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The preparation and characterization of $CH_3(R)Si(Cl)N(SiMe_3)_2$, $CH_3(R)Si(NH_2)$-$N(SiMe_3)_2$ and $CH_3(R)Si(NHSiMe_3)_2$ (R = H, CH_2=CH, Ph, Me) are described, as is the use of $CH_3(H)Si(NHSiMe_3)_2$ in the synthesis of $CH_3(H)Si\overline{N(SiMe_3)TiCl_2N(SiMe_3)}$.

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by

Gerard Mignani and Dietmar Seyferth

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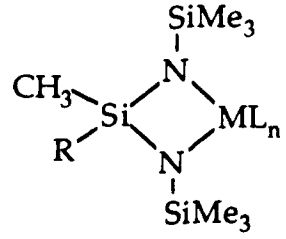
ABSTRACT

The preparation and characterization of $CH_3(R)Si(Cl)N(SiMe_3)_2$, $CH_3(R)Si(NH_2)N(SiMe_3)_2$ and $CH_3(R)Si(NHSiMe_3)_2$ (R = H, CH_2=CH, Ph, Me) are described, as is the use of $CH_3(H)Si(NHSiMe_3)_2$ in the synthesis of $CH_3(H)SiN(SiMe_3)TiCl_2N(SiMe_3)$.

INTRODUCTION

For the preparation of cyclic silametallaazanes of type 1, in particular those in which R is a reactive substituent such as H or CH_2=CH, we required the corresponding bis(trimethylsilylamino)silanes, $CH_3(R)Si(NHSiMe_3)_2$. Such compounds, we found, could be prepared readily by a Me_3Si-for-H rearrangement reaction first reported by Wannagat and Niederprüm in 1961.[2]



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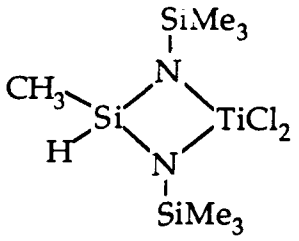
RESULTS AND DISCUSSION

Scheme 1 shows the synthetic route used. The 1:1 reaction of lithium bis(trimethylsilyl)amide with the respective dichlorosilane gave the expected $CH_3(R)Si(Cl)N(SiMe_3)_2$ compounds, 2, in acceptable yield. Their reaction with

anhydrous gaseous ammonia in hexane solution produced the $CH_3(R)Si(NH_2)N(SiMe_3)_2$ compounds, 3. It is advisable, at least when R = H, to carry out this reaction at low temperature. At –78°C, the yield of $CH_3(H)Si(NH_2)N(SiMe_3)_2$, 3c, was 75%; in a reaction carried out at 0°C its yield was only 35% and $[(Me_3Si)_2NSi(CH_3)(H)]_2NH$, 4, a by-product from the reaction of 2b and 3c, was formed in 23% yield. Products 2 and 3 are of limited thermal stability and should be distilled at reduced pressure.

The synthetic utility of these compounds is illustrated by the reaction of the dilithio derivative of $CH_3(H)Si(NHSiMe_3)_2$ with $TiCl_4$ in hexane to give 5.



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EXPERIMENTAL

General Comments

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques or a nitrogen-filled Vacuum Atmospheres drybox. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from Petrarch Systems, Inc., or Silar, and distilled from magnesium chips before use. *n*-Butyllithium was purchased from Aldrich. Organolithium reagents were titrated for RLi content by the Gilman double titration method.[3]

Proton NMR spectra were obtained either with a JEOL FX-90Q, a Bruker WM-250, or a Varian KL-300 NMR spectrometer using $CDCl_3/CHCl_3$ as a reference at 7.24 ppm downfield from tetramethylsilane.

1. Synthesis of $CH_3(R)Si(Cl)N(SiMe_3)_2$

A one-L, three-necked, round-bottomed flask equipped with a septum, an overhead mechanical stirrer and a condenser was flame-dried under nitrogen and charged with 80.37 g (0.49 mol) of $(Me_3Si)_2NH$ and 120 mL of dry hexane. *n*-Butyllithium (1.6 M in hexane, 0.49 mol) was added slowly at 0°C and the resulting mixture was stirred under nitrogen for 2 h at room temperature. Subsequently, it was cooled to 0°C and 60.77 g (0.52 mol) of CH_3SiHCl_2 was added slowly. The reaction mixture was stirred for 1 h at room temperature, centrifuged and filtered. The filtrate was evaporated to leave a clear oil. Distillation of the latter gave 87.0 g (72 %) of a clear oil, bp 65-67°C/8 Torr, which was identified as $CH_3(H)Si(Cl)N(SiMe_3)_2$.

Anal. Calcd. for $C_7H_{22}NClSi_3$: C, 35.03; H, 9.24; N, 5.83. Found: C, 35.14; H, 9.18; N, 6.03. The IR spectrum (KBr) showed ν (SiH) at 2190 cm^{-1}. The ^1H NMR spectrum ($CDCl_3$): δ 0.15 (s, 18H, Me_3Si), 0.63 (d, 3H, CH_3Si), 6.58 - 6.72 (broad, 1H, SiH).

Prepared by this procedure were:

$CH_3(CH_2=CH)Si(Cl)N(SiMe_3)_2$, 51% yield, bp 73-74°C/0.01 Torr, mp 61-62°C. **Anal.** Calcd. for $C_9H_{24}NClSi_3$: C, 40.63; H, 9.09. Found: C, 40.30; 9.02. IR (KBr): ν (C=C) 1595. ^1H NMR ($CDCl_3$): δ 0.24 (s, 18H, Me_3Si), 0.53 (s, 3H, CH_3Si), 5.84 (m, 3H, $CH=CH_2$).

$CH_3(C_6H_5)Si(Cl)N(SiMe_3)_2$, 70% yield, bp 89-90°/0.01 Torr. **Anal.** Calcd. for $C_{13}H_{26}NClSi_3$: C, 49.40; H, 8.79; N, 4.43. Found: C, 49.34; H, 8.34; N, 4.68. ^1H NMR ($CDCl_3$): δ 0.04 (s, 18H, Me_3Si), 0.55 (s, 3H, CH_3Si), 7.24 - 7.42 (m, 5H, Ph).

$(CH_3)_2Si(Cl)N(SiMe_3)_2$, 46% yield, bp 88-90°C/9 Torr (known compound[3]).

2. Synthesis of $CH_3(R)Si(NH_2)N(SiMe_3)_2$

The flask, as described in (1), was charged with 87.0 g (0.36 mol) of $CH_3(H)Si(Cl)N(SiMe_3)_2$ and 300 ml of dry hexane. The solution was cooled to −78°C and then gaseous NH_3 (dried by passage through KOH pellets) was bubbled into the solution through a gas dispersion tube that had been inserted through the septum. After 1 h, the NH_3 flow was stopped. The reaction mixture was centrifuged and filtered to remove NH_4Cl. Evaporation of the filtrate at reduced pressure gave a clear oil. Distillation of the latter (bp 48-49°C/3 Torr) gave 60.57 g (75%) of $CH_3(H)Si(NH_2)N(SiMe_3)_2$.

IR (KBr): ν (NH_2) 3490, 3410 ν (SiH) 2140 cm^{-1}. ^1H NMR: δ 0.18 - 0.24 (m, 21H, $SiCH_3$), 5.02 (s, broad, 1H, SiH).

When the reaction was carried out at 0°C for 2 h (instead of at −78°C), this compound was produced in 35% yield. A higher boiling product, bp 149-150°C/1 Torr, also was formed in 23% yield. It was identified as $[(Me_3Si)_2NSi(H)(CH_3)]_2NH$.

Anal. Calcd. for $C_{14}H_{45}N_3Si_6$: C, 39.65; H, 10.69; N, 9.90. Found: C, 39.66; H, 10.69; N, 9.98. IR (KBr): ν (NH) 2490; ν (SiH) 2145 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.10 (s, 42H, $SiCH_3$), 1.48 (broad s, 1H, NH), 4.75 (broad, 2H, SiH).

Prepared in similar manner were:

$CH_3(CH_2{=}CH)Si(NH_2)N(SiMe_3)_2$, (preparation at 0°C), 61% yield, bp 92-93°C/1 Torr, mp 67-68°C. **Anal.** Calcd. for $C_9H_{26}N_2Si_3$: C, 43.84; H, 10.62. Found: C, 43.75; H, 10.36. IR (KBr): ν (NH_2) 3510, 3415, ν ($CH{=}CH_2$), 1600 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.26 (s, 21H, $SiCH_3$), 5.77 - 6.24 (ABX, 3H, $CH_2{=}CH$, J_{AB} = 3.85 Hz, J_{BX} = 14.9 Hz, J_{AX} = 20.0 Hz).

$CH_3(C_6H_5)Si(NH_2)N(SiMe_3)_2$, (preparation at 0°C), 74% yield, bp 87-88°C/0.01 Torr. **Anal.** Calcd. for $C_{13}H_{28}N_2Si_3$: C, 52.63; H, 9.51. Found: C, 52.84;

H, 9.53. IR (KBr): ν (NH_2) 3480, 3400 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.17 (s, 18H, Me_3Si), 0.10 (s, 3H, CH_3Si), 6.99 - 7.22 (m, 5H, Ph).

$(CH_3)_2Si(NH_2)N(SiMe_3)_2$, (preparation at 25°C), 85% yield, bp 83-84°/9 Torr, mp 68-69°C. Known compound, bp 82-83°C/9 Torr, mp 73-74°C.[3]

3. Synthesis of $CH_3(R)Si(NHSiMe_3)_2$

$CH_3(H)Si(NH_2)N(SiMe_3)_2$, 12 g, was charged into a 50 mL, one-necked, round-bottomed flask equipped with a rubber stopper pierced with syringe needles for entrance and exit of an argon gas flow. The flask was heated with a sand bath at 220-230°C (external temperature) for 144 h with a slow flow of argon passing through the flask. Very slow distillation gave 5.70 g (48%) of $CH_3(H)Si(NHSiMe_3)_2$, bp 43-45°C/1 Torr. **Anal.** Calcd. for $C_7H_{24}N_2Si_3$: C, 38.12; H, 10.96. Found: C, 38.23; H, 10.93. IR (KBr): ν (NH) 3400, ν (SiH) 2140 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.19 (s, 21 H, $SiCH_3$), 4.41 (broad, 1H, SiH).

Similar pyrolyses (220-240°C/5-6 h) of the other $CH_3(R)Si(NH_2)N(SiMe_3)_2$ compounds gave the following:

$CH_3(CH_2{=}CH)Si(NHSiMe_3)_2$, 85% yield, bp 71-72°C/1 Torr. **Anal.** Calcd. for $C_9H_{26}N_2Si_3$: C, 43.84; H, 10.62; N, 11.36. Found: C, 44.22; H, 10.55, N, 11.36. IR (KBr): ν (NH) 3400, ν (C=C) 1605 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.20 (s, 18H, Me_3Si), 0.24 (s, 3H, CH_3Si), 5.77 - 6.19 (ABX, 3H, $CH{=}CH_2$, J_{AB} = 4.10 Hz, J_{BX} = 14.8 Hz, J_{AX} = 20.3 Hz).

$CH_3(C_6H_5)Si(NHSiMe_3)_2$, 89% yield, bp 83-84°C/0.3 Torr. **Anal.** Calcd. for $C_{13}H_{28}N_2Si_3$: C, 52.63; H, 9.51; N, 9.44. Found: C, 52.84; H, 9.50; N, 9.23. IR (KBr): ν (NH) 3380 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.05 (s, 18H, Me_3Si), 0.34 (s, 3H, CH_3Si), 7.18 - 7,60 (m, 5H, Ph).

$(CH_3)_2Si(NHSiMe_3)_2$, 84% yield, bp 72-73°C/10 Torr (known compound, bp 72°C/10 Torr[3]).

Preparation of Compound 5

The usual apparatus was charged with 4.83 g (21.4 mmol) of $CH_3(H)Si(NHSiMe_3)_2$ (98% pure by GLC) and 20 mL of dry hexane. To this solution was added, with stirring, under nitrogen, 43.9 mmol of *n*-BuLi (1.6 M in hexane). After the resulting mixture had been stirred at room temperature for 2 h, 100 mL of hexane was added and it was cooled to –40°C. Subsequently, 4.15 g (21.8 mmol) of $TiCl_4$ was added very slowly. The reaction mixture was stirred at room temperature for 16 h. It then was centrifuged. The supernatant solution was evaporated at reduced pressure, leaving a yellow solid. Two recrystallizations from pentane at –80°C gave 0.90 g (12%) of pure 5, mp 120°C.

Anal. Calcd. for $C_7H_{22}N_2Cl_2Si_3Ti$: C, 24.92; H, 6.57; N, 8.30. Found: C, 24.82; H, 6.96; N, 8.33. IR (KBr): ν (SiH) 2160-2120 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.29 (s, 18H, $NSiMe_3$), 0.59 (s, 3H, $SiCH_3$), 5.48 (s, broad, 1H, SiH).

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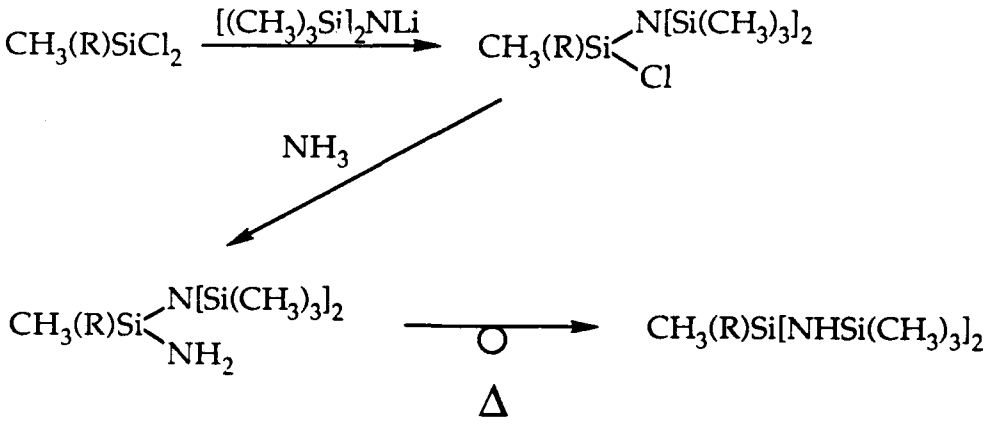
SCHEME 1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CH3(R)Si
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Cl
NH3
CH3(R)Si
N[Si(CH3)3]2
NH2
Δ
CH3(R)Si[NHSi(CH3)3]2