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Synthesis and chemical properties of 1,3-dichloro-1,3-dihydridodisilazanes

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Abstract

A trans-silylation route to 1,3-dichloro-1,3-dihydridodisilazanes, a novel class of polyfunctional disilazane, is described. Thus, heating hexamethyl- or heptamethyl-disilazane under reflux in the presence of an excess of dichlorohydrogenosilane R^1SiHCl_2, led to compounds of formula $(R^1ClHSi)_2NR^2$ (R^1 = Me, Et, Vi or Ph and R^2 = H; R^1 = Me and R^2 = Me) in high yield. The exchange of chlorinated organosilicon moieties was strongly facilited by a catalytic amount of $(^nBu_4N)F$. Interpretation of the results and a few chemical properties of these novel disilazanes are reported.

Key words: Silicon; Silazanes; Synthesis; Dichlorodisilazanes; Dihydridodisilazanes

1. Introduction

Since the pioneering work of Verbeek [1] and Yajima [2], considerable attention has focussed on research devoted to the preparation of silicon nitride- and silicon carbide-based ceramic materials by pyrolysis of organosilicon precursors. The properties of the final materials should strongly depend on factors such as the chemical composition and the backbone of the polymeric precursors. To improve our knowledge on the preparation of these ceramics and the mechanisms of their pyrolysis, the search for new polymers possessing well-defined backbones and suitable functional groups was necessary. Thus, we have reported a route for the preparation of novel poly(silylenesilazane) oligomers using original symmetrical 1,3-dichlorodisilazanes as the starting co-monomers [3–6]. We have shown that these oligomers can be thermally cross-linked and converted into polycarbosilazanes possessing $-CH_2-\overset{|}{\underset{|}{Si}}-\underset{|}{N}-$ links in the main backbone. In addition, they can be efficiently melt-spun affording, after hardening under various conditions and pyrolysis under an inert gas, small-diameter silicon carbonitride fibres exhibiting excellent thermomechanical properties [7,8].

In this paper, we report the preparation, the physico-chemical characterization and a few chemical properties of the starting 1,3-dichloro-1,3-dihydridodisilazanes.

2. Results and discussion

2.1. *Preparation of 1,3-dichloro-1,3-dihydridodisilazanes*

Alkyl-, aryl- and unsubtituted disilazanes are most commonly prepared by the condensation of two molecules of the corresponding monochlorosilane with ammonia or primary amines [9–11]. However, functional disilazanes are in a class of organosilicon compounds which are difficult to prepare. For example,

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attempts to obtain symmetrical 1,3-dichlorodisilazanes, *i.e.* disilazanes of structure $\mathrm{Cl{-}\overset{|}{\underset{|}{Si}}{-}\underset{|}{N}{-}\overset{|}{\underset{|}{Si}}{-}Cl}$, *via* the condensation of one Si–Cl bond of dichlorosilanes with ammonia were hitherto unsuccessful [12]. Kriegsmann *et al.* [13] succeeded in the preparation of $(ClMe_2Si)_2NH$, but only in poor yields, starting from $(PhMe_2Si)_2NH$. However, Silbiger and Fuchs [14] reported the first example of trans-silylation between hexamethyldisilazane and dimethyldichlorosilane involving replacement of the trimethylsilyl groups of the disilazane by chlorodimethylsilyl moieties in the presence of Al_2Cl_6 as the catalyst, leading to 1,3-dichloro-1,1,3,3-tetramethyldisilazane in good yield (eqn. (1))

$$2Me_2SiCl_2 + (Me_3Si)_2NH \xrightarrow[\text{refl.}]{Al_2Cl_6} (ClMe_2Si)_2NH + 2Me_3SiCl \quad (1)$$

(1)

They extended the trans-silylation reactions to cyclopolysilazanes $(Me_2SiNH)_x$ [15], and reactions involving various polychlorosilanes and silylamines or silazanes have been reported [16–20]. More recently, these reactions were used for the preparation of organosilicon ceramic precursors [21–23], including polymeric hydridochlorosilazanes [24].

Surprisingly, redistribution of Si–N and Si–Cl bonds has never been used for the preparation of disilazanes possessing both Si–H and Si–Cl bonds. Considering the large potential interest of these functional monomers in the field of organosilicon chemistry, we have investigated the trans-silylation reactions of hexamethyldisilazane in the presence of dichlorosilanes bearing alkyl, aryl and vinyl substituents.

We first re-examined the reaction between $(Me_3Si)_2NH$ and Me_2SiCl_2 without a catalyst. As reported previously [14], no reaction was observed, even in the presence of a large excess of dimethyldichlorosilane, but we have found that trans-silylation occurred smoothly with a catalytic amount of $(^nBu_4N)F$, yielding the expected 1,3-dichloro-1,1,3,3-dimethyldisilazane (**1**) in high yield after heating under reflux for a few hours. This result is consistent with previously reported work, since ammonium salts and fluoride ions catalyse redistribution of silylamino-derivatives and chlorosilanes [19,25].

We then have focussed our attention on the reaction with HMe_2SiCl and hexamethyldisilazane (eqn. (2))

$$2Me_2SiClH + (Me_3Si)_2NH \longrightarrow (HMe_2Si)_2NH + 2Me_3SiCl \quad (2)$$

(2)

With a small excess of chlorosilane (*i.e.* with a molar ratio of 2.5 : 1), but no catalyst, the reaction occurred slowly, and did not reach completion even after 48 h under reflux. Again, addition of a catalytic amount of $(^nBu_4N)F$ resulted in the fast and total conversion of hexamethyldisilazane to 1,1,3,3-tetramethyldisilazane (**2**).

Attempts to obtain intermediate mixed disilazanes by substitution of one trimethylsilyl group of hexamethyldisilazane, even in the absence of catalyst or upon changing the experimental conditions, for example, by lowering the temperature or using a deficiency of chlorosilane, were unsuccessful. In this last case, part of the starting hexamethyldisilazane did not react, and high boiling point products and undistillable oligomers were obtained. However, Silbiger and Fuchs had reported that the mixed chlorinated disilazane was obtained when aluminium chloride was used as the catalyst for the trans-silylation of hexamethyldisilazane and dichlorodimethylsilane [14].

To account for the enhancement in the disilazane reactivity in the presence of fluoride ion, we suppose that the first step of the reaction could be the formation of a fluorinated pentacoordinated organosilicon intermediate. The influence of hypervalent organosilicon intermediates on the catalysis of nucleophilic substitution at silicon has been extensively studied, especially by Corriu *et al.* [26]. Such hypervalent species could form more easily from dichlorosilane, since nucleophilic attack of F at silicon should be easier when electron-withdrawing chlorine atoms are attached to silicon. This feature might also facilitate subsequent nucleophilic attack at the trimethylsilyl group of hexamethyldisilazane followed by the release of trimethylchlorosilane, as depicted in eqns. (3) and (4).

$$\Sigma Me_2SiCl + (^nBu_4N)F \longrightarrow (^nBu_4N)^+(\Sigma Me_2SiClF)^- \quad (3)$$

$$(^nBu_4N)^+(\Sigma Me_2SiClF)^- + (Me_3Si)_2NH \longrightarrow (\Sigma Me_2Si{-}NH{-}SiMe_3) + Me_3SiCl + (^nBu_4N)F \quad (4)$$

$\Sigma = H$ or Cl

The substitution of the second trimethylsilyl group of the intermediate mixed disilazane might occur similarly, affording $(\Sigma Me_2Si)_2NH$.

Then, we have performed trans-silylation reactions using various dichlorohydrosilanes R^1SiHCl_2 ($R^1 = Me$, Et, Vi or Ph) and hexamethyl- or heptamethyl-disilazane, $(Me_3Si)_2NR^2$ ($R^2 = Me$ or H) (eqn. (5)).

$$2R^1SiHCl_2 + (Me_3Si)_2N{-}R^2 \longrightarrow (R^1ClHSi)_2N{-}R^2 + 2Me_3SiCl \quad (5)$$

The results are given in Table 1.

TABLE 1. Disilazanes prepared from trans-silylation of R^1SiHCl_2 and $(Me_3Si)_2NR^2$

R^1	R^2	Product no.	Yield (%)	b.p. (°C) (Torr)
Me	H	$(ClMe_2Si)_2N$-H **1**	60	75 (25)
Me	H	$(HMe_2Si)_2N$-H **2**	70	100 (760)
Me	H	$(ClHMeSi)_2N$-H **3**	95	41 (0.5)
Me	Me	$(ClHMeSi)_2N$-Me **4**	94	36 (0.5)
Et	H	$(ClHEtSi)_2N$-H **5**	94	50 (0.5)
Vi	H	$(ClHViSi)_2N$-H **6**	86	45 (0.5)
Ph	H	$(ClHPhSi)_2N$-H **7**	45	–

A small excess of methyldichlorosilane ($R^1 = CH_3$) reacts smoothly without catalyst with hexamethyldisilazane ($R^2 = H$) (molar ratio of 2.5 : 1), but the reaction does not reach completion even after some hours. The residual hexamethyldisilazane was detected by ^1H NMR spectroscopy. There were also resonances of the expected symmetrical disilazane, *i.e.* a doublet at 0.29 ppm (methyl groups) and a broad multiplet centred at 5.00 ppm (SiH protons). The intermediate mixed disilazane ($ClMeHSi$-NH-$SiMe_3$), was not observed. After longer reaction times, oligomeric products were also obtained. However, a catalytic amount of $(^nBu_4N)F$ immediately produced an exothermic reaction, and an increase in the reflux rate, and the trans-silylation reaction was complete after only a few hours, yielding compound **3**.

In contrast with methyldichlorosilane, in a molar ratio of 5 : 1, but no catalyst, disilazane **3** was obtained in quantitative yield after heating under reflux during 24 h.

From these observations, we infer that the first trimethylsilyl-group exchange may be reversible, as previously postulated for the redistribution reaction of aminosilanes and polysilazanes with chlorosilanes [19,23] (eqn. (6))

$$Me_3Si\text{-}NH\text{-}SiMe_3 + HR^1SiCl_2 \rightleftharpoons HR^1ClSi\text{-}NH\text{-}SiMe_3 + Me_3SiCl \quad (6)$$

Because silylamino moieties greatly prefer the most electron-deficient silicon [19], substitution of the second trimethylsilyl group of the intermediate disilazane by a mixed-silicon ligand containing both chlorine and nitrogen should lead to the expected symmetrical disilazane, the more stable product thermodynamically. This is consistent with the observed reactivity. According to the equilibrium eqn. (6), it is likely that this pathway could be easier with a large excess of chlorosilane. When a stoichiometric amount or a deficiency of chlorosilane is used, side reactions could occur. For instance, the intermediate mixed disilazane could undergo self-condensation or react with remaining hexamethyldisilazane, as depicted in eqns. (7) and (8).

$$2[HR^1ClSi\text{-}NH\text{-}SiMe_3] \longrightarrow HR^1ClSi\text{-}NH\text{-}HR^1Si\text{-}NH\text{-}SiMe_3 + Me_3SiCl \quad (7)$$

$$Me_3Si\text{-}NH\text{-}SiMe_3 + ClR^1HSi\text{-}NH\text{-}SiMe_3 \longrightarrow (Me_3Si\text{-}NH)_2SiR^1H + Me_3SiCl \quad (8)$$

The fact that high-boiling point products were found under these conditions supports this hypothesis.

On the basis of these results, disilazanes **3**–**7** were prepared conveniently and purified by distillation under high vacuum. However, disilazane **7** is thermally unstable, as it decomposed partly during distillation, resulting in an appreciably lower yield. This degradation is probably due to the $(^nBu_4N)F$ used as catalyst. Indeed, we have previously found that it facilitates

TABLE 2. ^1H NMR chemical shifts (200 MHz) and coupling constants of disilazanes [a]

Disilazane no.	$\delta(CH_3)$ (ppm)	$\delta(CH_2)$ (ppm)	δ(SiH) (ppm)	δ(N–H) (ppm)	$\delta(N\text{–}CH_3)$ (ppm)	δ(Vin) (ppm)	δ(Ph) (ppm)	$^3J(CH\text{–}SiH)$ (Hz)	$^3J(SiH\text{–}NH)$ (Hz)
1	0.28 (s)	–	–	1.2 (broad m)	–	–	–	–	–
2	0.16 (d)	–	4.74 (m)	– [b]	–	–	–	3.2	3.2
			4.76 (m)						
3	0.285 (d)	–	4.95 (dq)	1.2 (broad m)	–	–	–	2.50	5.0
	0.290 (d)	–	5.00 (dq)	–					
4	0.22 (d)	–	5.035 (q)	–	2.29 (s)	–	–	2.35	–
	0.23 (d)	–	5.050 (q)	–	2.28 (s)				
5	0.85 (m) [c]	0.63 (m)	4.92 (dt)	– [d]	–	–	–	2.25	5.5
			4.96 (dt)	– [d]					
6	–	–	5.15 (broad d)	1.2 (broad m)	–	5.83 (m)	–	– [e]	5.0
7	–	–	5.50 (d)	1.4 (broad m)	–	–	7.1 (m)	–	5.7
			5.55 (d)				7.5 (m)	–	5.3

[a] s = singlet, d = doublet, q = quartet, m = multiplet. [b] NH and CH_3(Si) overlapping signals. [c] A_3B_2 spectrum: $J(AB) = 7.7$ Hz. [d] NH and CH_3–CH_2 overlapping signals. [e] Not measured.

TABLE 3. ^{29}Si NMR data of disilazanes

Disilazane no.	δ(Si) (ppm)	^{1}J(Si–H) (Hz)	$^{2}J(\mathrm{Si–CH_3})$ (Hz)	^{2}J(Si–NH) (Hz)	^{3}J(Si–H) (Hz)
1	13.7	–	7.25	4	–
3	−5.2 −5.1	256.5	7.5	4.5	3.0
4	−0.75	251.0	7.5	–	[a]
5	−2.0 −1.75	257.0	–	[a]	[a]
6	−17.1 −17.2	275.5	–	[a]	[a]
7	−15.1 −15.2	259.5	–	[a]	[a]

[a] Not measured.

TABLE 4. IR Spectra of compounds **2–9**

Disilazane no.	Absorption bands (cm^{-1})
2	3380 m (νNH), 2960 s ($\nu \mathrm{aCH_3}$), 2900 w ($\nu \mathrm{sCH_3}$), 2110 vs (νSiH), 1420 w ($\delta \mathrm{aCH_3}$), 1250 s ($\delta \mathrm{sCH_3}$), 1170 s (γNH), 930 vs (νaSi–N–Si), 890 vs (δSiH), 840 m ($\rho \mathrm{CH_3}$), 760 m ($\nu \mathrm{SiCH_3}$)
3	3360 s (νNH), 2970 w ($\nu_a \mathrm{CH_3}$), 2200 s (νSiH), 1410 m ($\delta \mathrm{aCH_3}$), 1260 s ($\delta \mathrm{sCH_3}$), 1190 s (γNH), 950 s (νaSi–N–Si), 840 vs ($\rho \mathrm{CH_3} + \delta$SiH), 750 s ($\nu \mathrm{SiCH_3}$), 500 vs ($\nu$SiCl)
4	2970, 2950, 2900, 2820 w ($\nu \mathrm{CH_3}$), 2200 s (νSiH), 1410 vw ($\delta \mathrm{aCH_3}$), 1260 s ($\delta \mathrm{sCH_3}$), 1200 m, 1090, 1070 m (νCN), 950 vs (νaSi–N–Si), 850 vs ($\rho \mathrm{CH_3} + \delta$SiH), 750 m ($\nu \mathrm{SiCH_3}$), 500 s ($\nu$SiCl)
5	3360 s (νNH), 2960 vs ($\nu \mathrm{aCH_3}$), 2930 m ($\nu \mathrm{aCH_2}$), 2880 s ($\nu \mathrm{sCH_3}$), 2190 vs (νSiH), 1460 m ($\delta \mathrm{CH_2}$), 1240 m ($\mathrm{wCH_2}$), 1180 vs (γNH), 1010 m ($\mathrm{CH_2H_5}$), 970–950 vs (νaSi–N–Si + $\mathrm{C_2H_5}$), 810 vs (δSiH), 700 m ($\rho \mathrm{CH_2}$), 510 vs (νSiCl)
6	3360 s (νNH), 3150, 3050, 3020 w ($\nu \mathrm{CH_{eth}}$), 2200 vs (νSiH), 1600 m (νC=C), 14010 s ($\delta \mathrm{CH_2}$), 1190 vs (γNH), 1005 m (*trans* $\mathrm{wCH_{eth}}$, 950 vs (νaSi–N–Si + $\mathrm{wCH_2}$), 820 vs (δSiH + $\rho \mathrm{CH_3}$), 720 w ($\nu \mathrm{SiCH_3}$), 550 vs (νSiCl + $\gamma \mathrm{CH_{eth}}$)
7	3370 s (νNH), 3130, 3080, 3050, 3020 m ($\nu \mathrm{CH_{Ar}}$), 2200 vs (νSiH), 1960, 1900, 1830, 1780 vw (Ph ring overtones), 1590, 1490 w, 1430 s ($\nu \mathrm{CC_{Ar}}$), 1340 vw ($\delta \mathrm{CH_{Ar}}$), 1310 vw ($\nu \mathrm{CC_{Ar}}$), 1190–1180 vs (γNH + $\delta \mathrm{CH_{Ar}}$), 1120s ($\delta \mathrm{CH_{Ar}}$) 1000 vw ($\delta \mathrm{CCC_{Ar}}$), 945 vs (νaSi–N–Si + $\gamma \mathrm{CH_{Ar}}$), 830 vs (δSiH + $\rho \mathrm{CH_3}$ + $\gamma \mathrm{CH_{Ar}}$), 740 m ($\nu \mathrm{SiCH_3}$), 700 m ($\gamma \mathrm{CH_{Ar}}$), 620 vw ($\delta \mathrm{CCC_{Ar}}$), 530 s (νSiCl)
8	2960 m ($\nu \mathrm{CH_3}$), 2150 vs ($\nu \mathrm{SiH_2}$), 1415 vw ($\delta \mathrm{aCH_3}$), 1250 m ($\delta \mathrm{sCH_3}$), 980 vs (νaSi–N–Si), 945 vs ($\delta \mathrm{SiH_2}$), 895 vs ($\mathrm{wSiH_2}$), 760 s ($\nu \mathrm{SiCH_3}$), 520 w $\rho(\mathrm{SiH_2})$
9	2960 m ($\nu \mathrm{CH_3}$), 2140 vs (νSiH), 1560 vs (νSiD), 1410 vw ($\delta \mathrm{aCH_3}$), 1250 m ($\delta \mathrm{sCH_3}$), 970 vs (νaSi–N–Si), 890 s, 850 s ($\rho \mathrm{CH_3} + \delta$SiH), 680 ($\delta$SiD)

cross-linking of polycarbosilazanes at room temperature [27], as well as the nucleophilic condensation of Si–H and N–H bonds [28]. A similar result was found in the synthesis of compound **3**. Therefore, the route using a large excess of chlorosilane, but without catalyst, is preferred.

Heptamethyldisilazane also undergoes similar reactions giving disilazane **4** in 94% yield. Nevertheless, in the case of the more sterically hindered tris(trimethylsilyl)amine $(\mathrm{Me_3Si})_3\mathrm{N}$, no redistribution with $\mathrm{MeHSiCl_2}$ was observed, even in the presence of $(^{n}\mathrm{Bu_4N})\mathrm{F}$ and a large excess of chlorosilane.

For disilazanes **3–7**, which possess three different substituents on silicon, the expected diastereoisomers were observed, in nearly the same proportions, by ^{1}H (200 MHz) and ^{29}Si NMR spectroscopies (Tables 2 and 3). IR absorption bands and assignments [29,30] are given in Table 4. Mass spectra of these disilazanes (Table 5) are consistent with the fragmentation previously reported for disilazane **1** [29]. Thus, loss of 36 mass units (hydrogen chloride) is observed but, in our case, loss of hydrogen for disilazanes **2** –**7** (M-1 fragment) is important.

TABLE 5. Characteristic ions in the mass spectra (70 eV) of compounds **2–9**: m/z, relative intensities (%) and assignments

3	173 (19) (M); 172 (78) (M − H); 158 (100) ($\mathrm{M-CH_3}$); 138 (38) (M − CL); 136 (28) (M − H − HCl); 122 (47) ($\mathrm{M-CH_3-HCl}$)
4	187 (36) (M); 186 (53) (M − H); 172 (100) ($\mathrm{M-CH_3}$); 152 (38) (M − CL); 136 (18) ($\mathrm{M-CH_3-HCl}$); 108 (34) ($\mathrm{M-CH_3SiHCl}$); 72 (87) ($\mathrm{M-CH_3SiHCl-HCl}$)
5	201 (5) (M); 172 (100) ($\mathrm{M-C_2H_5}$); 144 (81) ($\mathrm{M-C_2H_5-C_2H_4}$)
6	196 (8) (M − H); 169 (100) ($\mathrm{M-C_2H_4}$); 141 (80) ($\mathrm{M-2C_2H_4}$)
7	297 (5) (M); 260 (18) (M − H − HCl); 218 (100) ($\mathrm{M-H-C_6H_6}$); 78 (63) ($\mathrm{C_6H_6}$)
8	149 (48) (M), 148 (100) (M − H); 134 (74) ($\mathrm{M-CH_3}$); 132 (43) ($\mathrm{M-NH_3}$); 102 (80) ($\mathrm{M-H-MeSiH_3}$)
9	152 (66) (M); 151 (98) (M − H); 150 (76) (M − D); 137 (94) ($\mathrm{M-CH_3}$); 135 (36) ($\mathrm{M-NH_3}$); 134 (40) ($\mathrm{M-NH_2D}$); 103 (100) ($\mathrm{M-H-MeSiHD_2}$ or $\mathrm{M-D-MeSiH_3}$)

2.2. Chemical properties of 1,3-dichloro-1,3-dihydridodisilazanes

Stability to moisture

The chlorinated disilazanes are very sensitive to moisture, and undergo explosive hydrolysis with water, with a vigorous evolution of ammonia and hydrogen chloride.

Thermal stability

Disilazanes **3–7** slowly decompose after several days at room temperature, under inert gas. For example, disilazane **3** gave a white precipitate of $\mathrm{NH_4Cl}$, oligomers, and $\mathrm{MeHSiCl_2}$. This degradation was considerably faster upon heating at reflux overnight. Un-

TABLE 6. ^{1}H NMR and ^{29}Si NMR spectra of trisilazanes **8** and **9**

δ (ppm), J (Hz)		8	9
^{1}H NMR	δ(Si–H)	4.63 (quartet)	4.63 (multiplet)
	δ(CH_3)	0.15 (triplet)	0.14 (multiplet)
	^{3}J(SiH–CH)	3.5	3.5
	^{2}J(H–D)	-	1.7
	^{3}J(H–D)	-	0.55
^{29}Si NMR	δ(Si)	−22.9	−23.2
	^{1}J(Si–H)	203.5	203.5
	^{1}J(Si–D)	-	31.0
	^{2}J(Si–H)	7.5	7.5
	^{3}J(Si–H)	3.5	3.5
	^{3}J(Si–D)	-	0.55

der an inert atmosphere at −20°C, all these 1,3-dichloro-disilazanes are stable for months.

Action of LiAlH$_4$ on 3

Ebsworth and Emeleus [31] found that the reaction of ammonia with MeH$_2$SiCl yields (MeH$_2$Si)$_3$N **8**, and not the expected disilazane (MeH$_2$Si)$_2$NH. Therefore, they considered this last derivative unstable under the conditions used. We attempted to prepare this disilazane by reduction of (ClHMeSi)$_2$NH with LiAlH$_4$ in ether. Again, the expected disilazane was not obtained, and the same trisilylamine **8** was formed in relatively low yield (24%), showing that trisilylation of nitrogen readily occurred, together with strong gas evolution (mainly H$_2$ and MeSiH$_3$). High-boiling point oligomers were also found. Very similar results were obtained with LiAlD$_4$, affording (MeHDSi)$_3$N **9**, showing clearly that the reduction of the Si–Cl bonds of chlorinated disilazanes in the presence of lithium aluminium hydride competes with the cleavage of Si–N bonds. Similar reactions were previously reported in the reduction of hexamethyldisilazane by metal hydrides [10,11].

Action of HCl

Strong acids are known to split Si–N bonds of silylamino-derivatives [12]. In **3**, we have shown that a very fast reaction occurred with anhydrous HCl, yielding dichloromethylsilane and ammonium chloride (eqn. (8)).

$$\mathrm{ClMeHSi{-}NH{-}SiHMeCl} + 3\mathrm{HCl} \longrightarrow \mathrm{NH_4Cl} + 2\mathrm{MeHSiCl_2} \qquad (9)$$

3. Experimental section

All reactions and transfers were carried out under dry argon, using a vacuum line and a glove box when necessary. All the vessels were oven-dried and filled with argon before use. The solvents were dried and distilled prior to use and kept over molecular sieves under argon.

NMR spectra were recorded on a Bruker WP 200 FT spectrometer in 5-mm tubes (^{1}H) or 10-mm tubes (^{29}Si) from solutions in CDCl$_3$ or C$_6$D$_6$ using TMS as internal standard. The ^{29}Si NMR spectra were obtained using the INEPT technique (^{1}J(Si–H) = 200 Hz, ^{2}J(Si–H) = 7 Hz). IR spectra of the liquids (4000–200 cm^{-1}) were obtained on a Perkin-Elmer PE 983 equipped with a 3600 data station, from films between TlBrI(KRS-5) plates. Mass spectra were recorded on a VG Micromass 70-70 F spectrometer using a 4000-V ion accelerating voltage and magnetic scanning. The ion source was operated at 70 eV and at 200 μA ionizing electron current. Elemental analysis were obtained from the Service Central d'Analyse du CNRS, 69390 Vernaison, France.

3.1. Synthesis of disilazanes 1–7

Preparation of **1**: the reaction was performed in a 500 ml four-necked round-bottomed flask equipped with a thermometer well, an inlet for the gas purge, a dropping funnel and a reflux condenser (circulation of decalin cooled at −10°C) connected to a drying column. After flame drying the flask and careful purging, hexamethyldisilazane (80.5 g, 0.5 mol) and three drops of (^{n}Bu$_4$N)F were introduced. Then dichlorodimethylsilane (184 g, 1.5 mol) was rapidly added. Then the mixture was heated under reflux for several hours and the temperature inside the flask rose steadily to 80°C. The ^{1}H NMR spectrum of the mixture showed the decrease of the singlet due to hexamethyldisilazane (0.1 ppm) and formation of a new signal at 0.45 ppm (strong singlet, Me$_3$SiCl). When the trans-silylation was complete, the condenser was replaced by a short Vigreux column, connected to vacuum line *via* a collector plunged into ice and a trap cooled by liquid nitrogen. As the mixture was heated, Me$_3$SiCl and Me$_2$SiCl$_2$ were recovered in the trap and the expected disilazane condensed in the collector (30 g, 60%). The product was kept under inert gas at −20°C. Anal. Found: C, 23.44; H, 6.25; Cl, 34.9; Si, 27.3; N, 6.58. C$_4$H$_{13}$NCl$_2$Si$_2$ calc.: C, 23.76; H, 6.43; Cl, 35.15; Si, 27.72; N, 6.93%.

Preparation of **3**: a similar reaction was carried out using a mixture of hexamethyldisilazane (80.5 g, 0.5 mol) and dichloromethylsilane (287.5 g, 2.5 mol). No catalyst was added. White vapours instantaneously formed and disappeared after a few minutes. The mixture was heated under reflux for several hours and the temperature inside the flask stabilized at 55°C. The ^{1}H NMR spectrum (60 MHz) of the mixture showed loss of hexamethyldisilazane and formation of three new signals: 0.45 ppm (strong singlet, Me$_3$SiCl), 0.30 ppm [doublet, (Cl*Me*HSi)$_2$NH] and 5.1 ppm [multiplet, (ClMe*H*Si)$_2$NH]. Usually the trans-silylation was complete after 24 h. The condenser was then replaced by a short Vigreux column connected to vacuum line *via* a receiver plunged into ice and a liquid nitrogen trap. As the mixture was heated, $MeHSiCl_2$ and Me_3SiCl were recovered in the trap and the expected disilazane condensed in the receiver (43.5 g, 85%). The product was kept under inert gas at −20°C.

Anal. Found: C, 13.4; H, 5.1; Cl, 40.5; Si, 31.7; N, 7.6. $C_2H_9NCl_2Si_2$ calc.: C, 13.80; H, 5.20; Cl, 40.80; Si, 32.20; N, 8.00%.

The others disilazanes were prepared according to similar procedures.

Reduction of disilazane 3 with $LiAlH_4$

The reaction was performed in a 250 ml three-necked round-bottomed flask equipped with a magnetic stirrer and fitted with a thermometer well, a dropping funnel and a reflux condenser with a circulation of decalin at 0°C, connected to a $CaCl_2$ column and a gas meter. After purging with argon, 1.7 g of $LiAlH_4$ (0.045 mol) and ether (75 ml) were introduced. To this suspension $(HMeClSi)_2NH$ (9.58 g, 0.055 mol) was added dropwise over 15 min with vigorous stirring. Substantial gas evolution was observed (1200 cm^3), which stopped as soon as the addition of disilazane was complete. Then the mixture was stirred overnight at room temperature before distillation under vacuum. The volatile fractions were condensed into a trap cooled with liquid nitrogen, yielding $(H_2MeSi)_3N$(4.22 g, 24% yield).

Similarly, $(MeHDSi)_3N$ was obtained from the reaction of $LiAlD_4$ with disilazane **3**.

^1H NMR and ^{29}Si NMR spectra of **8** and **9** are given in Table 6.

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