# New Method for the Synthesis of Silaheterocycles and the First Pentacoordinate Silanol

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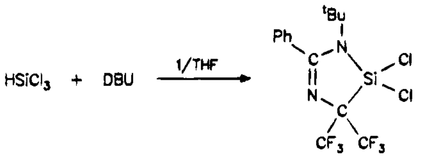
Trifluoromethyl-substituted 1,3-diazabutadienes, i.e., $(CF_3)_2C{=}NC(Ar){=}N^tBu$, **1**, have been used efficiently in the synthesis of heterocycles.[1] For example, **1** reacts with $GeCl_2$[2] and with $SnCl_2$[3] to give five-membered heterocycles, which can be isolated and structurally characterized in the case of germanium, **2**.[2]

The "Umpolung" thus effected at the carbon attached to the trifluoromethyl substituents (C(2)) is demonstrated by the course of hydrolysis.[3] On thermolysis, these heterocycles give imidazole derivatives, the germanium derivative **2** being more stable and hence needing more drastic conditions (160 °C/20 min) than its tin analogue. From these findings it may be anticipated that the silicon analogue should exhibit even higher stability. However, a preparative simple and high-yielding method for the generation of $SiCl_2$ is not available.[4]

Since $SiCl_2$ seems to be one of the most versatile building blocks for silaheterocyclic synthesis, a preparatively simple access to this carbene homologue or a source for it is highly desirable. It is well-known that $HSiCl_3$ easily is deprotonated by, e.g., amines (eq 1).[5] The $SiCl_3^-$ thus generated can be used

$$HSiCl_3 + NR_3 \xrightarrow{THF} [HNR_3][SiCl_3] \qquad (1)$$



(2)

**3**

according to eq 2 instead of $SiCl_2$:[6] with **1**, the formal [4 + 1] cycloadduct **3** is obtained.[7] The reaction sequence formally may be understood as a nucleophilic addition of $SiCl_3^-$ to the electrophilic C(2) atom of the diazabutadiene and subsequent cyclocondensation to give the heterocycle **3** (cf. ref 8), which is isolated from pentane as colorless crystals. The NMR data of **3** correspond to those of **2**.[2] The crystals of **3** are isomorphous to those of **2**. An X-ray structure determination[9] (Figure 1) proves the close resemblance of **3** and **2**. The $SiCl_2$ moiety is incorporated into a planar five-membered heterocycle. The silicon atom is surrounded tetrahedrally by two chlorine atoms, one nitrogen atom, and one carbon atom. All distances and angles correspond to the values derived from the germacycle **2**, if the different covalent radii of silicon and germanium are taken into account.

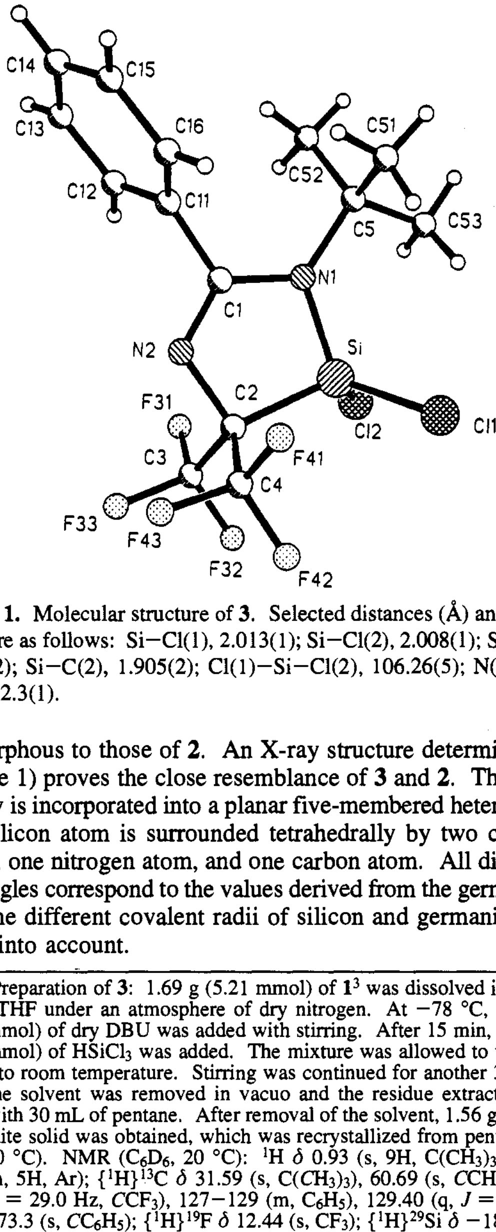


**Figure 1.** Molecular structure of **3**. Selected distances (Å) and angles (deg) are as follows: Si–Cl(1), 2.013(1); Si–Cl(2), 2.008(1); Si–N(1), 1.717(2); Si–C(2), 1.905(2); Cl(1)–Si–Cl(2), 106.26(5); N(1)–Si–C(2), 92.3(1).

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(1) (a) Burger, K.; Wassmuth, U.; Penninger, S. *J. Fluorine Chem.* **1982**, *20*, 813. (b) Burger, K.; Wucherpfennig, U.; Brunner, E. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1994; Vol. 60.

(2) Karsch, H. H.; Bienlein, F.; Heckel, M.; Steigelmann, O.; M.; Burger, K.; Cyrener, J. *Z. Naturforsch.* **1995**, *50b*, 289.

(3) Burger, K.; Penninger, S.; Greisel, M.; Daltrozzo, E. *J. Fluorine Chem.* **1980**, *15*, 1.

(4) Atwell, W. H.; Weyenberg, D. R. *Angew. Chem.* **1962**, *81*, 485; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 469.

(5) Benkeser, R. A. *Acc. Chem. Res.* **1971**, *94*, p 94.

(6) This method for silaheterocycle syntheses can be extended in a general sense: for instance, ${}^t\mathrm{Bu}\overline{\mathrm{NCH{=}CHN^tBuSiCl_2}}$ can be prepared easily in good yield by the reaction of $^tBuN{=}CHCH{=}N^tBu$ with the system $HSiCl_3$/DBU.

(7) Preparation of **3**: 1.69 g (5.21 mmol) of **1**[3] was dissolved in 30 mL of dry THF under an atmosphere of dry nitrogen. At −78 °C, 0.78 mL (5.21 mmol) of dry DBU was added with stirring. After 15 min, 0.53 mL (5.21 mmol) of $HSiCl_3$ was added. The mixture was allowed to warm up slowly to room temperature. Stirring was continued for another 3 h at 20 °C. The solvent was removed in vacuo and the residue extracted three times with 30 mL of pentane. After removal of the solvent, 1.56 g (70.7%) of a white solid was obtained, which was recrystallized from pentane (mp 98–100 °C). NMR ($C_6D_6$, 20 °C): $^1H$ $\delta$ 0.93 (s, 9H, $C(CH_3)_3$), 6.91–6.96 (m, 5H, Ar); $\{^1H\}^{13}C$ $\delta$ 31.59 (s, $C(CH_3)_3$), 60.69 (s, $CCH_3$), 67.27 (sept, $J$ = 29.0 Hz, $CCF_3$), 127–129 (m, $C_6H_5$), 129.40 (q, $J$ = 289 Hz, $CF_3$), 173.3 (s, $CC_6H_5$); $\{^1H\}^{19}F$ $\delta$ 12.44 (s, $CF_3$); $\{^1H\}^{29}Si$ $\delta$ −18.36. MS (CI, $^{35}Cl$): $m/z$ 423 ($M^+ + 1$), 367 (423 − $C_4H_8$).

(8) Sewald, N.; Riede, J.; Bissinger, P.; Burger, K. *J. Chem. Soc., Perkin Trans. 1* **1992**, 267.

(9) Crystal structure determinations of **3** and **5**: four-circle diffractometer CAD4 (Enraf-Nonius, Delft) with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å). **3**: $T$ = 23(2) °C, $C_{14}H_{14}Cl_2F_6N_2Si$, monoclinic, space group $P2_1/n$, $a$ = 7.989(1) Å, $b$ = 19.097(1) Å, $c$ = 12.239(1) Å, $\beta$ = 107.25(1)°, $V$ = 1783.3(3) Å$^3$. **5**: $T$ = 22(2) °C, $C_{14}H_{16}Cl_2F_6N_2OSi$, triclinic, space group $P1$, $a$ = 9.034(1) Å, $b$ = 9.074(1) Å, $c$ = 12.663(1) Å, $\alpha$ = 85.60(1)°, $\beta$ = 70.67(1)°, $\gamma$ = 73.57(1)°, $V$ = 9.394(2) Å$^3$. **3**/**5**: $D_{calc}$ = 1.577/1.560 g/cm$^3$, $Z$ = 4/2, $\mu$(Mo K$\alpha$) = 0.490/0.472 mm$^{-1}$, $F$(000) = 856/448, reflections collected 3872/3662, unique reflections 3872/3661, observed reflections 2740/2455 with $F > 4\sigma(F_o)$. Index ranges ($-10 \le h \le 9, 0 \le k \le 24, 0 \le l \le 15$)/($0 \le h \le 11, -10 \le k \le 11, -14 \le l \le 15$). Solution by direct methods with full-matrix least squares refinements on $F^2$ and absorption corrections with program DIFABS[10a,b] (for **3**) led to $R$ values of $R_1$ = 0.0425/0.0589 and $_wR_2$ = 0.1042/0.1598; rest electron density (min/max) was 0.286/−0.3499 (**3**) and 0.308/−0.392 e/Å$^3$ (**5**). Calculations were performed with programs CADSHEL, SHELXS-86, SHELXL-93, and SHELXTL-PLUS package.[10c−f]

(10) (a) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. (b) Walker, N. Program DIFABS, Version 9.0 (1993), BASF A6. (c) Kopf, J.; Rübcke, H.-Chr. Program CADSHEL, Version 3.1 (1993), University Hamburg. (d) Sheldrick, G. M. Program SHELXS-86, University of Göttingen. Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175–189. (e) Sheldrick, G. M. Program SHELXL-93, University of Göttingen. Sheldrick, G. M. *J. Appl. Crystallogr.*, in press. (f) Program Package SHELXTL-PLUS, Release 4.1 (1990), Siemens R3, Siemens Crystallographic Research Systems Instruments, Inc., Madison, WI 53719, 1989.

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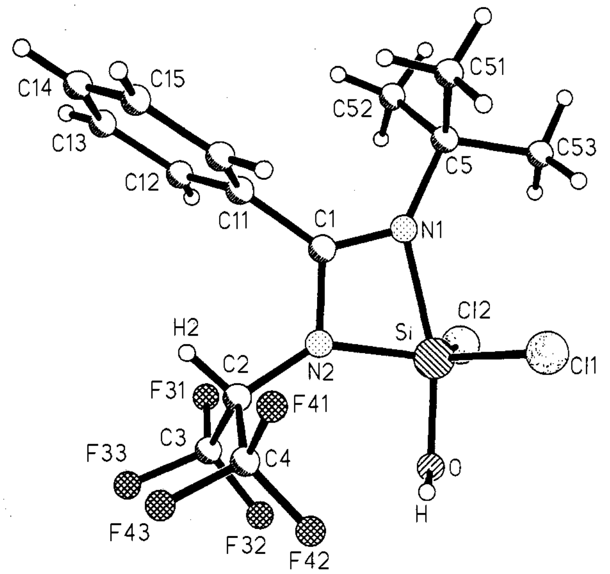
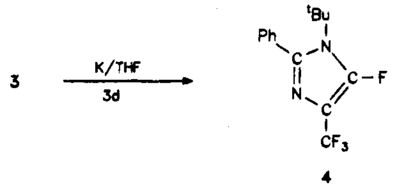


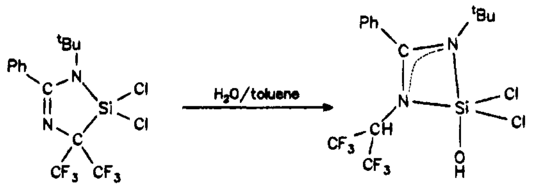
**Figure 2.** Molecular structure of **5**. Selected distances (Å) and angles (deg) are as follows: Si–Cl(1), 2.032(2); Si–Cl(2), 2.006(2); Si–O, 1.601(3); Si–N(1), 1.969(3); Si–N(2), 1.782(3); Cl(1)–Si–Cl(2), 117.3(1); Cl(1)–Si–O, 95.0(2); Cl(2)–Si–O, 93.9(2); N(2)–Si–O, 96.0(2); N(1)–Si–O, 164.5(2); N(1)–Si–N(2), 68.5(1).

In line with the expected trend (vide infra), the silaheterocycle **3** cannot be transformed into the imidazole simply on heating. It is stable up to 220 °C, when unspecific decomposition reactions occur. Under reducing conditions, however, **4** is formed in high yield (eq 3).[11,12] With excess water, $(CF_3)_2(H)CN(H)C(Ph){=}N^tBu$ is obtained, but with traces of water, an intermediate **5** is obtained as colorless needles (eq 4).[13]



(3)

**4**



(4)

**3** **5**

An X-ray structure determination of **5**[9] (Figure 2) constitutes the first structural proof for the "Umpolung"; i.e., the former electrophilic carbon atom of **1** acts as a nucleophilic center in the silaheterocycle **3**. The proton adds to this carbon atom (C(2)), whereas the hydroxyl group adds to the silicon atom. Thus an amidinate type of ligand is formed, chelated via the two nitrogen atoms to the trigonal bipyramidal coordinated silicon atom. Two chlorines and N(2) are arranged equatorially, and the N(1) atom and the hydroxyl group complete the distorted tbp arrangement in axial positions.

The equatorial/axial ligation of the two nitrogen atoms reduces the angle strain in the four-membered ring.[14] This strain is reflected in deviations of angles from ideal values. Most noteworthy, all silicon–element bonds are remarkably short, compared to other structures with a pentacoordinate silicon atom.[15] The Si–Cl and the Si–N(2) distances compare well with those of the tetrahedral **3**, and the Si–O distance even ranges at the lower limit for tetrahedral silanol structures. Although the axial Si–N(1) bond is longer than the equatorial Si–N(2) bond by 0.19 Å, it is exceptionally short compared to other axial Si–N bonds of pentacoordinated silicon.[15]

Therefore, one may conclude that amidinate ligands are particularly useful for stabilizing high coordination numbers at silicon (and probably other main group element centers), which presently is being investigated in our group. To the structural principle verified by the structure of **5** may well be attributed a key role in the amine-catalyzed hydrolysis of chlorosilanes.

The monomeric compound **5** represents the first stable silanol with a pentacoordinate silicon atom and the first stable dichlorosilanol.[16] No hydrogen chloride elimination is observed even on heating to +190 °C.

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**Supplementary Material Available:** Complete tables of crystal data, bond distances and angles, and atomic coordinates and displacement parameters (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) No silylene intermediate could be detected during this reduction.

(12) Preparation of **4** (eq 3): 1.54 g (3.64 mmol) of **3** was dissolved in dry THF under an atmosphere of dry nitrogen. At −78 °C 0.47 g (10.94 mmol) of potassium was added. The reaction mixture was allowed to warm up to room temperature with stirring and kept at 20 °C for another 36 h. The solvent was removed in vacuo and the residue extracted three times with 40 mL of toluene. After removal of the solvent and sublimation of the crude solid (165 °C, $10^{-2}$ mbar), 0.83 g (79.7%) of a yellow solid was obtained (mp 97 °C). NMR $CDCl_3$, 20 °C): $^1H$ $\delta$ 1.35 (s, 9H, $C(CH_3)_3$), 7.26–7.34 (m, 5H, $C_6H_5$); $\{^1H\}^{13}C$ $\delta$ 30.86 (s, $C(\mathit{C}CH_3)_3$), 60.50 (s, $\mathit{C}(CH_3)_3$), 109.88 (dq, $^2J = 40.0$ Hz, $^2J = 4.0$ Hz, $N\mathit{C}{=}C$), 124.95 (dq, $^1J = 266.2$ Hz, $^3J = 5.2$ Hz, $CF_3$), 127–129 (m, $C_6H_5$), 140.8 (d, $^3J = 8.0$ Hz, $N\mathit{C}{=}N$), 146.76 (dq, $^1J = 283.9$ Hz, $^3J = 2.8$ Hz, CF); $\{^1H\}^{19}F$ $\delta$ 11.37 (d, 3F, $^4J = 10.7$ Hz, $CF_3$), −58.67 (q, 1F, $^4J = 10.7$ Hz, (CF). MS (CI): *m/z* 286 ($M^+$), 231 ($M^+ - C(CH_3)_3$).

(13) Preparation of **5**: 0.83 g of **3** (1.96 mmol) was dissolved in 30 mL of wet toluene[17] and stored at 5 °C for 3 days; 0.51 g (1.16 mmol) of needle-shaped crystals precipitated (59.2%). Mp: 103–106 °C. NMR ($C_6D_6$, 20 °C): $^1H$ $\delta$ 0.89 (s, 9H, $C(CH_3)_3$), 3.79 (br, 1H, OH), 4.17 (sept, $J = 6.6$ Hz, $^1H$, $CH(CF_3)_2$), 6.73–6.95 (m, 5H, $C_6H_5$); $\{^1H\}^{13}C$ $\delta$ 28.35 (s, $C(\mathit{C}H_3)_3$), 56.95 (s, $\mathit{C}(CH_3)_3$), 58.16 (sept, $J = 34.6$ Hz, $\mathit{C}(CF_3)_2$), 123.63 (q, $J = 283.0$ Hz, $CF_3$), 127–129 (m, $C_6H_5$), 164.62 (s, NCN); $\{^1H\}^{19}F$ $\delta$ 6.23 (d, $J = 6.6$ Hz); $\{^1H\}^{29}Si$ $\delta$ −89.35 (s). MS (CI, $^{35}Cl$): *m/z* = 442 ($M^+ + 2$), 423 (442 − OH), 407 (442 − Cl).

(14) To our knowledge, there is only one example in the literature of a structurally characterized compound with a pentacoordinate silicon incorporated into a four-membered ring: van den Ancker, T.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1006.

(15) Chrit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448.

(16) Tetrahedral monochloro-substituted silanol derivatives are known, but not structurally characterized: Clegg, W.; Klingebiel, U.; Sheldrick, G. M. *Z. Naturforsch.* **1982**, *37b*, 423.

(17) Water content of the toluene used: 50–80 ppm (Karl-Fischer titration).