.6	−2.0
3	−12.6	6.1
3$^-$	−15.2; −14.8	4.9
4	−12.4	−2.7
4$^-$	−12.9	−3.9
5	−10.7	6.2
5$^-$	−11.4	7.02

Table 6
^{29}Si-NMR chemical shifts of silylamines and silylamides in toluene-d8/THF-d8 at 20°C (in ppm relative to TMS)

	N–$\underline{\text{Si}}$–N	$\underline{\text{Si}}$–N
1	−2.9	5.6
1$^-$	−9.4	2.3
2	−3.3	−2.8
2$^-$	−11	−7.2
3	−12.9	5.9
3$^-$	−17.7	2.8
4	−12.5	−2.75
4$^-$	−19	−6.4
5	−10.2	7.9
5$^-$	−16.1	3.1

Table 7
^{15}N-NMR chemical shifts of silylamines and silylamides in toluene-d8 at 20°C (in ppm relative to $MeNO_2$)

	Si–$\underline{\text{N}}$HMe or Si–$\underline{\text{N}}$LiMe or C–$\underline{\text{N}}$	Si–$\underline{\text{N}}$–Si
1	−370.0	−368.4
1$^-$		
2	−367.3	−367.6
2$^-$		
3	−372.3	−370.1
3$^-$	−367.7	−366.3
4	−369.5	−369.6
4$^-$		
5	−368.9	−367.5
5$^-$		
6	−331.2	0
6$^-$		

Table 8
^{15}N-NMR chemical shifts of silylamines and silylamides in toluene-d8/THF-d8 at 20°C (in ppm relative to $MeNO_2$)

	Si–$\underline{\text{N}}$HMe or Si–$\underline{\text{N}}$LiMe or C–$\underline{\text{N}}$	Si–$\underline{\text{N}}$–Si
1	−370.5	−368.4
1$^-$	−365.9	−365.6
2	−367.0	−367.4
2$^-$	−370.3	−370.3
3	−373.0	−370.3
3$^-$	−367.9	−366.9
4	−370.3	−369.5
4$^-$		
5	−368.9	−367.0
5$^-$		
6	−331.0	
6$^-$	−333.8	

Nevertheless, lowering the temperature of the NMR analysis induces significant changes in the ^{29}Si-NMR spectra. In the case of (**4**$^-$), new signals appear around − 12 and − 1 ppm in addition to the original signals at − 12.9 ([N–$\underline{\text{Si}}$(Me)(Vi)–N]) and − 3.9 ppm ([$Me_2Vi\underline{\text{Si}}$–N]) (Fig. 2). This might be related to the slowdown of equilibrium between aggregates with decreasing temperature.

An additional study has been realized on (**3**$^-$). Its NMR spectra have been recorded in the presence of increasing quantities of THF, ([THF]/[$\mathbf{3}^-$] = 0–5). In this case, only the most relevant NMR changes will be discussed (i.e. silicon and lithium chemical shifts). Results are presented in Table 11. In the polymerization of cyclodisilazanes, we were able to show that only one molar equivalent of THF (relative to the active centers) was needed to break the aggregates of ion pairs [1,2]. The ^{29}Si-NMR spectra tend to corroborate this result, since a significant upfield shift of [Si] chemical shift is observed, even for this low value of one equivalent (Fig. 3).

The evolution of ^{7}Li-NMR spectra is more complex (Table 11). Small quantities of THF induce a downfield shift up to one molar equivalent. Afterwards, the chemical shift decreases. At this time, this observation remains unexplained.

So, the deprotonation process of the studied silylamines leads to a reorganization of the electronic densities, particularly when vinyl groups are present. Considering the results obtained with the silylamines (**1**), (**3**) and (**5**), the effect of substituting a methyl group on silicon by a vinyl or a phenyl one can be enlightened.

In ^{1}H-NMR spectra, the chemical shift for [R–Si–$\underline{\text{Me}}$] increases as R is changed from methyl to vinyl and phenyl groups. This indicates a decrease in electronic density that is easily explained by the presence of electron-attracting groups. The same pattern is observed for the [NH$\underline{\text{Me}}$] chemical shift.

In ^{13}C-NMR analysis, the two main features are the low chemical shift of the [$\underline{\text{Me}}$–Si–vinyl] signal and the high one for [NH$\underline{\text{Me}}$] in (**5**) compared with (**1**) and (**3**). The former observation points out a higher electron density on the methyl group in [Me–Si–vinyl], compared with [Me–Si–Me] and [Me–Si–phenyl]. Since this higher density hardly comes from the methylamino group (δ_{NHMe} (**3**) and δ_{NHMe} (**1**) are similar), it can be assumed that this is partly coming from the vinyl group itself, as already reported by Delmulle [11]. In this case apparently, the phenyl group does not act the same way. From the chemical shift of the [NH$\underline{\text{Me}}$] group in (**5**), which is shifted downfield compared with (**1**) and (**3**), it can be inferred that in this compound (**5**), the $(p \rightarrow d)_\pi$ interaction through [Si–N] bond is maximum.

Table 9
^{7}Li-NMR characteristics of silylamides in toluene-d8 at 20°C (ppm relative to $LiClO_4$)

	δ (ppm)	$W_{1/2}$ (Hz)
$\mathbf{1}^-$	−2.21	21.8
$\mathbf{2}^-$	1.28	35.8
$\mathbf{3}^-$	−2.25; −2.8	19.8; 30
$\mathbf{4}^-$	1.25	25.8
$\mathbf{5}^-$	1.41	69.0
$\mathbf{6}^-$	−1.40	26.1

Table 10
^{7}Li-NMR characteristics of silylamides in toluene-d8/THF-d8 at 20°C (ppm relative to $LiClO_4$)

	δ (ppm)	$W_{1/2}$ (Hz)
$\mathbf{1}^-$	−2.49	16.7
$\mathbf{2}^-$	−0.29	13.9
$\mathbf{3}^-$	−2.40	21.1
$\mathbf{4}^-$	−0.39	15.6
$\mathbf{5}^-$	1.09	23.1
$\mathbf{6}^-$	−1.42	8.7

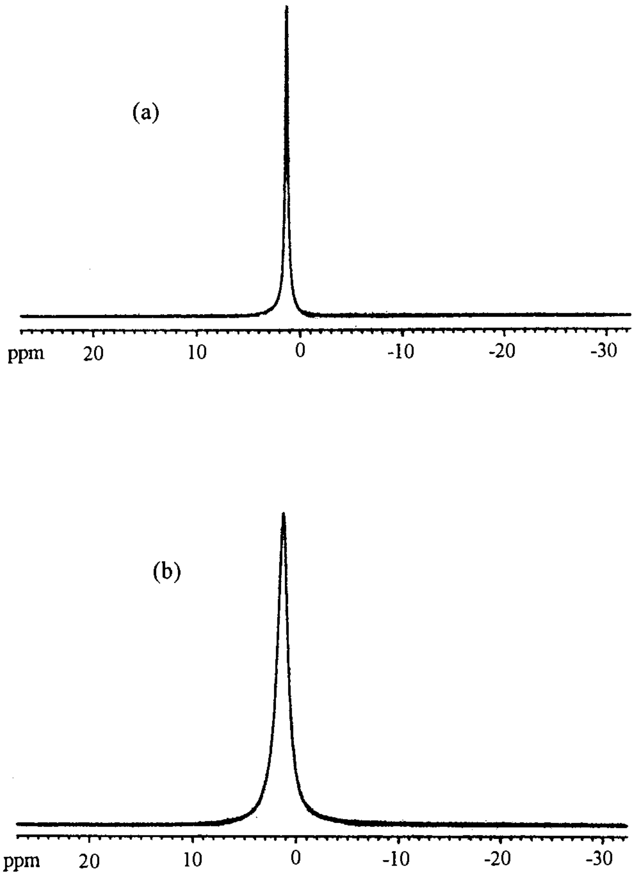


Fig. 1. ^{7}Li-NMR spectra of ($\mathbf{4}^-$) in toluene-d8; (a) at 20°C, (b) at − 30°C.

In the ^{29}Si-NMR spectra, the lowest chemical shift is observed for (**3**). This can be related to the position of the medium silicon atom, which is exposed to two types of $(p \rightarrow d)_\pi$ interactions, the weakest from the methylamino group and the strongest from the vinyl group.

The ^{15}N-NMR spectra lead to useful information. The highest shift is observed for (**5**) and the lowest for (**3**). Thus, the electronic density on the nitrogen of [NHMe] in (**5**) is lower than that of nitrogen in (**1**); on the contrary, that of nitrogen in (**3**) is the highest. This corroborates the fact that the $(p \rightarrow d)_\pi$ interaction through [Si–N] bond is maximum in (**5**) and minimum in (**3**), where the $(p \rightarrow d)_\pi$ interaction coming from the vinyl group is much greater than that coming from the methylamino group.

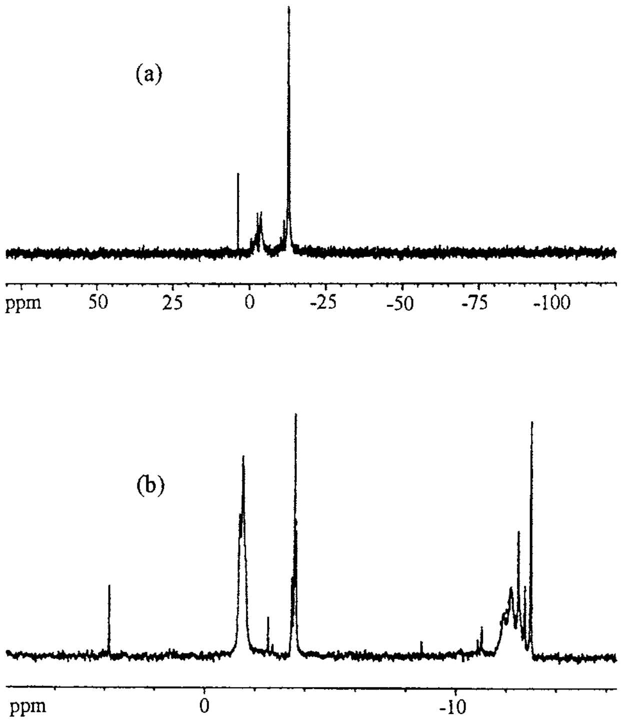


Fig. 2. ^{29}Si-NMR spectra of ($\mathbf{4}^-$) in toluene-d8; (a) at 20°C, (b) at − 30°C.

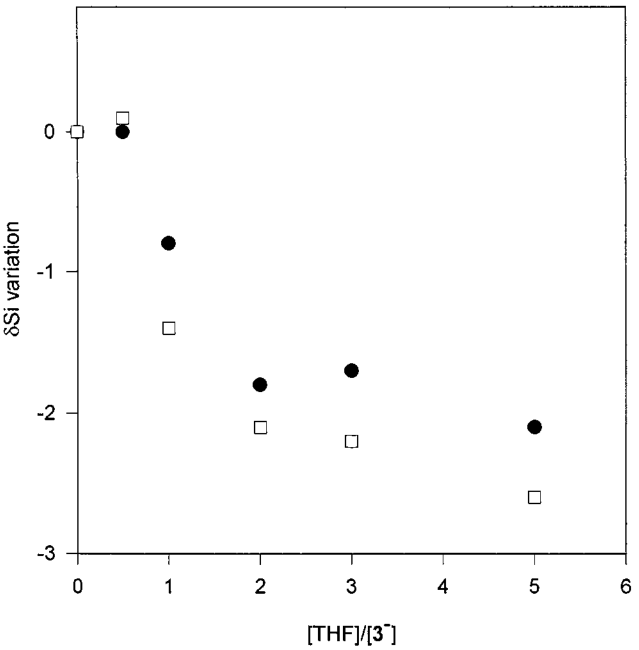


Fig. 3. Variations of ^{29}Si-NMR chemical shifts of ($\mathbf{3}^-$) with various amounts of THF at 20°C; (●) $\Delta\delta_{Si}$ for [Me_3Si], (□) $\Delta\delta_{Si}$ for [MeViSi].

3. Experimental

Dichlorosilanes and chlorosilanes (Roth-Sochiel) were stirred in the presence of magnesium for 18 h and trap-to-trap distilled. *N*-methyl *t*-butylamine (Aldrich) was stored on magnesium. Methylamine (Fluka), methyl lithium (Merck) and butyl lithium (Aldrich) were used without further purification. Bisaminosilanes (**7**) were prepared according to a previously published procedure [4]. Diethylether was distilled on CaH_2, toluene was distilled on sodium benzophenone and stored on a sodium mirror under high vacuum. Toluene-d8 and THF-d8 (SDS) were stored on sodium mirrors and trap-to-trap distilled.

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC 200 at 200 and 50.32 MHz, respectively. ^{29}Si- and ^{7}Li-NMR were carried out on a Bruker DPX200 at 39.8 and 77.77 MHz, respectively. ^{15}N-NMR was realized on a Bruker DPX400 at 20.28 MHz. All experiments were realized in 5 mm NMR tubes, except those for ^{15}N-NMR of nitranions, which were carried out in 10 mm tubes.

MS spectra were realized on an AutospecEQ spectrometer (electron impact mode, 70eV). GC chromatograms were realized on a DELSI DI 200 apparatus, equipped with a thermal conductibility detector using a macrobore column DB-1 (15 m × 0.53 mm). The program of temperature started at 50°C, for 2 min, and increased up to 240°C at 10°C min^{-1}.

3.1. Synthesis of silylamine (*1*)

A 250-ml three-necked flask equipped with a septum, a dropping funnel, a condenser topped with a gas outlet tube and a magnetic stirrer was flame-dried and charged with 7.6 g of bis(methylamino) dimethylsilane

Table 11
Influence of THF quantity on chemical shifts for ($\mathbf{3}^-$) at 20°C[a]

THF quantity (mol. eq.)	$\delta\underline{Si}Me_3$ (ppm)	$\delta\underline{Si}MeVi$ (ppm)	$\delta\underline{Li}$ (ppm)	$W_{1/2}$ (Hz)
0	4.9	−15.2/−14.8	−2.25/−2.80	19.8/30
0.5	4.9	−15.1	−2.08	15.2
1	4.1	−16.5	−2.06	17.3
2	3.1	−17.2	−2.16	18.7
3	3.2	−17.3	−2.38	23
5	2.8	−17.7	−2.4	21.1

[a] Chemical shifts relative to TMS for ^{29}Si-NMR and to $LiClO_4$ for ^{7}Li-NMR.

(0.065 mol) and 40 ml of diethylether. Through the funnel, methyl lithium (40 ml, 1.6 M) was added dropwise at 0°C over 30 min. The mixture was then stirred at 0°C for 2 h and 7 g of trimethylchlorosilane (0.065 mol) was then added dropwise at 0°C. The reaction mixture was stirred for 5 min and then allowed to settle. The supernatant liquid was recovered and the precipitated LiCl was washed with diethylether. Removal of the solvent in a rotatory evaporator was followed by vacuum trap-to-trap distillation of the crude product, leading to 6.9 g of (**1**) (56%).

The other silylamines (**2**)–(**5**) were synthesized following the same procedure starting from the corresponding bisaminosilanes. Yields ranged from 55 to 80%. The purity of the compounds was checked by GC and they were characterized by MS in addition to NMR.

EI MS; *m/z* 202 ($M^{+\bullet}$, 10); 187 ($M-CH_3$, 100); 171 (16); 158 (98); 146 (23); 73 (21); 59 (35).

EI MS; *m/z* 199 ($M-CH_3$, 100); 187(25); 170 (70); 158 (67); 142 (38).

EI MS; *m/z* 252 ($M^{+\bullet}$, 35); 237 ($M-CH_3$, 100); 208 (38); 121 (31).

3.2. Deprotonation of the amines

Compound (**2**) (0.28 g; 1.4 mmol) was introduced under nitrogen in a flame-dried reactor. Toluene (2 ml) was trap-to-trap distilled into this flask, which was then cooled to 0°C. BuLi (1.4 ml; 1.0M in pentane) was added under nitrogen. The mixture was then stirred at 0°C under vacuum for 2 h. Half of the solvent was removed by trap-to-trap distillation and the solution was poured into the NMR tube. After elimination of the remaining protonated solvent, deuterated solvents were trap-to-trap distilled into the NMR tube, which was then sealed under high vacuum.

The other amines have been deprotonated following the same procedure.

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