J. Am. Chem. Soc. **2001,** *123,* 10778−10779

Reversible Photocontrol of the Coordination Number of Silicon in a Tetrafluorosilicate Bearing a 2-(Phenylazo)phenyl Group

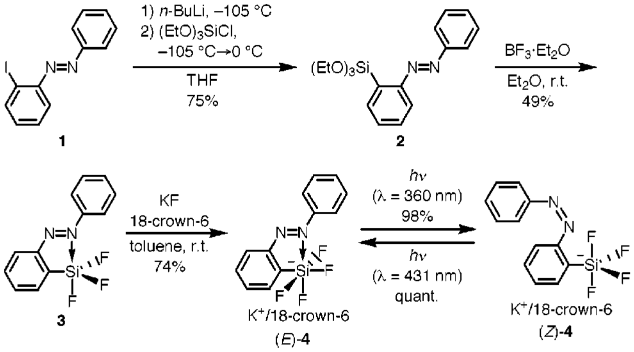
Naokazu Kano, Fuminori Komatsu, and
Takayuki Kawashima*

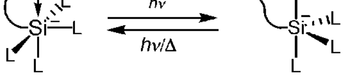
Department of Chemistry
Graduate School of Science
The University of Tokyo, 7-3-1 Hongo
Bunkyo-ku, Tokyo 113-0033, Japan

Received July 10, 2001

Highly coordinate organosilicon compounds constitute an important class of species in organosilicon chemistry and have been extensively studied in view of their structures, reaction mechanism, and synthetic application.[1] The coordination number of the silicon atom considerably influences not only the conformation around silicon but also the properties and reactivity of organosilicon compounds, especially in high coordination state. If the coordination number could be changed by external stimulations such as light, electricity, and magnetism, the structure and property of the compounds would be controlled without addition of an external reagent.[2] There has been no report on such a control of the coordination number despite its promising usefulness as a novel type of switch for the structure and property.[3] We recently reported versatile synthetic methods for azobenzenes with a silyl, germyl, or stannyl group at the 2-position, respectively.[4] A 2-(phenylazo)phenyl group is considered to act as a potential coordination site judging from the structural resemblance with the van Koten ligand, 2-(Me_2NCH_2)C_6H_4 group[5] and from many examples of transition metal complexes which show intramolecular coordination of an azo group.[6] Therefore, photo- and thermal isomerization of an azo unit which has been widely utilized for the switch of properties promoted by its geometrical change of the compound are expected to be effective for the control of the coordination number of the central atom.[7] We report here synthesis, structure, and reversible photoswitching of the coordination number of a silicon atom of potassium, 18-crown-6, tetrafluorosilicate bearing a 2-(phenylazo)phenyl group.

Scheme 1





2-Iodoazobenzene (**1**) was allowed to react successively with *n*-BuLi (1.03 equiv) and chlorotriethoxysilane (1.05 equiv) in THF at −105 °C and further at 0 °C to give 2-triethoxysilyl derivative **2** (75%) (Scheme 1).[4] Fluorination of **2** with $BF_3{\cdot}Et_2O$ (1.10 equiv) at room temperature in ether afforded the trifluoro[2-(phenylazo)phenyl]silane (**3**) (49%).[8] Treatment of **3** with KF (1.00 equiv) in the presence of 18-crown-6 (1.00 equiv) in toluene gave potassium, 18-crown-6, tetrafluoro[(*E*)-2-(phenylazo)phenyl]-silicate (**4**) (74%) as yellow solids.

In the ^{29}Si NMR spectra, (*E*)-**4** showed a quintet ($^1J_{\mathrm{Si-F}} = 193$ Hz) at δ −150.9 by coupling with four equivalent fluorine nuclei at room temperature in $CDCl_3$ and a doublet of double triplet at δ −153.7 coupled with three kinds of nuclei ($^1J_{\mathrm{Si-F}} = 149$, 186, and 214 Hz, respectively) at −90 °C, respectively, in CD_2Cl_2.[9] In the ^{19}F NMR spectra, a broad singlet at δ −127.4 in $CDCl_3$ at room temperature was split to two broad signals (δ −122.5 and −147.2) at −30 °C in CD_2Cl_2. They were further split to a pair of doublets at δ −121.6 ($^2J_{\mathrm{F-F}} = 21.3$ Hz) and −123.2 ($^2J_{\mathrm{F-F}} = 24.4$ Hz) and one double triplet at δ −147.2 ($^2J_{\mathrm{F-F}} = 21.3$ Hz, $^2J_{\mathrm{F-F}} = 24.4$ Hz) at −90 °C, respectively, in CD_2Cl_2. Such coupling patterns and chemical shifts, which are similar to those of a hexacoordinate tetrafluorosilicate with the van Koten ligand,[5b−d] indicate that nonequivalency of fluorine atoms in (*E*)-form due to the coordination of nitrogen atom of the azo group. Fast stereomutation of the ligands compared to the time scale of ^{19}F NMR spectroscopy would result in observation of a singlet at room temperature.

In UV/vis spectra of (*E*)-**4**, an absorption maximum due to $\pi-\pi^*$ transition of the azo group was observed at 334 nm in CH_2Cl_2. The color of (*E*)-**4** is yellow in sharp contrast to the red color of previously reported 2-silylazobenzenes, suggesting the perturbation of the electronic structure of the azo unit.[4] Isomerization of (*E*)-**4** could easily be done by irradiation ($\lambda = 360$ nm) in CH_2Cl_2 for 40 min to give orange-colored (*Z*)-**4**. (*Z*)-**4** showed its absorption maximum at 440 nm assignable to $n-\pi^*$ transition. Irradiation ($\lambda = 431$ nm) of the new absorption

---

[1] (a) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927. (b) Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, J. C. In *Chemistry of Hypervalent Compounds*; Akiba, K.-Y., Ed.; Wiley-VCH: New York, 1999; pp 81−146. (c) Kira, M.; Zhang, L.-C. In *Chemistry of Hypervalent Compounds*; Akiba, K.-Y., Ed.; Wiley-VCH: New York, 1999; pp 147−169. (d) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, 1998; Volume 2, Part 2, Chapter 23, pp 1339−1445.

[2] The changes of photophysical properties caused by hypercoordination of organosilicon compounds with addition/elimination of an external fluoride ion have been reported. See: Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 6793.

[3] Equilibrium between neutral hexacoordinate silicon complexes and ionic silicenium chlorides, which is temperature-, solvent-, counterion-, ligand-, and substituent-dependent, has been reported. See: Kingston, V.; Gostevskii, B.; Kalikhman, I.; Kost, D. *Chem. Commun.* **2001**, 1272.

[4] Kano, N.; Komatsu, F.; Kawashima, T. *Chem. Lett.* **2001**, 338.

[5] A bidentate ligand, $-C_6H_4-2-CH_2NMe_2$, was developed by van Koten: (a) van Koten, G.; Schaap, C. A.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *99*, 157. For hypervalent silicon compounds with the van Koten ligand, see: (b) Brelière, C.; Carré, F.; Corriu, R. J. P.; Saxce, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1981**, *205*, C1. (c) Weinmann, M.; Gehrig, A.; Schiemenz, B.; Huttner, G.; Nuber, B.; Rheinwald, G.; Lang, H. *J. Organomet. Chem.* **1998**, *563*, 61. (d) Belzner, J.; Dehnert, U.; Ihmels, H.; Hübner, M.; Müller, P.; Usón, I. *Chem. Eur. J.* **1998**, *4*, 852.

[6] Bruce, M. I.; Goodall, B. L. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; John Wiley & Sons: London, 1975; Chapter 9, p 259.

[7] (a) Archut, A.; Vögtle, F.; De Cola, L.; Azzellini, G. C.; Balzani, V.; Ramanujam, P. S.; Berg, R. H. *Chem. Eur. J.* **1998**, *4*, 699. (b) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3349. (c) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789.

[8] Boyer, J.; Brelière, C.; Carré, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C. *J. Chem. Soc., Dalton Trans.* **1989**, 43.

[9] (a) Brelière, C.; Carré, F.; Corriu, R. J. P.; Douglas, W. E.; Poirier, M.; Royo, G.; Man, M. W. C. *Organometallics* **1992**, *11*, 1586. (b) Carré, F.; Chuit, C.; Corriu, R. J. P.; Fanta, A.; Mehdi, A.; Reyé, C. *Organometallics* **1995**, *14*, 194.

10.1021/ja0165739 CCC: $20.00

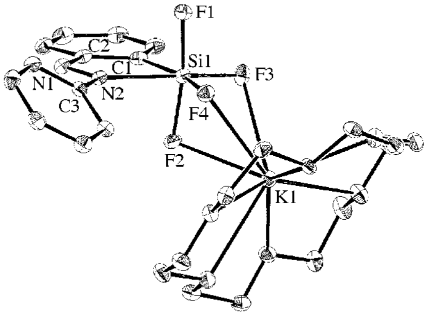


Figure 1. ORTEP drawing of (*E*)-**4** with thermal ellipsoid plot (30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Si1−F1, 1.672(2); Si1−F2, 1.687(2); Si1−F3, 1.647(2); Si1−F4, 1.661(2); Si1−C1, 1.909(4); N1−N2, 1.272(4); Si1−N2, 2.260(3); F1−Si1−F2, 168.4(1); F1−Si1−F3, 97.1(1); F1−Si1−F4, 88.9(1); F2−Si1−F3, 94.2(1); F2−Si1−F4, 87.2(1); F3−Si1−F4, 95.8(1); C1−Si1−F1, 90.7(1); C1−Si1−F2, 90.1(1); C1−Si1−F3, 99.6(2); C1−Si1−F4, 164.5(2); N2−Si1−F1, 84.4(1); N2−Si1−F2, 84.5(1); N2−Si1−F3, 175.9(1); N2−Si1−F4, 88.0(1); N2−Si1−C1, 76.6(1).

maximum led to the recovery of (*E*)-**4** with a decrease of its absorption.

In variable-temperature ^{19}F NMR spectra, the signal of (*Z*)-**4** was observed at δ −114.7 as a broad singlet and did not split even at −70 °C in contrast to that of (*E*)-**4**. The ratio of (*E*)-**4**:(*Z*)-**4** is estimated as 2:98 by the integral of ^{19}F NMR spectra of the reaction solution after irradiation for 40 min. Furthermore, the higher concentration of the solution of (*Z*)-**4** was, the broader the signal became, suggesting the intermolecular fluorine exchange. The ^{29}Si NMR spectra of (*Z*)-**4** at −65 °C showed a quintet at δ −122.8, which is lower field by 28 ppm than that of (*E*)-**4**. These results suggest that fluorine nuclei exchange faster than the time scale of ^{19}F NMR spectroscopy even at −65 °C both intra- and intermolecularly and that (*Z*)-**4** bears a pentacoordinate structure around a silicon atom in the absence of coordination of the nitrogen atom. The (*Z*)-isomer of **4** thus obtained is stable under argon at ambient temperature for a few days in the solid state, and it gradually isomerizes to (*E*)-isomer at room temperature in solution state even in the dark.

The structures of both (*E*)- and (*Z*)-stereoisomers were finally determined by X-ray crystallographic analysis.[10] In the (*E*)-isomer, the N2 atom on the azobenzene unit is directed to the Si1 atom despite the steric repulsion of a bulky silicate group (Figure 1).[4] The interatomic N2−Si1 distance (2.260(3) Å), which is almost same as those of highly coordinate organosilicon compounds with the van Koten ligand, is much shorter than the sum of the corresponding van der Waals radii (3.65 Å).[5b−d,11] Taking into consideration that a hypervalent bond is generally long, the intramolecular interaction between N2 and Si1 evidently exists in (*E*)-**4**, presenting the hexacoordinate structure of the silicon. (*E*)-**4** was shown to have a distorted octahedral configuration suggested by the bond angles (76.6(1)−99.6(2)°) around Si1 atom.

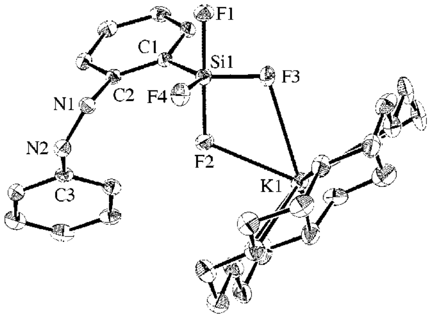


Figure 2. ORTEP drawing of (*Z*)-**4** with thermal ellipsoid plot (30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Si1−F1, 1.670(3); Si1−F2, 1.698(3); Si1−F3, 1.617(3); Si1−F4, 1.611(3); Si1−C1, 1.888(4); N1−N2, 1.259(5); F1−Si1−F2, 178.2(1); F1−Si1−F3, 90.4(1); F1−Si1−F4, 90.4(1); F2−Si1−F3, 88.8(1); F2−Si1−F4, 88.5(1); F3−Si1−F4, 115.3(1); C1−Si1−F1, 91.3(2); C1−Si1−F2, 90.5(2); C1−Si1−F3, 117.8(2); C1−Si1−F4, 126.8(2).

In (*Z*)-**4**, the silicon atom evidently lacked Si1−N2 interaction and adopted a pentacoordinate state with a trigonal bipyramidal structure with F1 and F2 atoms at apical positions and with F3, F4, and C1 atoms at equatorial positions, respectively, (TBP → SP 22.3%) (Figure 2).[12] The bond lengths of Si1−F1 (1.670(3) Å) and Si1−F2 (1.698(3) Å) bonds are significantly longer than those of Si1−F3 (1.617(3) Å) and Si−F4 (1.611(3) Å) bonds. Such elongation of apical bonds is indeed characteristic of TBP structure around a pentacoordinate silicon atom. Structural changes between (*E*)-**4** and (*Z*)-**4** were found on the widening of the bond angles of C1−Si1−F4 (164.5(2)°) and the narrowing of F3−Si1−F4 (95.8(1)°) and C1−Si1−F3 (99.6(2)°) in (*E*)-**4** compared to those of (*Z*)-**4** (126.8(2)°, 115.3(1)°, and 117.8(2)°, respectively). Thus, configuration around the silicon atom in **4** has completely been changed between distorted octahedral and TBP structures by photoirradiation. Such a change around the silicon atom by irradiation has never been reported as far as we know. In this case, the N1−N2 bond length (1.272(4) Å) of the (*E*)-isomer is almost same as that of azobenzenes without donation of the nitrogen atom, indicating little structural perturbation of the azobenzene unit regardless of the coordination of N2 to Si1.[4,13]

Interestingly, the coordination state can visually be recognized with ease by the change of the colors from yellow to red because the azo unit in **4** works as a coordination site in the (*E*)-form as well as a chromophore. Furthermore, irradiation of the silicate **4** caused changes of their stabilities to the humidity. Although the (*E*)-**4** isomer easily handled without any special care in the air, the (*Z*)-**4** isomer is easily hydrolyzed in the aerial humidity. We believe that this new strategy, that is, the photoswitching of the coordination number of highly coordinate main-group element compounds promising the control of the structures, spectral properties, and reactivities, would be useful for the construction of molecular devices.

Acknowledgment. We thank Shin-etsu Chemical Co., Ltd., and Tosoh Finechem Corp. for the generous gift of chlorosilanes and alkyllithiums, respectively.

Supporting Information Available: Synthetic procedures and spectral data for **2**, **3**, (*E*)-**4**, and (*Z*)-**4** (PDF). X-ray crystallographic files in CIF format for (*E*)-**4** and (*Z*)-**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0165739

---

(10) Crystallographic data. (*E*)-**4**: $C_{24}H_{33}F_4KN_2O_6Si$, orthorhombic, $P2_12_12_1$, $a = 9.3340(2)$ Å, $b = 16.3190(8)$ Å, $c = 18.1480(8)$ Å, $V = 2764.3(2)$ Å^3, $Z = 4$, MW = 588.71, $T = 150$ K, R = 0.046, wR2(all data) = 0.147, GOF = 1.01. (*Z*)-**4**: $C_{24}H_{33}F_4KN_2O_6Si$, triclinic, P-1, $a = 13.445(2)$ Å, $b = 14.836(2)$ Å, $c = 15.750(2)$ Å, $\alpha = 74.097(6)°$, $\beta = 69.804(3)°$, $\gamma = 79.731(2)°$, $V = 2823.4(7)$ Å^3, $Z = 4$, MW = 588.71, $T = 103$ K, R = 0.066, wR2(all data) = 0.138, GOF = 1.28. The unit cell contains two independent molecules, which have a similar conformation around the silicon atom in (*Z*)-**4**.

(11) (a) Klebe, G. *J. Organomet. Chem.* **1987**, *332*, 35 (b) Brelière, C.; Carré, F.; Corriu, R. J. P.; Poirier, M.; Royo, G.; Zwecker, J. *Organometallics* **1989**, *8*, 1831 (c) Probst, R.; Leis, C.; Gamper, S.; Herdtweck, E.; Zybill, C.; Auner, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1132 (d) Handwerker, H.; Leis, C.; Probst, R.; Bissinger, P.; Grohmann, A.; Kiprof, P.; Herdtweck, E.; Blumel, J.; Auner, N.; Zybill, C. *Organometallics* **1993**, *12*, 2162 (e) Belzner, J.; Schar, D.; Kneisel, B. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 1840.

(12) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(13) (a) Allmann, R. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; John Wiley & Sons: London, 1975; Chapter 2, p 43. (b) Harada, J.; Ogawa, K.; Tomoda, S. *Acta Crystallogr.* **1997**, *B53*, 662.