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New cyclodisilazane monomers

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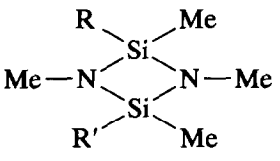
Abstract

N,N'-Dimethylcyclodisilazanes [SiMeR–NMe–SiMeR'–NMe] (R = R' = Me, Vi, or Et and R = Me, R' = Vi, Et, or Ph where Vi = vinyl) have been prepared in good yield by cyclization of bis(methylamino)silanes with chlorosilanes. ^{1}H, ^{13}C, ^{29}Si and ^{15}N NMR spectra have been assigned. The four-membered cyclic structure of the compounds have been confirmed by mass spectrometry and IR absorption measurements.

1. Introduction

The first four-membered silazane ring with alternating Si–N bonds was synthesized in 1953 by Schlumb and Towle [1] and several reviews concerning cyclodisilazane synthesis have been published since [2–5], although applications of such compounds are few. Nevertheless, *N,N'*-dimethylcyclodisilazanes have been described recently as interesting monomers [6] and the only one so far which can be used for the synthesis of linear and high-molar-mass polysilazanes [7,8].

In our study of cyclosilazane synthesis, characterization and polymerization [8], various *N,N'*-dimethylcyclodisilazanes (1) with different substituents on the silicon atoms were used as monomers.



(1)

R = R' = Me: D_{2NMe}

R = R' = Vi or Et: $D^{R'}_{2NMe}$

R = Me, R' = Vi, Et, or Ph: $D^{R'}_{NMe}D_{NMe}$

Although D_{2NMe} and $D^{Ph}_{NMe}D_{NMe}$ have already been prepared by Lienhard and Rochow [9,10], comprehensive characterization of these and other monomers is reported in this paper for the first time.

2. Results and discussion

The monomers were prepared by the method of Lienhard and Rochow [9,10], which was later used by Fink [11] and by Seyferth *et al.* [6]. This synthesis is a two-step reaction, as shown in Scheme 1.

The typical solvent is diethyl ether which was refluxed over benzophenone/sodium and distilled under dinitrogen before use. Chlorosilanes (Aldrich and Petrarch) were vacuum distilled from magnesium chips by a trap-to-trap technique. Reactions were carried out under dinitrogen.

2.1. Synthesis of bis(methylamino)silanes

A 1-litre three-necked flask equipped with a septum, a cold condenser (−60°C) and a magnetic stirrer, was flame-dried, charged with $MeRSiCl_2$ and diethyl ether, and cooled to 0°C.

Gaseous methylamine (Fluka) was admitted to the solution through a glass tube until the dissolution of precipitated methylammonium salt in the excess of amine was complete. The reaction mixture was allowed to warm to room temperature overnight as the excess of amine evaporated. The re-precipitated methylammonium chloride was filtered off and washed with

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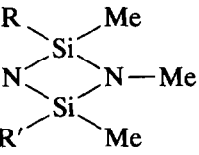
$$MeRSiCl_2 + 4MeNH_2 \longrightarrow MeRSi(NHMe)_2 + 2(MeNH_3)Cl$$

$$MeRSi(NHMe)_2 \xrightarrow[-2\ MeH]{+2\ MeLi} MeRSi(NLiMe)_2 \xrightarrow[-2\ LiCl]{+MeR'SiCl_2}$$



Scheme 1.

TABLE 1. Synthesis of bis(methylamino)silanes, $MeRSi(NHMe)_2$

R	Diethyl ether (ml)	$MeRSiCl_2$ (ml (mol))	$MeRSi(NHMe)_2$ (g (mol))	b.p. (°C/mmHg)	Yield (%)
Me	300	65.0(0.536)	43.5(0.367)	59/136 [a]	69
Vi	150	35.0(0.270)	21.7(0.167)	56/58 [b]	62
Et	150	23.6(0.175)	15.9(0.120)	51/60	69

[a] lit.: 57–58°C/132 mmHg [12] and 109°C [46]. [b] lit.: 65–66°C/78 mmHg [12].

diethyl ether. The solvent was removed from the combined organic phase and the residue was distilled (on a 30cm Vigreux column). All experimental conditions and the corresponding results are reported in Table 1.

The ^1H NMR spectra are consistent with literature reports [6]. NMR data are given in Table 2.

2.2. *Synthesis of N,N'-dimethylcyclodisilazanes*

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 bis(methylamino)silane and diethyl ether. Through the funnel, methyllithium (Merck, 1.6 mol l^{-1} in diethyl ether) was added dropwise at 0°C over 2 h. The mixture was then stirred at 0°C for another 2 h and $MeR'SiCl_2$ was added dropwise at 0°C for 5 min. The reaction mixture was stirred for another 10 min and then allowed to settle (usually 30 min). The super-

TABLE 2. NMR chemical shifts of bis(methylamino)silanes, $RMeSi(NHMe)_2$

R	^1H NMR	^{13}C NMR	^{29}Si NMR
Me	−0.27 (s, 6H, $SiMe_2$) 0.25 (s, 2H, NHC) 2.22 (s, 6H, NH*Me*)	−3.3 (s, 2C, $SiMe_2$) 26.7 (s, 2C, NHMe)	−6.21
Vi	−0.08 (s, 3H, Si*Me*Vi) 0.45 (s, 2H, NHC) 2.37 (s, 6H, NH*Me*) 5.75 < δ < 6.00 (multiplet ABX, 2H + 1H, SiMe*Vi*)	−4.2 (s, 1C, Si*Me*Vi) 27.1 (s, 2C, NHMe) 132.2 (s, 1C, $SiCH{=}CH_2$) 137.2 (s, 1C, $SiCH{=}CH_2$)	−16.22
Et	−0.16 (s, 3H, Si*Me*Et) 0.30 (s, 2H, NHC) 0.36 (q, J = 7.90 Hz, 2H, $SiCH_2Me$) 0.80 (t, J = 7.92 Hz, 3H, $SiCH_2$*Me*) 2.36 (s, 6H, NH*Me*)	−5.1 (s, 1C, Si*Me*Et) 6.1 (s, 1C, $SiCH_2Me$) 7.0 (s, 1C, $SiCH_2$*Me*) 27.2 (s, 2C, NHMe)	−4.54

TABLE 3. Synthesis of *N,N'*-dimethylcyclodisilazanes

D_{2NR}	R	R'	$MeRSi(NHMe)_2$ (g (mol))	Diethyl ether (ml)	MeLi (1.6 M/ether (ml (mol))	$MeR'SiCl_2$ (ml (mol))	D_{2NR} (g (mol))	n_D^{20}	m.p. (°C)	Yield (%)
D_{2NMe}	Me	Me	9.5(0.080)	120	100(0.160)	9.7(0.080)	9.6(0.055)	1.4210	17	69
D^{Vi}_{2NMe}	Vi	Vi	9.5(0.080)	120	100(0.160)	10.4(0.080)	9.5(0.048)	1.4540	−60	60
D^{Et}_{2NMe}	Et	Et	11.0(0.080)	120	100(0.160)	10.8(0.080)	11.6(0.057)	1.4370	−29	72
$D^{Vi}_{NMe}D_{NMe}$	Me	Vi	9.5(0.080)	120	100(0.160)	10.4(0.080)	8.0(0.043)	1.4365	−53	54
$D^{Et}_{NMe}D_{NMe}$	Me	Et	4.3(0.036)	60	45(0.072)	5.4(0.036)	4.4(0.023)	1.4288	–	65
$D^{Ph}_{NMe}D_{NMe}$	Me	Ph	4.7(0.040)	60	50(0.080)	6.5(0.040)	6.1(0.026)	1.4963	–	65

TABLE 4. NMR chemical shifts of N,N'-dimethylcyclodisilazanes

D_{2NR}	^{1}H NMR	^{13}C NMR	^{29}Si NMR	^{15}N NMR
D_{2NMe}	0.13 (s, 12H, $SiMe_2$) 2.43 (s, 6H, NMe)	0.5 (s, 4C, $SiMe_2$) 26.9 (s, 2C, NMe)	8.05	−362.4 (^1J(Si–N) = 14.0 Hz)
D^{Vi}_{2NMe}	0.29–0.30 (2s, 6H, Si*Me*Vi) 2.44 (s, 6H, NMe) 5.80 < δ < 6.10 (mult. ABX, 2(2H + 1H), SiMe*Vi*)	−2.5–4 (2s, 2C, Si*Me*Vi) 26.8 (s, 2C, NMe) 134.6 (s, 2C, $SiCH{=}CH_2$) 138.4–138.5 (2s, 2C, $SiCH{=}CH_2$)	−4.24–4.18 (2s, 2Si, SiMeVi)	−364.7 (^1J(Si–N) = 14.9 Hz)
D^{Et}_{2NMe}	0.00 (s, 6H, Si*Me*Et) 0.50 (q, J = 7.80 Hz, 4H, $SiCH_2Me$) 0.82 (t, J = 7.80 Hz, 6H, $SiCH_2$*Me*) 2.34 (s, 6H, NMe)	−1.9 (s, 2C, Si*Me*Et) 6.8 (s, 2C, $SiCH_2$*Me*) 9.1 (s, 2C, $SiCH_2Me$) 27.1 (s, 2C, NMe)	8.69–9.14 (2s, 2Si, SiMeEt)	
D^{Vi}_{NMe}, D_{NMe}	0.07–0.09 (2s, 6H, $SiMe_2$) 0.17 (s, 3H, Si*Me*Vi) 2.34 (s, 6H, NMe) 5.70 < δ < 6.10 (mult. ABX, 2H + 1H, SiMe*Vi*)	−2.6 (s, 1C, Si*Me*Vi) 0.3–0.5 (2s, 2C, $SiMe_2$) 26.7 (s, 2C, NMe) 134.1 (s, 1C, $SiCH{=}CH_2$) 138.5 (s, 1C, $SiCH{=}CH_2$)	−5.56 (s, 1Si, SiMeVi) 8.56 (s, 1Si, $SiMe_2$)	−364.0 (^1J(Si–N) = 14.9 Hz) (^1J(Si–N) = 14.1 Hz)
D^{Et}_{NMe}, D_{NMe}	0.05 (s, 3H, Si*Me*Et) 0.07–0.08 (2s, 3H, $SiMe_2$) 0.53 (q, J = 7.81 Hz, 2H, $SiCH_2Me$) 0.89 (t, J = 7.87 Hz, 3H, $SiCH_2$*Me*) 2.38 (s, 6H, NMe)	−1.5 (s, 1C, Si*Me*Et) 0.2–0.4 (2s, 2C, $SiMe_2$) 6.7 (s, 1C, $SiCH_2$*Me*) 9.2 (s, 1C, $SiCH_2Me$) 27.0 (s, 2C, NMe)	7.89 (s, 1Si, $SiMe_2$) 9.33 (s, 1Si, SiMeEt)	−365.4
D^{Ph}_{NMe}, D_{NMe}	0.37–0.41 (2s, 6H, $SiMe_2$) 0.63 (s, 3H, Si*Me*Ph) 2.56 (s, 6H, NMe) 7.50 (massif, 3H, SiMe*Ph*) 7.70 (massif, 2H, SiMe*Ph*)	−2.3 (s, 1C, Si*Me*Ph) 0.5–0.8 (2s, 2C, $SiMe_2$) 27.0 (s, 2C, NMe) 127.9 (s, 2C, $SiPh(C_3)$) 129.8 (s, 1C, $SiPh(C_4)$) 134.2 (s, 2C, $SiPh(C_2)$) 138.2 (s, 1C, $SiPh(C_1)$)	−2.76 (s, 1Si, SiMePh) 9.36 (s, 1Si, $SiMe_2$)	-

natant liquid was recovered and the precipitated LiCl was washed with diethyl ether (2 × 50 ml). Removal of the solvent in a rotary evaporator was followed by vacuum trap-to-trap distillation of the crude product. All the experimental details and results are presented in Table 3.

Other workers have described [6,9–11] cyclodisilazane distillation after removal of the precipitated LiCl by filtration or centrifugation. In our case, such a process led to the cyclodisilazane polymerization and the formation of higher silazane rings.

The NMR data on D_{2NMe} are consistent with literature values [6] and corroborate the expected structures (Table 4). Mass spectrometry (MS) measurements systematically indicate the presence of both a molecular ion M and a base peak, which appears at M-15 (loss of a methyl group) or at M-29 (loss of an ethyl group) (Fig. 1.) We cannot explain the M-42 peak which is present in all mass spectra, but further research is in progress. MS can be used to distinguish the four-membered ring structures from the six- and higher-membered rings. IR spectra show characteristic asymmetric SiNSi stretch bands at 860–870 cm^{-1}; these values are 60 cm^{-1} lower than those of cyclotrisilazanes [10,13].

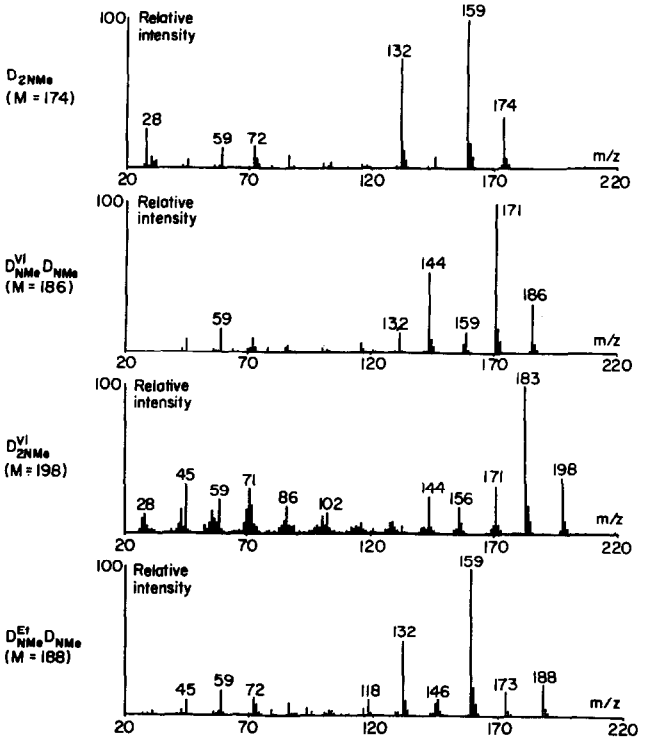


Fig. 1. Mass spectra of cyclodisilazanes.

3. Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer at 250 and 62.9 MHz, respectively. $CDCl_3$ was used as the solvent and for the internal deuterium lock. All spectra were measured on 20–50% solutions, at room temperature, in 5-mm sample tubes. ^{29}Si and ^{15}N NMR were carried out on a Bruker AC 200 spectrometer at 39.8 and 20.3 MHz in C_6D_6 and $CDCl_3$ solutions (10-mm sample tubes), respectively. Chemical shifts were referred to internal TMS (^{29}Si) and to external $MeNO_2$ (^{15}N). $^{1}J(^{15}N-^{29}Si)$ coupling constants were measured from ^{29}Si satellites in ^{15}N NMR spectra at the natural abundances of the isotopes, using an INEPT pulse sequence for accumulation according to Kupče's [14,15] and Wrackmeyer's [16] experimental conditions.

The mass spectra were recorded by direct introduction on a VG Micromass-16-F spectrometer (ionization conditions: 70 eV, 100 μA, 200°C).

The IR spectra of thin liquid films were recorded on a FT-IR Nicolet 320 spectrometer.

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