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Pentacoordinate Silyl Cations Stabilized by Coordination with Oxygen Donors: Crystal Structure, Charge Distribution, and Stereodynamics

Inna Kalikhman,*,† Sonia Krivonos,† Lutz Lameyer,‡ Dietmar Stalke,‡ and Daniel Kost*,†

Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva 84105, Israel, and Institut für Anorganische Chemie, Universität Würzburg, D-97074 Würzburg, Germany

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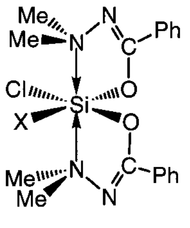
*Summary: Attempted preparation of neutral hexacoordinate silicon chelates with two O→Si dative bonds (**4**), in analogy to previously reported bis-N→Si isomers (**2**), resulted in unexpected formation of pentacoordinate siliconium complexes (**5** and **6**), characterized by a crystal structure. The barrier for inversion of configuration at silicon was determined by selective inversion recovery NMR measurements:* $\Delta G^* = 20.5 \pm 0.2$ *kcal* mol^{-1}.

Free tricoordinate silicon cations (silicenium) are exceedingly unstable and have only recently been first realized.[1,2] A silicenium ion can be stabilized by coordination with two intramolecular donors, to form a stable (pentacoordinate) siliconium complex. These have been reported with N→Si coordination[3,4] and most recently also with O,[5,6] S,[6] and P[6] donor ligands, involving ortho-substituted phenyl chelates ($(o\text{-}ZCH_2C_6H_4)_2$-Si−X, where Z is the donor atom and X is a monodentate ligand, usually H). These recent reports prompt us to communicate results on the facile preparation and characterization of a new class of ionic pentacoordinate siliconium compounds, with bis-O→Si coordination and O,N-chelate connectivity (**5**; SiN_2O_2C ligand framework). Previously reported siliconium bis-chelates had H as the monodentate ligand, in most cases,[3a,c,4,6] and required elaborate ligand exchange reactions, or special non-nucleophilic counterions, to obtain analogues with any other monodentate ligand.[3b,d] In contrast, the present work describes the facile spontaneous formation of ionic complexes with a variety of monodentate ligands. The complexes have been characterized, and their facile formation, charge distribution, and stereodynamic behavior are discussed.

Results. Synthesis. The reaction of *N′*,*N′*-dimethyl-*O*-(trimethylsilyl)benzhydrazide ($Me_2NN{=}C(Ph)OSiMe_3$) with trichlorosilanes (**1**, $XSiCl_3$; X = Me, Ph, CH_2Cl, CH_2Ph) was reported to yield the neutral hexacoordinate silicon chelates **2** with two N→Si dative bonds.[7]



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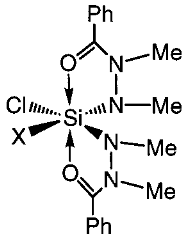

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In sharp contrast, the reaction of *N*,*N′*-dimethyl-*N′*-(trimethylsilyl)benzhydrazide (**3**)[8a] with **1** does *not* result in the expected hexacoordinate bis-O→Si chelates **4a**−**d**, which are isomers of **2**, but rather in the pentacoordinate siliconium chloride complexes **5** (eq 1).[8b] This is evident from the relative downfield shift in the ^{29}Si NMR spectra, characteristic of pentacoordination, and is supported by the equivalence of the two chelate rings (Table 1), as required by **5**. Equivalence of the

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† Ben Gurion University of the Negev.

‡ Universität Würzburg.

(1) For reviews see: (a) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191. (b) Lickiss, P. D. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester U.K., 1998; pp 557−594. (c) Olah, G. A.; Heiliger, L.; Li, X. Y.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1990**, *112*, 5991.

(2) (a) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlman, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001. (b) Lambert, J. B.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 400. (c) For computational evidence, see: Müller, T.; Zhao, Y.; Lambert, J. B. *Organometallics* **1998**, *17*, 278.

(3) (a) Brelière, C.; Carré, F.; Corriu, R. J. P.; Wong, C. M. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2333. (b) Chauhan, M.; Chuit, C.; Corriu, R. J. P.; Reyé, C. *Tetrahedron Lett.* **1996**, *37*, 845. (c) Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reyé, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1311. (d) Chauhan, M.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reyé, C. *Organometallics* **1996**, *15*, 4326.

(4) (a) Belzner, J.; Schär, D.; Kneisel, B. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 1840. (b) Schär, D.; Belzner, J. In *Organosilicon Chemistry III*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1997; pp 429−434.

(5) (a) Ovchinnikov, Yu. E.; Pogozhikh, S. A.; Razumovskaya, I. V.; Shipov, A. G.; Kramarova, E. P.; Bylikin, S. Yu.; Negrebetsky, V. V.; Baukov, Yu. I. *Russ. Chem. Bull.* **1998**, *47*, 967. (b) Kramarova, E. P.; Smirnova, L. S.; Artamkina, A. G.; Shipov, A. G.; Baukov, Yu. I.; Ovchinnikov, Yu. E.; Mozzhukhin, A. O.; Struchkov, Yu. T. *Zh. Obshch. Khim.* **1993**, *63*, 2275.

(6) Berlekamp, U.-H.; Jutzi, P.; Mix, A.; Neumann, B.; Stammler, H.-G,; Schoeller, W. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 2048.

(7) (a) Kalikhman, I. D.; Gostevskii, B. A.; Bannikova, O. B.; Voronkov, M. G.; Pestunovich, V. A. *Metalloorg. Khim.* **1989**, *2*, 937; *Chem. Abstr.* **1990**, *112*, 1188926r. (b) Kost, D.; Kalikhman, I.; Raban, M. *J. Am. Chem. Soc.* **1995**, *117*, 11512. (c) Kalikhman, I.; Kost, D.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1253. (d) Kost, D.; Krivonos, S.; Kalikhman, I. In *Organosilicon Chemistry III*; Auner, N., Weis, J.; Eds.; VCH: Weinheim, Germany, 1997; pp 435−445. (e) Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T.; Kost, D. *Organometallics* **1997**, *16*, 3255. (f) Kost, D.; Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T. *J. Am. Chem. Soc.* **1998**, *120*, 4209.

(8) (a) **3** was prepared by trimethylsilylation of *N*,*N′*-dimethylbenzhydrazide, as described previously for *N′*,*N′*-dimethyl-*O*-(trimethylsilyl)-benzhydrazide.[7a,b] (b) **5a** was prepared by stirring a 2.62 g (11 mmol) solution of **3** and 1.3 g (8.7 mmol) of **1** in 20 mL of $CHCl_3$ at room temperature for 8 h under argon, followed by removal of volatiles at 0.5 Torr. The remaining oil was boiled in 30 mL of hexane to yield 2.16 g (5.33 mmol, 97%) of **5a**: white powder, mp 182−183 °C. Anal. Calcd for $C_{19}H_{25}ClN_4O_2Si$: C, 56.35; H, 6.22; Cl, 8.75; N, 13.85; Si, 6.94. Found: C, 56.15; H, 6.10; Cl, 8.82; N, 13.95; Si, 6.30. **5b**−**d** were prepared analogously to **5a**. Selected NMR data are listed in Table 1.

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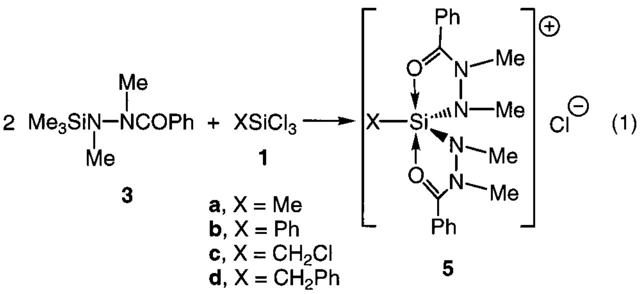
Table 1. ^{1}H (500.13 MHz), ^{13}C, and ^{29}Si Chemical Shifts (δ in ppm, Relative to Internal TMS) for Complexes 5a–d, 6, and 9 in $CDCl_3$ Solution

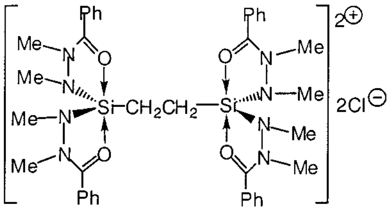
	^{29}Si	C=O	CN*C*H$_3$	SiN*C*H$_3$	CNC*H*$_3$	SiNC*H*$_3$
5a	−79.0	160.4	36.8	31.9	3.86	3.27
5b	−94.8	160.3	37.2	32.6	3.79	3.30
5c	−91.7	159.4	36.7	32.0	3.64	3.07
5d	−86.6	159.6	36.2	31.6	3.70	3.20
6-I	−81.3	159.0	36.8	31.1	3.84	3.26
6-II	−81.6	158.9	36.8	31.1	3.84	3.28
9	−78.3	163.0	32.7[a]	30.9	3.60	3.07
	−78.9[a]	162.8[a]	32.7[a]	30.6[a]	3.56	3.05
	−78.9[a]	162.8[a]	32.6	30.6[a]	3.54	2.88
	−79.3	162.5	32.0	30.4	3.52	2.80

[a] Accidental equivalence of two groups.



rings down to 175 K makes a possible "flip flop"[9] exchange of chelates highly unlikely.

A crystal structure confirming the pentacoordinate nature of **5** was obtained for the dication dichloride **6**, prepared from $Cl_3SiCH_2CH_2SiCl_3$ and **3** (Figure 1).[10]



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Molecular Structure of Dication 6. The molecular geometry derived from the crystal structure of **6** clearly confirms the ionic nature of the complex: the Si–Cl distances are greater than 7 Å, and the chloride anions are solvated by hydrogen bonding to chloroform molecules.

The geometry around each of the silicon atoms in **6** (Table 2) is a distorted trigonal bipyramid (TBP). The oxygen atoms occupy axial positions, and the O–Si–O angle is 168.8°. The dative O→Si bonds (1.802 and 1.807 Å) are exceptionally short relative to those in other pentacoordinate complexes,[11–13] including the reported ionic disiloxane complexes.[5]

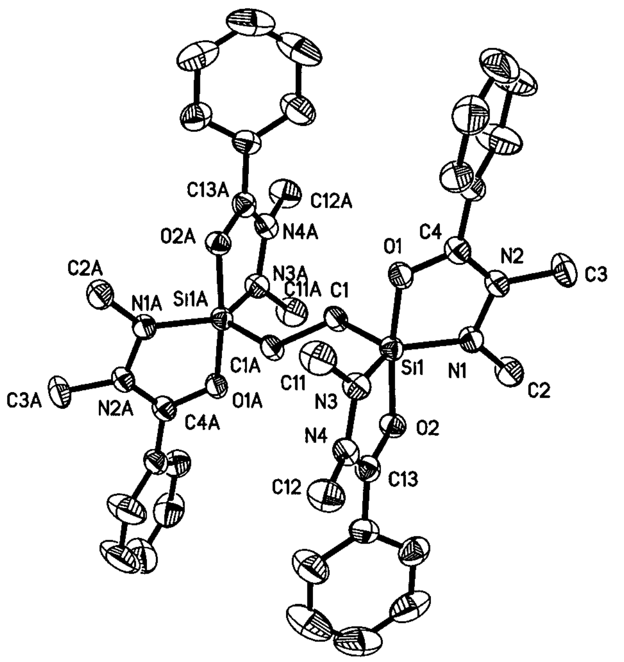

Figure 1. Crystal structure of **6**: formula $C_{44}H_{54}Cl_{20}N_8O_4Si_2$; triclinic, space group $P\bar{1}$; unit cell a = 1072.78(14) pm, b = 1352.8(2) pm, c = 1417.3(2) pm, α = 108.12(2)°, β = 110.77(2)°, γ = 100.75(2)°; determined at 173(2) K. The complete data can be found in the Supporting Information.

Table 2. Selected Bond Lengths (Å) for 6

Si(1)–N(1)	1.755(3)	Si(1)–N(3)	1.770(3)
Si(1)–O(1)	1.802(2)	Si(1)–O(2)	1.807(2)
Si(1)–C(1)	1.878(3)	N(3)–N(4)	1.409(4)
N(1)–N(2)	1.405(4)	N(4)–C(13)	1.310(5)
N(2)–C(4)	1.293(5)	C(13)–O(2)	1.293(4)
C(4)–O(1)	1.304(4)		

6 may exist in two diastereomeric forms. The crystal of **6** features a molecular inversion center, and hence, the isolated diastereomer is the *meso* form.

The solution NMR spectra indicated the presence of both diastereomers of **6**, **6-I**, and **6-II** (*meso* and *d,l*), as expected. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **6** (Table 1) are analogous and similar to those of **5a–d** and lead to the structural assignment of the latter.

Charge Distribution Analysis for 6. Computational[2c,14] and experimental[2a,b] evidence suggests that while the silicon atom is positively charged in a free silicenium compound, it is effectively neutral in donor-stabilized siliconium complexes (i.e., most of the positive charge is transferred to the donor atoms); this is evident from the huge difference in ^{29}Si chemical shifts between the two classes of compounds (>200 ppm in the former and <−50 ppm in the latter). Thus, the term "siliconium" should be referred to in a formal sense. This charge distribution is supported by a bond length analysis of **6**: the strong coordination of oxygen to silicon, as evident from the short O–Si distances, affects the carbonyl bond length. The C=O bonds in **6** are substantially longer than average amide or hydrazide C=O bonds,[15] and the C–N bonds are likwise shorter than typical amide C–N bonds.[15] In fact, the C–O and C–N

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[9] Auner, N.; Probst, R.; Hahn, F.; Herdtweck, E. *J. Organomet. Chem.* **1993**, *459*, 25.

[10] **6** was prepared by adding 97 mg (0.325 mmol) of $Cl_3SiCH_2CH_2SiCl_3$ to a solution of **3** (307 mg, 1.3 mmol) in 3 mL of chloroform under dry argon. After 1 h at room temperature, half of the solvent was removed under vacuum, and the solution was placed at −10 °C for 24 h, after which crystals separated in quantitative yield. A single crystal was taken directly for X-ray analysis.

[11] Lukevics, E.; Pudova, O. A. *Khim. Geterotsikl. Soedin.* **1996**, 1605; *Chem. Abstr.* **1997**, *126*, 157528w.

[12] Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Apeloig, Y., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, p 1339.

[13] Mercado, R.-M. L.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1999**, *18*, 906.

[14] Kraka, E.; Sosa, C. P.; Gräfenstein, J.; Cremer, D. *Chem. Phys. Lett.* **1997**, *279*, 9.

[15] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

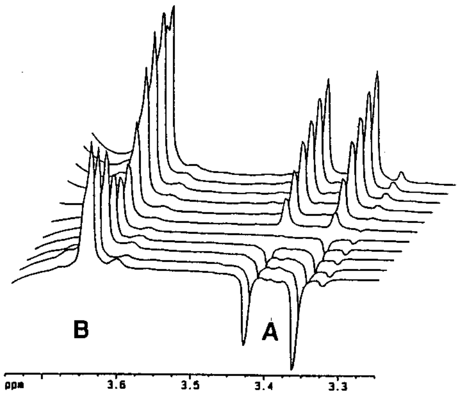
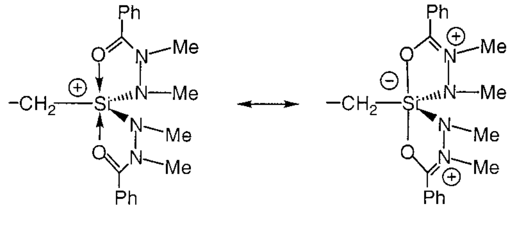


Figure 2. Stack plot of the ^{1}H (500.13 MHz) selective inversion recovery (SIR) spectra of **9** in nitrobenzene-d_5 solution at 360 K.[18]

distances in **6** are essentially equal, at 1.30 ± 0.01 Å. Examination of numerous relevant amide and hydrazide silicon complexes[16] shows that the C−O distance varies between 1.20 and 1.35 Å, while the C−N bond falls in the range 1.34−1.27 Å (depending on whether the sequence N−C=O→Si or N=C−O−Si is more important). Clearly, both the C−O and C−N bonds in **6** are near the middle of each bond length range, and hence, **6** may best be described as a hybrid between equal parts of **7** and **8** (eq 2). The resulting charge distribution is 0.5 positive charge on each of the ammonium nitrogens and zero charge on silicon. It follows that the formation of these formally cationic silicon complexes (**5** and **6**) is facilitated by the ability of the hydrazide moiety to redistribute the charges so that the positive charge is effectively removed from silicon and transferred to the nitrogen atoms.

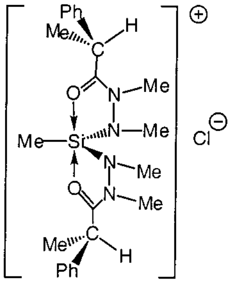


(2)

7 **8**

This extraordinary ability of the oxygen atoms to distribute the positive charge, relative to other donor atoms, through the amide resonance (eq 2) accounts for the facile formation of the ionic complexes in this work, with large monodentate ligands: the better donor ability of the oxygen atoms makes the silicon atom less susceptible to further coordination and, hence, stabilizes the pentacoordinate **5** relative to **4**.

Inversion of Configuration at Silicon. The NMR spectra of **5a**−**d** do not permit the observation of internal ligand-exchange reactions. To enable an NMR kinetic study, the analogous complex **9** was prepared,[17] having two additional chiral carbon centers (Table 1).



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The presence of three chiral centers, one at silicon and two constitutionally equivalent carbon centers, generates three diastereomers in solution: *RRR*, *RSR*, and *RRS* = *SRR* and their respective enantiomers. The first two stereoisomers have C_2 symmetry axes and, hence, have equivalent chelate rings and give rise to two *N*-methyl signals each. The last two stereoisomers are identical but give rise to four *N*-methyl signals, because of nonequivalence of the chelate rings. Thus, in the ^{1}H NMR spectrum of the mixture of isomers there are eight nearly equal *N*-methyl singlets, divided in two groups for the CN*Me* and SiN*Me* groups.

The inversion of configuration at silicon is relatively slow, making the coalescence measurement impractical. The barrier was determined by utilizing the selective inversion recovery (SIR) NMR technique.[18] The SIR method was applied to the exchange of *N*-methyl groups in the essentially equally populated diastereomers (Figure 2). The first-order rate constant is $k = 2.74\ \mathrm{s}^{-1}$, corresponding to a free energy of activation $\Delta G^* = 20.5 \pm 0.2$ kcal mol^{-1} for epimerization at the silicon center.

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Supporting Information Available: Text giving experimental procedures and physical properties of new compounds, figures giving NMR spectra of **5c**,**d**, **6**, and **9**, and tables giving crystallographic data for **6**, in addition to crystallographic files, in CIF format, for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) (a) Kalikhman, I.; Krivonos, S.; Ellern, A.; Kost, D. *Organometallics* **1996**, *15*, 5073. (b) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Baukov, Yu. I.; Kramarova, E. P.; Oleneva, G. I. *J. Organomet. Chem.* **1987**, *327*, 167.

(17) **9** was prepared in analogy to **5a**; three diastereomers had formed which could not be separated and were characterized by the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the mixture.

(18) (a) Blanca, B.-D. M.; Maimon, E.; Kost, D. *Angew. Chem.* **1997**, *109*, 2294; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2216. (b) Orrell, K. G.; Sik, V. *Annu. Rep. NMR Spectrosc.* **1993**, *27*, 103. (c) Kalikhman, I.; Girshberg, O.; Lameyer, L.; Stalke, D.; Kost, D. *Organometallics* **2000**, *19*, 1927.