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Communications

Hexacoordinate Complexes of Silacyclobutane: Spontaneous Ring Opening and Rearrangement

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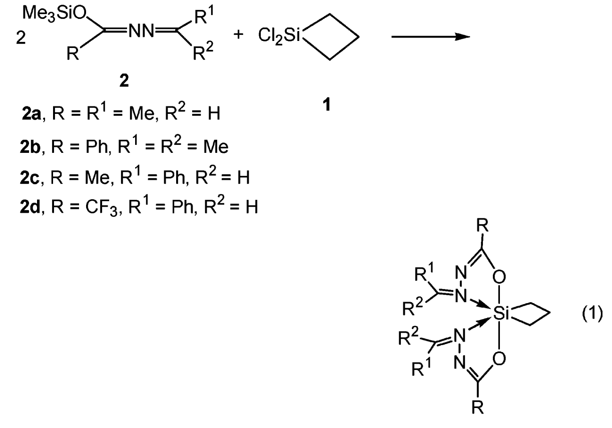
Summary: The title compounds were prepared and were found to undergo ring opening and molecular rearrangement under mild conditions and no catalysis, forming a carbon−carbon bond and closing a new chelate ring. The rearrangement product depends on whether α-protons are present. Reactants and products are characterized by crystal structures.

This communication describes the preparation of hexacoordinate silacyclobutane complexes and their facile uncatalyzed ring opening and skeletal rearrangement under mild conditions. The rearrangement leads to a neutral pentacoordinate silicon complex, involving carbon−carbon bond formation and closure of a new chelate-ring. Silacyclobutane chemistry[1] is of considerable interest, due to its facile ring opening and consequent reactivity in anionic polymerization.[2] Its thermal[3] and photochemical[3a,4,5] reactivity has been reported, forming silenes and disilacyclobutanes.[3] Silacyclobutanes undergo reactions with carbenes,[6] aldehydes, and epoxides.[7] However, all of these reactions require strong bases, thermolysis at elevated temperatures, or photochemical initiation. In contrast, the present work reports facile spontaneous silacyclobutane ring expansion.

The transsilylation reaction[8] of 1,1-dichlorosilacyclobutane (**1**) with *O*-(trimethylsilyl)-*N*-(alkylideneimino)-hydrazides (**2**;[9,10] eq 1) in chloroform solution at room temperature leads smoothly to the neutral hexacoordinate silacyclobutane complexes **3**.[11] To the best of our knowledge there has only been one previous report of a hexacoordinate silacyclobutane compound, with a substantially different structure (four phosphorus ligands).[12]



2

1

2a, R = R^1 = Me, R^2 = H

2b, R = Ph, R^1 = R^2 = Me

2c, R = Me, R^1 = Ph, R^2 = H

2d, R = CF$_3$, R^1 = Ph, R^2 = H

3a-d

Under mild conditions (7 h in boiling acetonitrile or several days at room temperature in chloroform) **3a**,**b** rearrange, respectively, to **4a**,**b**, neutral *penta*coordinate complexes with a new carbon−carbon bond closing a new chelate ring, while the four-membered ring opens and forms an *n*-propyl ligand (eq 2).[13] This remarkable rearrangement, which proceeds without any catalysis,

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(10) **2b** has been described previously.[9] Details of the synthesis and spectral properties of **2a**,**c**,**d** are given in the Supporting Information.

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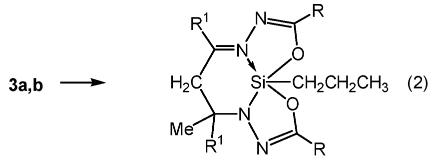
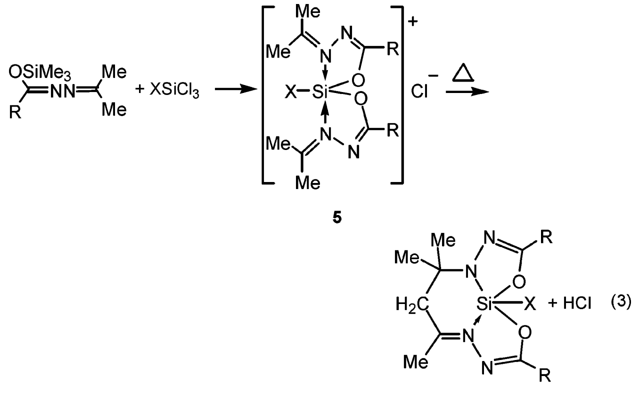


4a, R = Me, R^1 = H
4b, R = Ph, R^1 = Me

is reminiscent of a previously reported rearrangement which takes place in pentacoordinate siliconium ion salts, initiated by proton abstraction by the halide counterion (eq 3).[14] The close resemblance of these two



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6
6a, R = X = Me
6b, R = Ph; X = C_6H_{11}
6c, R = CF_3; X = Me

reactions suggested that they might proceed by similar routes, i.e., initial ring opening and formation of a silapropyl carbanion, followed by α-proton abstraction and nucleophilic attack on the neighboring imino carbon to close a six-membered chelate ring. However, the possibility of a radical reaction cannot be ignored at this point. The mechanistic ambiguity is under investigation and will be reported later.

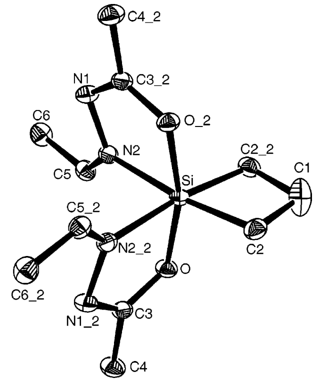
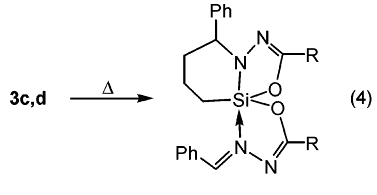


Figure 1. Molecular structure of **3a** in the crystal, depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si–O, 1.8051(12); Si–N, 1.9919(16); Si–C, 1.9016(19); O–Si–O, 164.39(9); N–Si–N, 86.39(9); C–Si–C, 78.53(12), O–Si–N2, 88.65(6); O–Si–N2A, 79.95(6).

In the absence of protons in positions α to the imino carbon, such as in the benzaldimino complexes **3c**,**d**, no proton abstraction is possible, and hence a different rearrangement takes place: silacyclobutane ring opening leads to a γ-silapropyl intermediate (whether radical or carbanion), which attacks the most electrophilic atom in the system, the imino carbon, adds to the double bond, and closes a new six-membered chelate ring (eq 4).



7c, R = Me
7d, R = CF_3

This reaction involves ring expansion of the silacyclobutane to a six-membered azasilacyclohexane ring, accompanied by transformation of one of the dative N→Si bonds to a regular covalent bond.

The evidence for these findings is as follows: crystal structures have been determined for a representative silacyclobutane complex and rearrangement products (**3a**, **4b**, and **7c**),[15] and the resulting molecular structures are depicted in Figures 1–3. The results of microanalyses and spectral data are given in the Supporting Information.

3 is of interest also because it is the first reported hydrazide-based hexacoordinate complex with two monodentate carbon ligands.[8] The nitrogens in **3** are cis and

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(11) (a) Typical synthesis of bis[*N*-(ethylideneimino)acetimidato-*N*,*O*]silacyclobutane (**3a**): in a partly evacuated flask a mixture of 1.155 g (6.70 mmol) of **2a** and 0.471 g (3.34 mmol) of **1** in 5 mL of ether was stirred for 20 h at room temperature. The volatiles were removed under vacuum, and the solid residue was washed with 10 mL of hexane and dried. **3a** was obtained: yield 0.890 g (3.32 mmol, 99%); mp 130–133 °C. A single crystal for X-ray analysis was grown from an ether–THF mixture. ^{1}H NMR: δ 1.13 (m, 4H, CH_2Si), 1.42 (m, 2H, CH_2), 2.04 (s, 6H, OCMe), 2.06 (d, $^3J_{HH} = 5.4$ Hz, 6H, *Me*CH), 7.21 (q,$^3J_{HH} = 5.4$ Hz, 2H, *H*CMe). ^{13}C NMR: δ 12.4, 33.1 (CH_2), 15.9, 18.7 (CH_3), 152.4 (HC=N), 171.7 (OC=N). ^{29}Si NMR: δ −134.7. Anal. Calcd for $C_{11}H_{20}N_4O_2Si$: C, 49.23; H, 7.51; N, 20.88. Found: C, 49.47; H, 6.78; N, 20.66. (b) **3c** is initially formed as the nearly pure *E,Z* isomer, as is evident from the NMR spectra, and upon mild heating it is converted almost exclusively to the C_2-symmetric *E,E* isomer. Further heating brings about the rearrangement discussed below.

(12) Karsch, H. H.; Richter, R.; Witt, E. *J. Organomet. Chem.* **1996**, *521*, 185.

(13) Preparation of compound **4b**: a solution of 1.329 g (5.35 mmol) of **2b** and 0.309 g (2.61 mmol) of **1** in 5 mL of chloroform was kept for 116 h at room temperature. The volatiles were removed under vacuum, and the oily residue was crystallized in 10 mL of ether, giving **4b** as orange crystals: mp 147–148 °C; yield 0.415 g, 0.986 mmol, 38%). ^{1}H NMR: δ 0.77–0.85 (m, 4H, CH_2CH_2), 0.94 (t,$^3J_{HH} = 6.5$ Hz, 3H, *Me*CH_2), 1.44 (m, 2H, CH_2), 1.23 (s, 3H, MeC), 1.59 (s, 3H, MeC), 2, 53 (s, 3H, MeC=N), 2.58, 2.82 (ABq, $^2J_{HH} = 15.5$ Hz, 2H, CH_2), 7.30–8.21 (m, 10H, Ph). ^{13}C NMR: δ 17.7 (Me), 17.9 (CH_2), 21.9 (CH_2), 22.2 (Me), 26.6 (Me), 30.6 (Me), 46.7 (CH_2), 53.7 (C), 124.9–132.3 (Ph), 151.9, 166.9, 170.3 (C=N). ^{29}Si NMR: δ −86.9. Anal. Calcd for $C_{23}H_{28}N_4O_2Si$: C, 65.68; H, 6.71; N, 13.32. Found: C, 65.75; H, 6.55 N, 13.40.

(14) Gostevskii, B.; Kalikhman, I.; Sivaramakrishna, A.; Kocher, N.; Deuerlein, S.; Leusser, D.; Stalke, D.; Kost, D. *Organometallics* **2004**, *23*, 4346.

(15) (a) Crystal data for **3a**: $T = 100(2)$ K, monoclinic, space group $C2/c$; $a = 15.901(3)$ Å, $b = 7.3668(12)$ Å, $c = 12.472(2)$ Å; $\alpha = 90°$, $\beta = 109.739(2)°$, $\gamma = 90°$. $Z = 4$, $V = 1375.1(4)$ Å^3, $R_F = 0.0497$ ($R_{wF} = 0.1096$) for $I > 2\sigma(I)$, 5959 reflections collected, 1655 independent reflections. Full-matrix least squares on F^2 was used for refinement (b) Crystal data for **4b**: $T = 100(2)$ K, orthorhombic, space group $Pca2_1$; $a = 11.1551(10)$ Å, $b = 9.0352(8)$ Å, $c = 43.602(4)$ Å; $\alpha = \beta = \gamma = 90°$. $Z = 8$, $V = 4394.6(7)$ Å^3, $R_F = 0.0716$ ($R_{wF} = 0.1413$) for $I > 2\sigma(I)$, 36 931 reflections collected, 10 464 independent reflections. Full-matrix least squares on F^2 was used for refinement. (c) Crystal data for **7c**: $T = 100(2)$ K, monoclinic, space group $C2/c$; $a = 31.124(3)$ Å, $b = 8.5609(7)$ Å, $c = 31.249(3)$ Å; $\alpha = 90°$, $\beta = 96.615(2)°$, $\gamma = 90°$. $Z = 16$, $V = 8270.7(12)$ Å^3, $R_F = 0.0536$ ($R_{wF} = 0.1216$) for $I > 2\sigma(I)$, 35 720 reflections collected, 9970 independent reflections. Full-matrix least squares on F^2 was used for refinement.

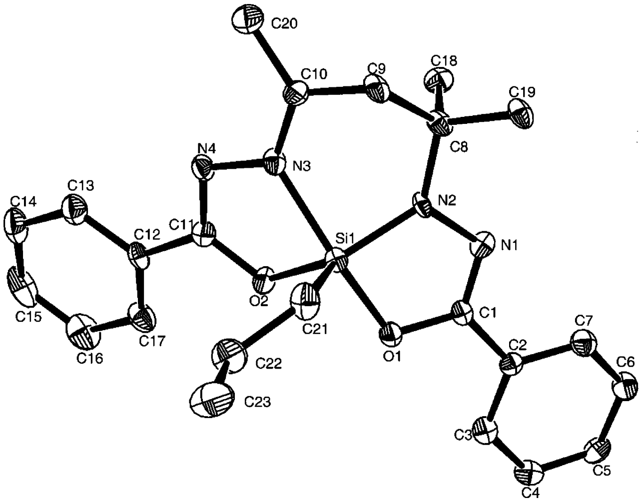

Figure 2. Molecular structure of **4b** in the crystal, depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si−O1, 1.733(3); Si−O2, 1.746(3); Si−N2, 1.755(3); Si−N3, 1.981(3); Si−C, 1.868(4); N2−C8, 1.467(5); N3−C10, 1.289(4); O1−Si−N3, 160.63(13); O2−Si−N2, 133.68(14), N2−Si−N3, 89.31(13); O1−Si−O2, 89.66(12); O1−Si−C, 101.45(17); O2−Si−C, 108.49(16); N2−Si−C, 117.56(17); N3−Si−C, 97.34(17).

Table 1. ^{29}Si Chemical Shifts (ppm) for Compounds 3a−d, 4a,b, and 7c,d in CDCl$_3$ Solution at 300 K

	3a	**3b**	**3c**	**3d**	**4a**	**4b**	**7c**	**7d**
δ(^{29}Si)	−134.7	−119.0	−131.3	−132.1	−86.6	−86.9	−74.6	−70.6

the oxygens trans relative to each other, in contrast to numerous previously analyzed SiO$_2$N$_2$XY hexacoordinate compounds, in which nitrogens were in trans positions.[9,16] Further evidence for the hexacoordination of compounds **3a**−**d** in solution is found in their ^{29}Si NMR spectra (Table 1): the ^{29}Si chemical shifts fall well within the range of hexacoordinate complexes with similar ligand frameworks, with either X or Y being a halogen.[8,9,16] **3b** shows significant temperature dependence of the ^{29}Si chemical shift (δ −123.1 ppm at 257 K and −112.6 ppm at 330 K, in CDCl$_3$ solution), suggesting that some N−Si dissociation may take place in an equilibrium between hexa- and pentacoordinate complexes.[17]

The various solution NMR spectra (^{1}H, ^{13}C, and ^{29}Si) of the rearrangement products **4** agree with the crystal structure of **4b**, proving the identity of the compounds in the crystal and in solution. Thus, the appearance of the ^{1}H and ^{13}C NMR signals typical of the *n*-propyl group provide evidence for the structure of **4**. Likewise, the conversion of one of the *C*-methyl groups in **3a**,**b** to a CH$_2$ group in **4** is apparent in the NMR spectra and is evidence for the structure of **4** in solution.

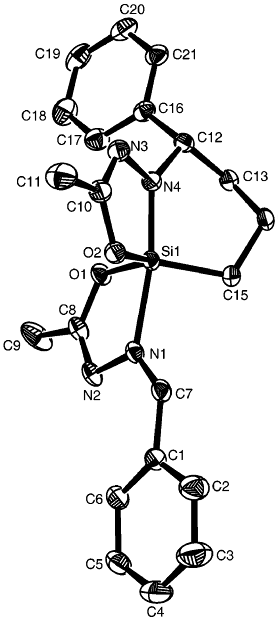

Figure 3. Molecular structure of **7c** in the crystal, depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (corresponding to one of the two independent molecules in the unit cell): Si1−O1, 1.7248(12); Si1−O2, 1.7017(12); Si1−N1, 2.0438(15); Si1−N4, 1.7579(15); Si1−C15, 1.8637(17); N1−Si1−N4, 169.45(6); O1−Si1−O2, 113.57(6); O1−Si1−C15, 113.18(7), O2−Si1−C15, 131.17(7).

The two rearrangement reactions described above feature unusually facile ring opening, accompanied by carbon−carbon bond formation and chelate ring expansion, and may offer new synthetic routes for organic and organosilicon compounds.

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Supporting Information Available: Text giving experimental and spectral details for new compounds, and tables of crystal data for **3a**, **4b**, and **7c**; crystal data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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