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The Flash Vacuum Thermolysis of 1,3-Diisopropyl- and 1,3-Ditertiobutyl-2,2,4,4-tetramethylcyclodisilazanes

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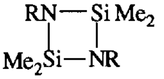
Abstract: The FVT of 1,3-diisopropyl- and 1,3-ditertiobutyl-2,2,4,4-tetramethylcyclodisilazanes was investigated by low temperature NMR and coupling with HRMS. The first of them, apparently unchanged up to 925°C, appeared to be in equilibrium with N-isopropyl-1,1-dimethylsilanimine. At the same temperature, the second one gave mainly the reactive 1-tertiobutyl-3-isopropenyl- and 1,3-diisopropenyl-2,2,4,4-tetramethylcyclodisilazanes.Copyright © 1996 Elsevier Science Ltd

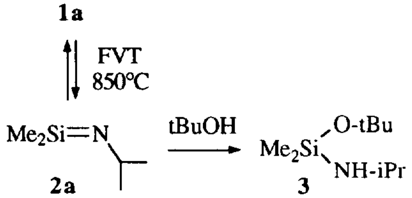
Cyclodisilazanes, when N,N'-disubstituted by aromatic or alkyl groups, are rather stable, well-investigated compounds.[1-4] The less hindered among them, hexamethylcyclodisilazane, can polymerize rapidly to high molar mass polysilazanes, most suitable intermediates for the mineralization into silicon carbonitride ceramics, and is thus of particular importance.[5] On the other hand, the 2,2,4,4-tetramethylcyclodisilazanes, bearing on the nitrogens alkenyl groups or hydrogen atoms, are expected to be unstable compounds and remained experimentally unknown.

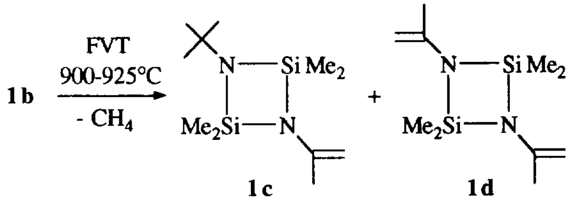


1a R = iPr
1b R = tBu

Cyclodisilazanes **1a** and **1b** are possible precursors, by thermal monomerization, of the reactive, still elusive silanimines **2a** and **2b** ($Me_2Si{=}N\text{-}tBu$). Thus, in the context of our work[6,7] aimed at generating unhindered silanimines by flash vacuum thermolysis (FVT), we have investigated and report herein the thermal behaviour (under FVT conditions) of these cyclodisilazanes, conveniently prepared by the reported method[8] (see also ref.[9]).

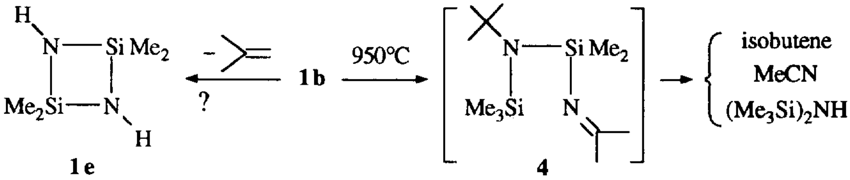
Compound **1a** was found to be apparently stable up to 925°C in our FVT conditions (oven: 20 cm length x 1.6 cm i.d., pressure: 10^{-5} hPa). Such a thermal stability, already reported for 1,3-diphenyl- and 1,3-bis(trimethylsilyl)cyclodisilazanes,[1] however doesn't exclude the possibility of a thermal equilibrium with N-isopropyl-1,1-dimethylsilanimine (**2a**). Although the presence of this latter was not demonstrated by FVT/HRMS coupling, its intermediacy seems likely in the FVT of **1a** at 850°C in the presence of tertiobutanol, which gave in 30% yield compound **3**[10], the addition product of **2a** with this alcohol (no reaction occured at 25°C in solution between **1a** and tertiobutanol). The characteristics of **3** are analogous to those of a sample prepared according to the general method[11] by reaction of tertiobutanol and isopropanamine on dichlorodimethylsilane. Above 925°C, a progressive elimination of propene from the isopropyl groups of **1a** also took place.





The ditertiobutyltetramethylcyclodisilazane **1b** underwent, as main decomposition pathway at 900-925°C, a demethylation of the tertiobutyl groups leading to the unsaturated cyclodisilazanes **1c** and **1d**, obtained in *ca.* 70% yield (**1c** + **1d**) determined by NMR (-60°C, quantitative standard of benzene), with a **1c**/**1d** ratio of 1:0.6 at 900°C and 1:1.1 at 925°C. Owing to the rapid polymerization of **1c** and **1d** in solution, their signals were no more visible after warming the sample up to room temperature and, thus, these compounds have been characterized by low temperature IR and NMR spectrometry, as well as, in the gas phase, by FVT/HRMS coupling.[10]

The amount of **1c** and **1d** decreased noticeably at 950°C and the formation of isobutene, methyl cyanide and hexamethyldisilazane became important. By analogy with our previous results,[7] the loss of isobutene from **1b** to give the cyclodisilazane **1e** was also to be expected, but the presence of this compound has not been confirmed in the FVT/HRMS of **1b** and an important SiMe3 ion at m/z 73.0550 (calcd. C_3H_9Si 73.0474) was observed in the spectrum. Thus, the formation of the above products can be due more likely to a methyl migration accompanied by ring opening into an intermediate such as **4**, which then fragments upon FVT.



The FVT of cyclodisilazanes **1a** and **1b** in coupling with photoelectron spectroscopy, which enabled us to characterize directly the silanimines **2a** and **2b** in the gas phase, will be reported shortly.[12]

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10. Spectral data for **3**, **1c**, and **1d** [apparatus: Perkin-Elmer 1420 (IR), Bruker AC 250 (NMR), Jeol JMS D300 (HRMS)]: **3**: NMR ($CDCl_3$): δ^1H 0.08 (s, 6 H), 1.07 (d, J 6.2 Hz, 6 H), 1.27 (s, 9 H), 3.12 (hept, J 6.2 Hz, 1 H); $\delta^{13}C$ 1.01, 27.80, 32.10, 42.76, 71.73 ppm; **1c** + **1d**: IR (solid film at -196°C): strong absorptions at 2960, 1635, 1378, 1310, 1252, 1098, 897, 838 and 802 cm^{-1}; **1c**: NMR (-60°C, $CDCl_3$): δ^1H 0.38 (12 H), 1.16 (9 H), 1.83 (3 H), 3.59 (1 H), 3.64 (1 H); $\delta^{13}C$ 3.98, 24.16, 33.90, 84.66, 148.31 ppm (tetrasubstituted t-Bu carbon not assigned); HRMS (60 eV): $M^{+\cdot}$ 242.1615 (calcd. $C_{11}H_{26}N_2Si_2$ 242.1634), $M^{+\cdot}$ - CH_3 227.1378 (calcd. $C_{10}H_{23}N_2Si_2$ 227.1399); **1d**: NMR: δ^1H 0.49 (12 H), 1.85 (6 H), 3.67 (2 H), 3.73 (2 H); $\delta^{13}C$ 2.08, 24.02, 86.57, 147.09 ppm; HRMS: $M^{+\cdot}$ 226.1292 (calcd. $C_{10}H_{22}N_2Si_2$ 226.1321).
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