Synthesis, X-ray Structure, and Electronic Properties of Oligosilanes Containing Pentacoordinate Silicon Moieties at Internal Positions

Ibrahim El-Sayed,[†] Yasuo Hatanaka,^{*,†} Chizuru Muguruma,[†] Shigeru Shimada,[†] Masato Tanaka,^{*,†} Nobuaki Koga,[‡] and Masuhiro Mikami[†]

National Institute of Materials and Chemical Research Tsukuba, Ibaraki 305-8565, Japan Graduate School of Informatics and Sciences Nagoya University, Nagoya 464-8601, Japan

Received August 17, 1998

Polysilanes represent a novel class of materials with unique electronic and optical properties, which exhibit an extensive electron delocalization along the polymer backbone.¹ The electronic properties of these polymers are affected by the polymer conformation, the degree of polymerization, and the substituents attached to the polymer chain.² Although the introduction of hypervalent silicon moieties into the polysilane backbone is expected to cause a strong perturbation to the electronic structure of the polymers,³ little is known about the influence of coordination number and valence state on the polymer properties. Several efforts have been made to introduce hypervalent silicon atoms into disilanes⁴ and trisilanes;⁵ however, the synthesis of oligosilanes containing pentacoordinate silicon moieties in the internal positions has not been realized yet.⁶ We report herein the synthesis, characterization, and the spectral properties of trisilane 3 containing a pentacoordinate silicon atom and tetrasilane 4 having two adjacent pentacoordinate silicon atoms at the internal positions.

We chose *N*-[(chlorosilyl)methyl]amide systems for the present study, because the five-membered rings involving intramolecular $O \rightarrow Si$ coordination by amides were found to be very stable, compared to other systems.⁷ Pentacoordinate trisilane **3** was prepared in a high yield by the reaction of *N*-methyl-*N*trimethylsilylacetamide with trisilane **1** in hexane at room temperature (Scheme 1). The similar reaction with tetrasilane **2** (1:1 mixture of diastereomers) selectively gave *dl*-isomer of pentacoordinate tetrasilane **4**; ¹H NMR analysis of the reaction

[†] National Institute of Materials and Chemical Research.

For reviews, see: (a) Miller, R. D.; Michl, J. Chem. Rev. 1989, 89, 1359.
 (b) Zeigler, J. M., Fearson, F. W. G., Eds.; Silicon-Based Polymer Science, Advances in Chemistry Series 224; American Chemical Society: Washington, DC. 1990.
 (c) West, R. J. Organomet, Chem. 1986, 300, 327.

Washington, DC, 1990. (c) West, R. J. Organomet. Chem. 1986, 300, 327.
 (2) (a) Harrah, L. A.; Zeigler, J. M. Macromolecules 1987, 20, 601. (b)
 Miller, R. D.; Farmer, B. L.; Fleming, W.; Sooriyakumaran, R.; Rabolt, J. J.
 Am. Chem. Soc. 1987, 109, 2509. (c) Miller, R. D.; Sooriyakumaran, R.
 Macromolecules 1988, 21, 3120. (d) Hsiao, Y.-L.; Waymouth, R. M. J. Am.
 Chem. Soc. 1994, 116, 9779. (e) Seki, T.; Tanigaki, N.; Yase, K.; Kaito, A.;
 Tamaki, T.; Ueno, K. Macromolecules 1995, 28, 5609 and references therein.

(3) (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99. (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

(4) (a) Sawitzki, G.; Schnering, H. G. Chem. Ber. 1976, 109, 3728. (b)
Grobe, J.; Henkel, G.; Krebs, B.; Voulgarakis, N. Z. Naturforsch. 1984, 39b, 341. (c) Kira, M.; Sato, K.; Kabuto, C.; Sakurai, H. J. Am. Chem. Soc. 1989, 111, 3747. (d) Belzner, J.; Ihmels, H.; Noltemeyer, M. Tetrahedron Lett. 1995, 36, 8187. (e) Tamao, K.; Asahara, M.; Kawachi, A. J. Organomet. Chem. 1996, 521, 325.

(5) (a) Kummer, D.; Balkir, A.; Köster, H. J. Organomet. Chem. **1979**, 178, 29. (b) Tamao, K.; Tarao, Y.; Nakagawa, Y.; Nagata, K.; Ito, Y. Organometallics **1993**, 12, 1113.

(6) Weak intramolecular coordination of the furyl ring oxygen with the tris(trimethylsilyl)silyloxy group in the chromium–carbene complex has been reported. However, the ²⁹Si chemical shift for the coordination center at the very low field (31.4 ppm) is unusual as a pentacoordinate silicon atom:¹⁵ Schubert, U.; Wiener, M.; Köhler, F. H. *Chem. Ber.* **1979**, *112*, 708. Quite recently, Tamao and co-workers have reported the synthesis of pseudo-pentacoordinate tetrasilanes having 8-amino-1-naphthyl groups which weakly interact with the internal silicon atoms: Tamao, K.; Asahara, M.; Saeki, T.; Toshimitsu, A. *Chem. Lett.* **1999**, 335.

Scheme 1



mixture showed that there was no trace amount of *meso-4*.⁸ These compounds are colorless crystals and fairly stable in the air but rapidly hydrolyzed in polar solvents containing water.

The X-ray analysis of 3 and 4 revealed the almost ideal trigonal bipyramidal (TBP) structure with the chlorine and the oxygen atoms in the axial positions (Figure 1). The TBP character of the internal silicon atoms of the pentacoordinate oligosilanes is markedly high; the %TBPe value for 3 estimated from the three equatorial-to-equatorial angles is 99%, and this value for 4 (average of the two pentacoordinate silicon centers) is 98%.⁹ The Si-Cl bond lengths (2.367(1) Å for 3, 2.3217(6) and 2.3704(5) Å for 4) and the Si–O distances $(1.947(2) \text{ Å for } 3 \ 1.981(1) \text{ and}$ 1.943(1) Å for 4) are normal as [3 + 2] TBP coordination.¹⁰ The sum of the three equatorial angles (359.9° for 3, 360.0° and 359.1° for 4) indicates almost complete planarity of the equatorial planes in 3 and 4. The Si1-Si2 bond length (2.3362(5) Å) in 4 is comparable to a tetrahedral Si(sp³)-Si(sp³) bond (2.33-2.37 Å),¹¹ while the bond between the two equatorial silicon atoms can be formally regarded as $Si(sp^2)$ - $Si(sp^2)$.^{12,13} The relatively long Si_{eq} -Si_{eq} bond length, however, is quite reasonable in view of the sterically crowded coordination sphere of pentacoordinate silicon species.14

The ²⁹Si NMR spectra of **3** and **4** in C₆D₆ solution showed that the chemical shifts for the internal silicon atoms (-63.71 ppm for **3** and -61.88 ppm for **4**) are markedly upfield-shifted by ca. 60 ppm from those of tetracoordinate trisilane **1** (0.53 ppm) and tetrasilane **2** (-0.43 and 1.33 ppm), proving the effective O \rightarrow Si coordination.¹⁵ Strong coordination in these molecules is also supported by the IR spectra (in KBr) which exhibited the ν (CO) bands at 1603 cm⁻¹ for **3** and 1607 cm⁻¹ for **4**. The ν (CO)

of analogous (Me₂ClSi)CH₂N(Me)(C=O)Me (**5**) also appeared at the same region (1598 cm⁻¹),^{7a} indicating that replacement of

(8) All new compounds exhibited satisfactory spectral and analytical data.
 (9) For the %TBPe value, see: Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. Organometallics 1992, 11, 2099.

(10) (a) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Gostevskii, B. A.; Kalikhman, I. D.; Bannikova, O. B.; Voronkov, M. G.; Pestunovich, V. A. J. Organomet. Chem. **1988**, 356, 23. (b) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Oleneva, G. I.; Kramarova, E. P.; Shipov, A. G.; Baukov, Yu. I. J. Chem. Soc., Chem. Commun. **1988**, 683.

(11) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Part 1, Chapter 3.

(12) Musher, J. I. Angew. Chem., Int. Ed. Engl. 1969, 8, 54.

(13) Natural bond orbital analysis at the RHF/6-31G(d,p) level on model compound **6** (see text) showed that the hybridization of the central silicon orbitals used in bonding to the equatorial Si atoms is $sp^{2.37}$ (69.9% of *p*).¹⁸ Thus, it is reasonable to assume sp^2-sp^2 character of the Si_{ea}-Si_{ea} bond in **4**.

(14) Bond lengths in pentacoordinate silicon species are usually longer than in related tetracoordinate species: (a) Deiters, J. A.; Holmes, R. R. J. Am. Chem. Soc. 1990, 112, 7197. (b) Schomburg, D.; Krebs, R. Inorg. Chem. 1984, 23, 1378. (c) Atoji, M.; Lipscomb, W. N. Acta Crystallogr. 1954, 7, 597.

(15) The ²⁹Si chemical shifts for pentacoordinate Si usually exhibit an upfield shift relative to tetracoordinate Si.^{3a}

[‡] Nagoya University.

^{(7) (}a) Hillyard, R. W., Jr.; Ryan C. M.; Yoder, C. H. J. Organomet. Chem. **1978**, 153, 369. (b) Yoder, C. H.; Ryan, C. M.; Martin, G. F.; Ho, P. S. J. Organomet. Chem. **1980**, 190, 1 and references therein. (c) Pestunovich, V. A.; Valery, F. S.; Voronkov, M. G. In Progress in Organosilicon Chemistry; Marciniec, B., Chojnowski, J., Eds.; Gordon and Breach Publishers: Basel, Switzerland, 1995; pp 69–82.



Figure 1. X-ray structures of 3 and 4. Selected bond distances (Å) and angles (deg). 3: Si1-Si2 = 2.329(1), Si1-O1 = 1.947(2), Si1-Cl1 = 2.367(1), Si1-C1 = 1.903(3); Si2-Si1-Si3 = 122.73(4), Si2-Si1-C1= 122.1(1), Si3-Si1-C1 = 115.1(1), Cl1-Si1-O1 = 170.70(6). 4: Si1-Si3 = 2.3395(6), Si1-Si2 = 2.3362(5), Si2-Si4 = 2.3447(7), Si1-Cl1 = 2.3217(6), Si1-O1 = 1.981(1), Si2-Cl2 = 2.3704(5), Si2-O2= 1.943(1); C1-Si1-Si2 = 116.96(5), C1-Si1-Si3 = 123.03(5), Si2-Si1-Si3 = 119.09(2), Cl1-Si1-O1 = 172.03(4), C5-Si2-Si4 = 117.30(6), Si1-Si2-Si4 = 126.27(2), Si1-Si2-C5 = 116.41(6), Cl2-Si2-O2 = 172.49(4).



Figure 2. UV spectra of (a) 3, (b) 2-chloroheptamethyltrisilane, (c) 4 in isooctane solution, and (d) 4 in acetonitrile solution.

two equatorial methyl groups in 5 by two silyl groups has no influence on the strength of the O-Si bond.¹⁶ This result is somewhat surprising, because the presence of an electropositive ligand such as silicon in the equatorial position is supposed to weaken the coordination bond.^{3,7c}

The UV spectra of 3 and 4 are shown in Figure 2, in which the spectrum of 2-chloroheptamethyltrisilane is also given for comparison. In isooctane solution, 3 exhibited a strong absorption at 227 nm ((a), $\epsilon = 7045$ cm⁻¹ M⁻¹), which can be assigned to $\sigma \rightarrow \sigma^*$ transition of the Si–Si bond.^{1a,17} It should be noted that the absorption maximum of 3 appears at the longest wavelength among various $Me_3SiSi(X)MeSiMe_3$ (X = halogen, N, O, S, Me).¹⁷ For example, compared with the spectrum of (Me₃Si)₂Si-(Cl)CH₃ ((b), $\lambda_{max} = 215$ nm, $\epsilon = 7300$ cm⁻¹ M⁻¹), the λ_{max} of 3 is red-shifted by 12 nm. The strong bathochromic shift is apparently a result of an electronic perturbation of the Si-Si bond by the pentacoordinate moiety. To gain an insight of this point, ab initio calculations (CIS/6-31G**) were carried out on model

compounds, (H₃Si)₂Si(Cl)CH₂NHCHO 6 and (H₃Si)₂Si(Cl)CH₃ 7, where the structures were optimized at the B3LYP/6-31G** level.¹⁸ The calculated λ_{max} of **6** was red-shifted by 6.2 nm from



that of 7, and the strongest absorption was mainly originated by the $\sigma_{SiSi} \rightarrow \sigma^*_{SiSi}$ transition in both molecules. Compared with the corresponding orbitals of 7, the σ_{SiSi} orbital of 6 is substantially destabilized, whereas the σ^*_{sisi} orbital of **6** is slightly destabilized. The lone pair orbital on oxygen shifts up the σ_{SiSi} orbital of 6 in energy, while it does not affect the $\sigma *_{\rm SiSi}$ orbital of the different symmetry. Thus, the red shift in the absorption spectra of 6 is theoretically explained as the result of an interaction between the oxygen lone pair orbital and the σ_{SiSi} orbital.

In striking contrast, the λ_{max} of **4** ((c), 207 nm, $\epsilon = 8400 \text{ cm}^{-1}$ M⁻¹ in isooctane) appeared at the shorter-wavelength region relative to 3, although the presence of the two pentacoordinate silicon moieties are expected to be more effective in destabilizing the σ_{SiSi} . We attribute this unusual spectral property of 4 primarily to a conformational effect on the electronic structure. Recent studies on conformationally constrained tetrasilanes have clearly demonstrated that pseudo-gauche conformation (the Si-Si-Si-Si dihedral angle (ω) = 55°) causes a significant decrease of absorbance in the longer-wavelength region above 220 nm.¹⁹ As suggested by the crystal structure of 4 ($\omega = 57.14(4)^{\circ}$), the lowest energy conformation of 4 in solution seems to be gauche-like (conformer A in Scheme 2);²⁰ this conformation would be responsible for the disappearance of the absorption in the longerwavelength region. Our hypothesis is strengthened by the observation that the UV spectrum of 4 displayed a solventsensitive red shift of the λ_{max} in acetonitrile solution (Figure 2d), suggesting that greater contribution of other conformer like **D** in polar solvent gave rise to the observed red shift.²¹ However, at the present stage, it is difficult to separate the inherent electronic effects of the two pentacoordinate silicon moieties on the electronic structure of 4 from the conformational effects; further study is needed to clarify this point.

Currently, we are studying the electronic properties of various types of hexa- and pentacoordinate oligosilanes as well as the synthesis of pentacoordinate polysilanes with high molecular weights.

Acknowledgment. We are grateful to Professor Keiji Morokuma, Emory University, for helpful discussion and to the Japan Science and Technology Corporation (JST) for financial support through the CREST (Core Research for Evolution Science and Technology) program and for a postdoctoral fellowship to I.E.-S.

Supporting Information Available: Experimental details and characterization data for all new compounds, including tables of crystal data, atomic coordinates, bond distances, and angles for 3 and 4 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA982943O

⁽¹⁶⁾ The strength of the O-Si coordination bond is reflected in the shift of the v(CO): Macharashvili, A. A.; Shklover, V. E.; Chernikova, N. Yu.; Antipin, M. Yu.; Struchkov, Yu. T.; Baukov, Yu. I.; Oleneva, G. I.; Kramarova, E. P.; Shipov, A. G. J. Organomet. Chem. 1989, 359, 13. (17) Pitt, C. G. J. Am. Chem. Soc. 1969, 91, 6613.

⁽¹⁸⁾ Detailed accounts of the calculated structures and the energies will be reported elsewhere. All calculations were carried out using the program Gaussian 94, Revision E.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gaussian 94, Revision E.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.;
Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.;
Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.;
Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B.
B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.;
Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.;
Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.
(19) (a) Plitt H. S. Michl J. Chem. Phys. Lett. 1992, 198, 400 (b) Imbof. (19) (a) Plitt, H. S.; Michl, J. Chem. Phys. Lett. 1992, 198, 400. (b) Imhof, R.; Teramae, H.; Michl, J. Chem. Phys. Lett. 1997, 270, 500.

⁽²⁰⁾ Other conformers depicted in Scheme 2 seem to be less stable, due to the steric repulsion between the neighboring rings (conformer B) or an enhanced dipole moment derived from the highly polarized Si-Cl bonds (conformers C and D).

⁽²¹⁾ Oka, K.; Fujiue, N.; Dohmaru, T.; Yuan, C.-H.; West, R. J. Am. Chem. Soc. 1997, 119, 4074.