Pentacoordinate Silicon Complexes

An Unexpected, Sterically Driven, Methyl Halide Elimination in Pentacoordinate Siliconium Halide Salts: Silicon Complexes with Equatorial Nitrogen Coordination**

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Donor-stabilized silyl cation salts have recently drawn considerable attention.[1–6] Several reactions leading to such complexes[2–6] and the utility of these complexes as catalysts have been reported.[7] While dozens of previously reported pentacoordinate (as well as hexacoordinate) silicon complexes with a dimethylamino donor group (**1, 2**) are thermally stable,[8] we now report that certain pentacoordinate siliconium halide salts undergo a facile and quantitative elimination of a methyl halide to produce neutral pentacoordinate silicon complexes with unprecedented equatorial nitrogen coordination (Scheme 1).

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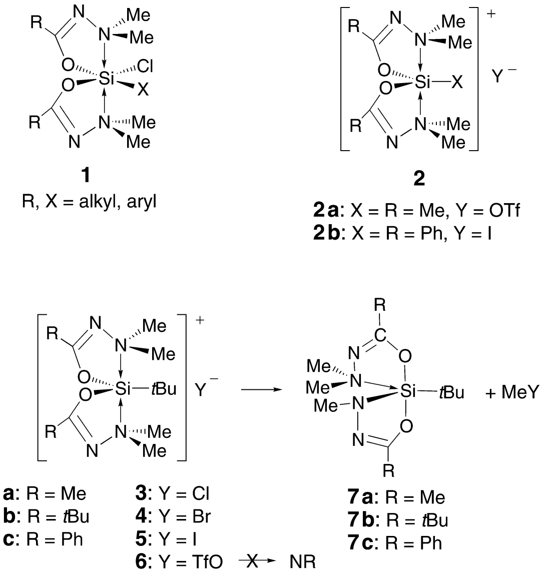
[**] Donor-stabilized silyl cations, part 6. For parts 1–5 see reference [6]. This work was supported by the German Israeli Scientific R&D Foundation (GIF), grant I-628-58.5/1999.



Scheme 1. Elimination of a methyl halide from bis-(N→Si)-coordinated siliconium salts **3**–**5** to give neutral, singly (N→Si)-coordinated complexes **7**.

tert-Butylsiliconium chlorides **3a**–**c** were obtained by transsilylation of $t\mathrm{BuSiCl_3}$ with the corresponding *N*-dimethylamino-*O*-trimethylsilylimidates $[\mathrm{Me_3SiOC(R){=}NNMe_2}]$ and readily converted into the siliconium halides or triflates **4**–**6** by treatment with $\mathrm{Me_3SiY}$.[6c]

A unique feature of the *t*Bu-substituted compounds **3**–**5** is that under mild heating (65 °C) they quantitatively undergo methyl halide elimination to form novel, neutral pentacoordinate complexes **7** (Scheme 1).[9] In this reaction, one of the two initially equivalent $\mathrm{Me_2N}$ groups loses a methyl substituent to produce a complex with one covalent and one dative N–Si bond. The products of elimination were isolated and characterized by X-ray crystal-structure analysis (Figure 1 a)[10] and by standard methods.

The progress of the elimination reaction (at 65 °C, in $\mathrm{CDCl_3}$, in a flask sealed under vacuum) was monitored by ^{1}H and ^{29}Si NMR spectroscopy, and was found to depend on the counterion: With respect to the halide the order of reactivity is I > Br > Cl (50 % elimination after 85, 130, and 175 min, respectively, from **5c, 4c**, and **3c**), whereas the siliconium triflates **6a**–**6c** did not react. It is thus evident that nucleophilic attack of the anion at one of the *N*-methyl groups is involved in the rate-determining step of the elimination.

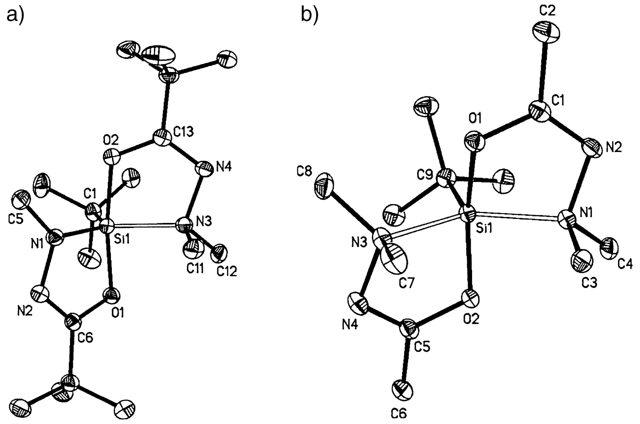


Figure 1. Crystallographic molecular structures of **7b** (a) and **6a** (b) at the 50 % probability level. Hydrogen atoms omitted for clarity. For **6a** only the cation is shown; the separate triflate anion has been omitted.

The special observations made regarding the *t*Bu complexes **3**–**6** can be rationalized in terms of steric bulk: a) the direct formation of **3** by transsilylation (in contrast with analogues **2**, which contain X = Me, Ph, or $\mathrm{PhCH_2}$ in place of the *t*Bu group and are formed via the neutral hexacoordinate species **1**) results from the difficulty in accommodating both the *t*Bu and the halide ligands next to each other; b) likewise, steric repulsion between the adjacent *t*Bu and $\mathrm{Me_2N}$ groups in **3**–**5**, which is at least partly released by elimination, may account for the facile loss of the methyl halide. These arguments are strengthened by comparison of the crystal structures of the relevant complexes (**6a, 7b**, Figure 1, Table 1).[10]

Table 1: Selected bond lengths and angles for **6a** and **7b**.

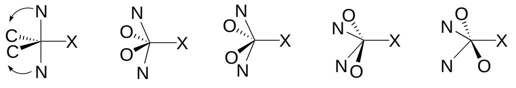
	Si–O [Å]	Si–N [Å]	Si–C [Å]	O-Si-O [°]	N-Si-N [°]
6a	1.7240(8) 1.7266(8)	1.9397(10) 1.9470(10)	1.8964(11)	152.22(4)	133.54(4)
7b	1.7844(7) 1.7591(7)	1.7265(9) 1.9496(9)	1.9115(10)	165.74(4)	121.51(4)

The striking feature of the structure of the elimination product **7b** is that the $\mathrm{Me_2N}$ donor ligand, as well as the covalent Si–N bond, occupy *equatorial* positions in the slightly distorted trigonal bipyramidal (TBP) complex. To the best of our knowledge, no equatorial coordination by a nitrogen ligand has been reported in pentacoordinate silicon complexes.[8]

The molecular structure of **6a**, the triflate analogue of the elimination precursors **3a**–**5a**,[11] was also unexpected: Even in the elimination precursor the nitrogen ligands occupy the equatorial-like and the oxygen ligands the axiallike positions, as judged from the corresponding N-Si-N (133.54°) and O-Si-O (152.22°) bond angles. This is in sharp contrast to all previously reported crystal structures for analogous siliconium salts **2** with different X ligands, in all of which the nitrogen ligands occupy essentially axial positions.[6c]

Like the elimination itself, the uncommon N,N-diequatorial geometry in **7b** and **6a** must also be imposed by steric requirements: The bulky *t*Bu ligand prefers to have the smaller oxygen ligands in its vicinity (~ 90° bond angle) over the relatively large *N*-methylamino and *N,N*-dimethylamino groups. The latter are therefore placed at greater distances from the *t*Bu group by opening up the bond angles (~ 120°). These substantial modifications of the crystal structures of *t*Bu-substituted complexes are in line with the observation that only *tert*-butylsiliconium halide complexes undergo facile methyl halide elimination, whereas methyl- and benzylsiliconium complexes **2** resist this reaction, and the bulkier **2b** undergoes a much slower elimination (50 % MeI elimination after 90 h at 65 °C).

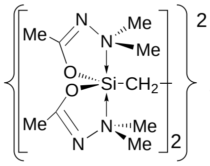
The uncommon molecular geometries found in the crystal structures of **7b** and **6a** can be viewed within a larger framework as points along a hypothetical Berry pseudorotation reaction coordinate.[12] A single pseudorotation process is depicted schematically in Figure 2. Each point along the pseudorotation coordinate has a corresponding crystal structure, and thus the entire process can be followed crystallographically, in a Burgi–Dunitz sense.[13]



	TBP1	35% TBP1	SP	31% TBP2	TBP2
NSiN	171.2	155.6	146.9	133.5	121.5
OSiO (CSiC)	119.8	134.3	146.0	152.2	165.7
Compound	**9**	**2a**	**8**	**6a**	**7b**

Figure 2. Schematic progress along a Berry pseudorotation coordinate, with corresponding molecular structures and N-Si-N and O-Si-O angles (°). For references, see text. TBP = trigonal bipyramidal, SP = square planar.

The progress along the reaction coordinate is evident from the variation in the N-Si-N and O-Si-O (or C-Si-C) angles, which determine the overall geometry. Initially the geometry corresponds to TBP1, with two *trans*-diaxial nitrogen ligands (**9**).[2a] This is the common geometry for pentacoordinate bischelates with two nitrogen donor ligands.[8] The N-Si-N angle gradually decreases along the series, while the O-Si-O angle increases, via a distorted TBP (**2a**, ~65 % TBP1→SP),[6c] through pure square planar (SP) geometry (**8**; evidenced by the N-Si-N ≃ O-Si-O angles),[6e] then through another distorted TBP with axiallike oxygen ligands (**6a**), and finally to the TBP2 geometry of **7b**, which is essentially an inverted TBP in which axial and equatorial groups have exchanged their positions. Throughout this process the *t*Bu group acts as a "pivot" for the pseudorotation.



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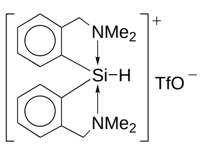

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As mentioned above, most pentacoordinate bischelates of silicon with two N→Si dative bonds have TBP1 geometry. Clearly this geometry is preferred. It is only the steric strain introduced by the *t*Bu group in **3**–**5** and **7**, or in the binuclear **8**, that pushes the geometry towards the other end of the reaction coordinate and enables the demonstration of stable points along the entire pseudorotation coordinate. The methyl halide elimination described herein may provide a new synthetic route to MeN-Si compounds.

Experimental Section

4a–c–6a–c were obtained from **3a–c**[6c] by reaction with excess Me_3SiY in 80–97 % yield. **6a**: $Me_3SiOSO_2CF_3$ (0.777 g, 3.5 mM) was added as a solution in hexane to **3a**[6c] (0.977 g, 3.4 mM), and the mixture was stirred for 2 h at room temperature. The volatile components were removed at 0.02 mmHg, leaving **6a** (1.205 g, 88 %) as a white precipitate, m.p. 197–198 °C, which was recrystallized for X-ray analysis from CH_2Cl_2. ^1H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 1.07$ (s, 9H, *t*Bu), 2.08 (s, 6H, CMe), 3.05, 3.12 ppm (2 s, 6H, NMe_2); ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): $\delta = 16.9$ (CCH_3), 23.0 (Me_3C), 29.7 ($(CH_3)_3C$), 49.7, 51.8 (NMe_2), 120.6 (q, $^1J = 321$ Hz, CF_3), 169.0 ppm (C=N); ^{29}Si NMR (99.4 MHz, $CDCl_3$, 300 K): $\delta = -61.2$ ppm. **7b**: A solution of **3b** (0.804 g, 1.97 mM) in $CHCl_3$ (5 mL) was kept in a preevacuated flask immersed in a 90 °C bath for 6 days. The volatiles were removed at 0.02 mmHg, and the residue was recrystallized from hexane, to give **7b** (0.386 g, 55 %), m.p. 77–78 °C. ^1H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 0.86$ (s, 9H, *t*Bu-Si), 1.09 (s, 18H, *t*Bu-C), 2.40 (s, 3H, NMe), 2.88, 3.01 ppm (2 s, 6H, NMe_2); ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): $\delta = 25.0$ (Me_3CSi), 27.3, 27.7, 29.3 ($(CH_3)_3C$), 33.9, 35.1 (Me_3CC), 36.8 (NMe), 47.8, 49.0 (NMe_2), 160.9, 176.8 ppm (C=N); ^{29}Si NMR (99.4 MHz, $CDCl_3$, 300 K): $\delta = -73.1$ ppm; elemental analysis: calcd for $C_{17}H_{36}N_4O_2Si$: C 57.26, H 10.18, N 15.71. Found: C, 57.21; H, 10.29; N, 15.59. **7a** and **7c** were prepared in the same way as **7b** and were characterized by analogy based on their NMR spectra. **7a**: ^1H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 0.85$ (s, 9H, *t*BuSi), 1.85, 1.93 (2 s, 6H, MeC), 2.56 (s, 3H, NMe), 3.00, 3.90 ppm (2 s, 6H, NMe_2); ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): $\delta = 16.0$, 17.0 (CCH_3), 24.1 (Me_3CSi), 28.7 ($(CH_3)_3C$), 36.0 (NMe), 49.7, 56.9 (NMe_2), 169.1, 170.2 ppm (C=N); ^{29}Si NMR (99.4 MHz, $CDCl_3$, 300 K): $\delta = -71.8$ ppm. **7c**: ^1H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 1.03$ (s, 9H, *t*BuSi), 2.79, 3.32 (2 s, 6H, NMe_2), 3.47 (s, 3H, NMe), 7.30–8.10 ppm (m, 10H, Ph); ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): $\delta = 24.6$ (Me_3CSi), 28.8 ($(CH_3)_3C$), 36.8 (NMe), 48.4, 50.0 (NMe_2), 124.9–132.4 (Ph), 152.8, 166.1 ppm (C=N); ^{29}Si NMR (99.4 MHz, $CDCl_3$, 300 K): $\delta = -71.7$ ppm.

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[10] **6a**: $T = 100(2)$ K, triclinic, space group: $P\bar{1}$; $a = 8.0805(4)$, $b = 11.0395(6)$; $c = 11.6194(6)$ Å; $\alpha = 83.063(1)$; $\beta = 75.121(1)$; $\gamma = 81.860(1)°$, $Z = 2$, $V = 987.79(9)$ Å^3. $R_F = 0.0269$ ($wR_F = 0.0737$) for $I > 2\sigma$. **7b**: $T = 100(2)$ K, triclinic, space group: $P\bar{1}$; $a = 7.5031(5)$, $b = 11.7898(8)$; $c = 12.0470(8)$ Å; $\alpha = 82.708(1)$; $\beta = 87.980(1)$; $\gamma = 84.512(1)°$, $Z = 2$, $V = 1051.93(12)$ Å^3. $R_F = 0.0345$ ($wR_F = 0.0906$) for $I > 2\sigma$. CCDC-195084 (**6a**) and CCDC-195085 (**7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[11] The exact precursors to **7b** (**3b**–**5b**) did not yield suitable crystals for X-ray crystal-structure analysis. However, the identical ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3b** and **6b**, as well as previous experience with siliconium salts with different counterions,[6c] indicate that the siliconium ion portions of **3b** and **6b** are equivalent. The replacement of the remote substituent R = *t*Bu in **6b** by R = Me in **6a** is not expected to have a substantial effect on the geometry about the silicon atom.

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