Synthesis and Molecular Structures of Novel Isopropyl-substituted Oligosilanes

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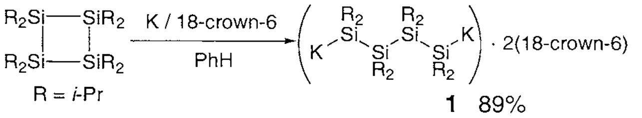
The cyclotetrasilane $[(i\text{-Pr})_2Si]_4$ reacts with K in benzene in the presence of 18-crown-6 to give the 1,4-dipotassio compound $K[(i\text{-Pr})_2Si]_4K$ (**1**). The reaction of **1** with $(i\text{-Pr})_2SiCl_2$ and Me_3SiCl leads to the formation of the sterically crowded oligosilanes, $[(i\text{-Pr})_2Si]_5$ (**2**) and $Me_3Si[(i\text{-Pr})_2Si]_4SiMe_3$ (**3**), respectively. The molecular structures of the resulting oligosilanes, **2** and **3**, display some unusual features.

We wish to report the synthesis and X-ray structures of novel isopropyl-substituted oligosilanes **2** and **3**, which can be obtained from the reaction of 1,4-dipotassio tetrasilane **1** with $(i\text{-Pr})_2SiCl_2$ and Me_3SiCl, respectively.

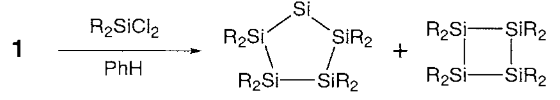
Cleavage of silicon–silicon bonds by alkali metals is one of the important methods for the synthesis of the silyl derivatives of group 1 metals.[1] To date, several examples have appeared in the literature about the ring-opening metallation of small-ring polysilanes, cyclotrisilanes and cyclotetrasilanes, leading to α, ω-dimetallo polysilanes.[2] However, such a reaction only proceeds satisfactorily when the silicon atoms possess at least one aromatic substituent, however the analogous reaction of peralkylated cyclopolysilanes has not been yet reported.[2-4] We found that the ring-opening reaction of $[(i\text{-Pr})_2Si]_4$ with K smoothly proceeds in the presence of 18-crown-6, producing 1,4-dipotassio tetrasilane **1**.

Treatment of a benzene solution of $[(i\text{-Pr})_2Si]_4$ with two equivalents of K in the presence of 18-crown-6 at reflux temperature for 3 h under argon yielded a very air-sensitive pale-yellow powder, $K[(i\text{-Pr})_2Si]_4K$ (**1**).[5,6]



1 89%

Compound **1** is reactive towards $(i\text{-Pr})_2SiCl_2$ and Me_3SiCl. Thus, treatment of **1** with $(i\text{-Pr})_2SiCl_2$ produced the cyclopentasilane $[(i\text{-Pr})_2Si]_5$ (**2**) in 35% isolated yield along with $[(i\text{-Pr})_2Si]_4$ (47%).[7] The formation of **2** is useful, since **2** can not be prepared by the coupling reaction of $(i\text{-Pr})_2SiCl_2$ with Li; the reaction yields only $[(i\text{-Pr})_2Si]_4$.[8]



2 35% 47%

The molecular structure of **2** was established by X-ray crystallography (Figure 1).[9] The molecule has no crystallographic symmetry axis and the ring structure in **2** is significantly distorted from the ideal cyclopentasilane geometry. The Si–Si bond lengths vary from 2.405(1) to 2.444(1) Å with an average of 2.422 Å, compared to $[(i\text{-Pr})_2Si]_4$ where no variation is virtually observed (2.373(4) Å),[10] and these values are the longest among the Si–Si bond lengths in the cyclopentasilanes.[11] The Si_5 ring adopts the twist-envelope (*TE*) conformation; the long Si-Si bond lengths allow the *TE* conformation to avoid destabilizing steric interactions between the isopropyl substituents.

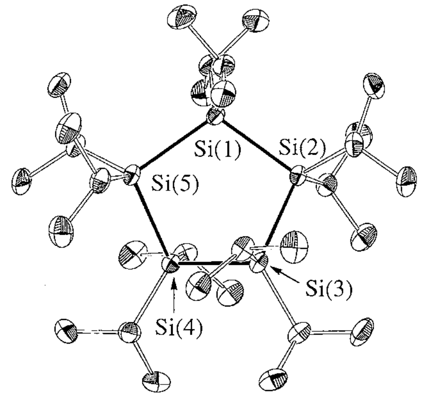
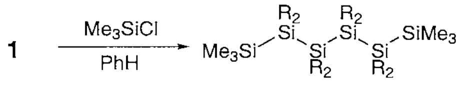


Figure 1. The molecular structure of **2** shown at the 30% probability level. Selected bond lengths (Å) and angles (°); Si(1)-Si(2) 2.441(1), Si(1)-Si(5) 2.444(1), Si(2)-Si(3) 2.405(1), Si(3)-Si(4) 2.409(1), Si(4)-Si(5) 2.410(1), Si(1)-Si(2)-Si(3) 99.79(3), Si(2)-Si(3)-Si(4) 100.51(3), Si(3)-Si(4)-Si(5) 100.46(3), Si(4)-Si(5)-Si(1) 99.89(3), Si(5)-Si(1)-Si(2) 108.77(3).

The reaction of **1** with Me_3SiCl produced linear hexasilane **3** in good yield.[12]



R = *i*-Pr **3** 79%

An X-ray crystallographic study of **3** disclosed some unusual structural features (Figure 2).[13] The dihedral angle Si(2)-Si(3)-Si(4)-Si(5) framework is 172° indicating that the Si_4 framework has a nearly *all-trans* conformation.[14] The Si-Si

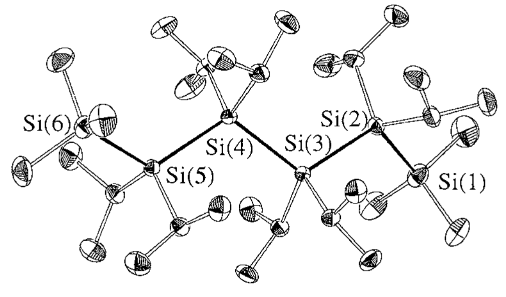


Figure 2. Molecular structure of **3** shown at the 30% probability level. Selected bond lengths (Å) and angles (°); Si(1)-Si(2) 2.385(1), Si(2)-Si(3) 2.449(1), Si(3)-Si(4) 2.480(1), Si(4)-Si(5) 2.443(1), Si(5)-Si(6) 2.405(1), Si(1)-Si(2)-Si(3) 113.53 (1), Si(2)-Si(3)-Si(4) 115.35(4), Si(3)-Si(4)-Si(5) 113.06(4), Si(4)-Si(5)-Si(6) 120.92(4). Dihedral angles (ref. 14); Si(1)-Si(2)-Si(3)-Si(4) -148.08(4)°, Si(2)-Si(3)-Si(4)-Si(5) 173.37(4)°, Si(3)-Si(4)-Si(5)-Si(6) 163.90(4)°.

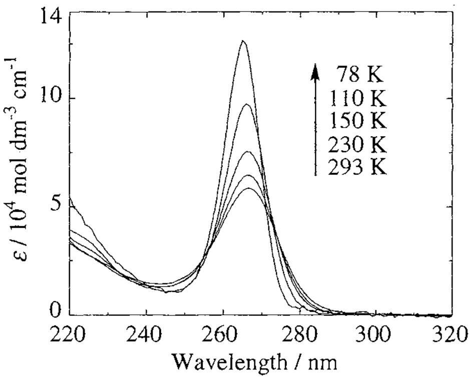


Figure 3. Variable-temperature ultraviolet spectra of **3** in 3-methylpentane.

bond lengths in the framework range between 2.405(1) and 2.480(1) Å; the longest bond length is the central Si(3)-Si(4) bond. The structural features observed for the Si_4 unit may result from the steric requirements for the isopropyl substituents at the two vicinal silicon atoms to avoid severe steric repulsions.

Another interesting point worthy of mention is the UV absorption properties of **3**; it exhibits intense lowest-energy absorption at 267 nm (ε 5.56 x 10^4, in 3-methylpentane). This is similar in position but much stronger than the absorption of $Me(SiMe_2)_6Me$ (260 nm, ε 2.11 x 10^4).[16] Figure 3 also shows that the absorption band does not show any bathochromic shift but a significant hyperchromic one upon cooling. This behavior is rationalized by assuming that the strained *all-trans* form of the Si_4 backbone is retained even in solution.[17-19]

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References and Notes

1 For recent reviews, see: a) P. D. Lickiss and C. M. Smith, *Cood. Chem. Rev.*, **145**, 75 (1995). b) K. Tamao and A. Kawachi, *Adv. Organomet. Chem.*, **38**, 1 (1995). c) J. Balzner and U. Dehnert, in "The Chemistry of Organic Silicon Compounds", ed by Z. Rappoport and Y. Apeloig, John Wiley, New York (1998), Vol. 2, Part 1, Chap. 14.

2 A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **83**, 1921 (1961). H. Gilman and G. L. Schwebke, *J. Am. Chem. Soc.*, **86**, 2693 (1964). M. F. Lemanski and E. P. Schram, *Inorg. Chem.*, **15**, 2515 (1976). J. Belzner, U. Dehnert, and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, **33**, 2450 (1994).

3 For the reduction of peralkylcyclopolysilanes to that of radical anions, a) E. Carberry, R. West, and G. E. Glass, *J. Am, Chem. Soc.*, **91**, 5446 (1969). b) C. L. Wadsworth, R. West, Y. Nagai, H. Watanabe, H. Matsumoto, and T. Muraoka, *Chem. Lett.*, **1985**, 1525.

4 An example of the silyl-anion mediated ring-opening reactions of $(Et_2Si)_4$ has been reported; Y. Hatanaka and T. Hiyama, 40th Symposium on Organometallic Chemistry, Sapporo, November 1993, Abstr., p. 136.

5 Typical procedure: a mixture of K (172 mg, 4.4 mmol), $[(i\text{-}Pr)_2Si]_4$ (1.00 g, 2.2 mmol), and 18-crown-6 (1.16 g, 4.4 mmol) in benzene (40 ml) was refluxed for 3 h. Decantation and washing with pentane of the resulting precipitate afforded **2** as a yellow powder (1.57 g, 89% yield as a complex of two 18-crown-6 molecules). ^1H NMR (THF) δ 0.92 - 0.96 (m, 56H), 3.54 (s, 48H); ^{13}C NMR (THF) δ 14.4, 14.9, 22.3, 22.7, 22.9, 23.0, 70.1; ^{29}Si NMR (THF)δ -65.6, -4.2. An attempt to determine the crystal structure of **2** failed due to its high sensitivity to moisture and air.

6 Dipotassium compound **1** can also be prepared in THF, however, the reaction of **1** with Me_3SiCl in THF resulted in the regeneration of $[(i\text{-}Pr)_2Si]_4$ (93% yield) instead of **3**.

7 To a suspension of **1** prepared from K (79 mg, 2.0 mmol), $[(i\text{-}Pr)_2Si]_4$ (457 mg, 1.0 mmol), 18-crown-6 (530 mg, 2.0 mmol) and benzene (30 ml) was added $(i\text{-}Pr)_2SiCl_2$ (193 mg, 1.0 mmol) and heated at reflux for 1 day. Preparative HPLC gave 269 mg of $[(i\text{-}Pr)_2Si]_4$ (47%) and **2** (201 mg, 35%); mp 202 °C (sublimed); ^1H NMR (C_6D_6) δ 1.43 (d, 60H, J = 7.3 Hz), 1.64 (sept, 10H, J = 7.3 Hz); ^{13}C NMR (C_6D_6) δ 16.29, 24.02; ^{29}Si NMR (C_6D_6) δ -14.77; IR (KBr, cm^{-1}) 2953, 2866, 1456, 1385, 1360, 1223, 1016, 878; UV (nm, hexane) 274 (ε 1500), 265 (ε 1600); MS *m/z* (%) 570 (M^+, 7), 527 (100), 157 (77); Anal. Found: C, 62.42; H, 12.19%. Calcd for $C_{30}H_{70}Si_5$: C, 63.07; H, 12.35%.

8 H. Watanabe, T. Muraoka, M. Kageyama, and Y. Nagai, *J. Organomet. Chem.*, **216**, C45 (1981).

9 Crystallographic data for **2**: $C_{30}H_{70}Si_5$ (MW = 571.31), triclinic, $P\bar{1}$, a = 10.578(1) Å, b = 17.961(4) Å, c = 10.566(2) Å, α = 91.46(2)°, β = 111.55(1)°, γ = 95.21(1)°, V = 1855 (1) Å^3, Z = 2, D_{calc} = 1.022 gcm^{-3}, μ = 18.97 cm^{-1}, R = 0.038 (R_W = 0.049) for 5086 observed reflections [I > 3σ(I)].

10 H. Watanabe, M. Kato, T. Okawa, Y. Kougo, Y. Nagai, and M. Goto, *Appl. Organomet. Chem.*, **1**, 157 (1987).

11 For a recent review, see; E. Hengge, and R. Janoschek, *Chem. Rev.*, **95**, 1495 (1995).

12 To a suspension of **1** prepared from $[(i\text{-}Pr)_2Si]_4$ (2.01 g, 4.39 mmol), 18-crown-6 (2.31 g, 8.76 mmol), and K (350 mg, 8.76 mmol) in benzene (30 ml) was added Me_3SiCl (990 mg, 9.13 mmol). Preparative HPLC gave 2.10 g (yield 79%) of **3** and 85 mg (9 %) of $[(i\text{-}Pr)_2Si]_4$: mp 87 °C; ^1H NMR (C_6D_6) δ 0.39 (s, 18H), 1.29 (d, 12H, J = 7.3 Hz), 1.30 (d, 12H, J = 7.3 Hz), 1.33 (d, 12H, J = 7.3 Hz), 1.34 (d, 12H, J = 7.3 Hz), 1.61 (sept, 4H, J = 7.3 Hz), 1.67 (sept, 4H, J = 7.3 Hz); ^{13}C NMR (C_6D_6) δ 4.7, 15.1, 16.0, 22.4, 23.0, 23.2, 23.3; ^{29}Si NMR (C_6D_6) δ -13.5, -13.4, 1.1; IR (KBr, cm^{-1}) 2951, 2866, 1458, 1385, 1364, 1242, 1003, 847, UV (nm, hexane) 267 (ε 55600), 228 (sh, ε 14000). MS *m/z* (%) 559 ($[M-C_3H_7]^+$, 2), 301 (100), 259 (58), 217 (64); Anal. Found: C, 59.79; H, 12.39%. Calcd for $C_{30}H_{74}Si_6$: C, 59.71; H, 12.36%.

13 X-ray diffraction experiment was done at –100°C. Crystallographic data for **3**: $C_{30}H_{74}Si_6$ (MW = 603.43), monoclinic, $P2_1/c$, a = 17.430(1) Å, b = 11.861(1) Å, c = 20.898(1) Å, β = 112.695(1)°, V = 3985.9(2) Å^3, Z = 4, D_{calc} = 0.999 gcm^{-3}, μ = 2.25 cm^{-1}, R = 0.048 (R_W = 0.038) for 5013 observed reflections [I > 3σ(I)].

14 The dihedral angles Si(1)-Si(2)-Si(3)-Si(4) and Si(3)-Si(4)-Si(5)-Si(6) are -148.08(4)° and 163.90(4)°, respectively (Figure 2). The dihedral angles are defined as follows (ref. 15): If in a fragment Si(A)-Si(B)-Si(C)-Si(D), looking along Si(B) towards Si(C), Si(A)-Si(B) has to be rotated clockwise (< 180°) to eclipse Si(C)-Si(D), the Si(A)-Si(B)-Si(C)-Si(D) dihedral angle is positive. If clockwise is replaced by anticlockwise, positive is replaced by negative.

15 For the definition of dihedral angles, see: J. E. Anderson, in "The Chemistry of Alkanes and Cycloalkanes", ed by S. Patai and Z. Rappoport, John Wiley, New York (1992), Chap. 3, p. 96.

16 H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organomet. Chem.*, **2**, 369 (1964).

17 For conformational effects in the ultraviolet spectra of oligosilanes, see; R. D. Miller, and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).

18 Examples of oligosilanes which were constrained to an *all-trans* conformation in solution, see; a) S. Mazieres, M. K, Raymond, G. Raabe, A. Prodi, and J. Michl, *J. Am. Chem. Soc.*, **119**, 6682 (1997). b) A. Toshimitsu, M. Terada, H. Tsuji, M. Asahara, and K. Tamao, 45th Symposium on Organometallic Chemistry, Tokyo, September 1998, Abstr., p. 6.

19 Figure 3 also shows that a slight blue-shift (3 nm) with lower temperatures occurs for oligosilane **2**. Professor M. Kira (Graduate School of Science, Tohoku University) suggested for us that the origin of the blue shift for the lower temperatures observed in **2** is ascribed to a parabolic dependence of the transition energies on the Si-Si-Si bond angles. We are grateful to Prof. Kira for sending us a preprint on the synthesis, structure, and spectroscopic properties of perhexyloligosilanes (K. Obata and M. Kira, *Organometallics*, in press) .