Hexakis(fluorodimethylsilyl)benzene, Hexakis(methoxydimethylsilyl)benzene, and Related Compounds. Novel Neutral Pentacoordinate Structures for Silicon and Merry-Go-Round Degenerate Fluorine Migration[1]

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Received October 27, 1993

As a part of studies on persilylated π-electron systems, particularly on persilylated benzenes,[2] we are interested in hexakis(fluorodimethylsilyl)benzene (**1**) for its possible dynamic properties as a gear-meshed structure[3] and for possible nonclassical neutral pentacoordinate silicon atoms.[4] Herein we report the novel structure of **1** and related phenomena involving neutral pentacoordinate fluorosilane (Scheme 1).

Compound **1** was prepared by the reaction of hexakis(bromodimethylsilyl)benzene[2a] and antimony trifluoride in dry benzene as colorless crystals in 20% yield.[5] X-ray crystallographic analysis[6] revealed that the benzene ring was slightly distorted into a boat form with a gear-meshed structure (Figure 1). Distances of the bonding Si–F bonds (average 1.68 Å) are longer than the standard tetracoordinate Si–F (1.50 Å) and neutral pentacoordinate Si–F (apical, 1.60 Å) bonds,[7] while the nonbonding Si–F distances (average 2.39 Å) are much shorter than the value of 2.63 Å, the minimal nonbonded approach between Si and F.[8] The distance (*h*) between a silicon atom and the center of the triangle formed by three carbon atoms of substituents of silicon is 0.29–0.34 Å. The *h* value should be 0 for the trigonal bipyramid and 0.6 Å for the tetrahedral structures. All the F–Si–F angles are nearly linear (171.9–178.9°, average 176°). On the whole, all the silicon atoms adopt a nearly trigonal bipyramidal configuration (Figure 1).

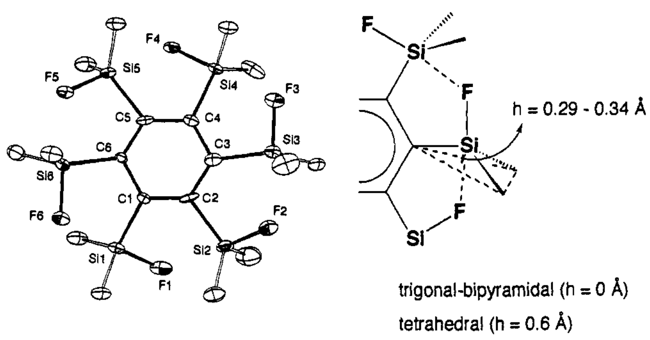


Figure 1. Molecular structure of hexakis(fluorodimethylsilyl)benzene: top view and geometry around silicon.

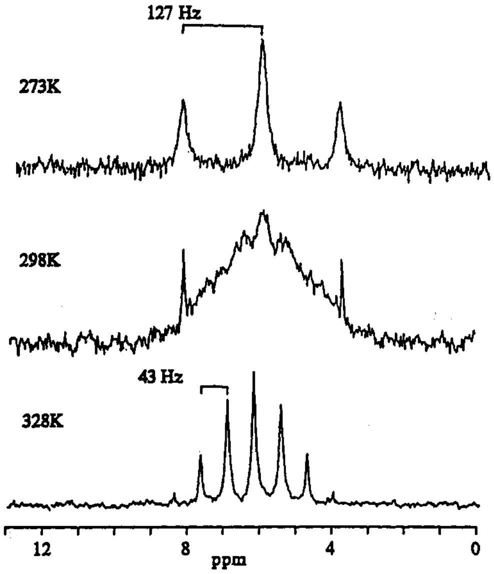
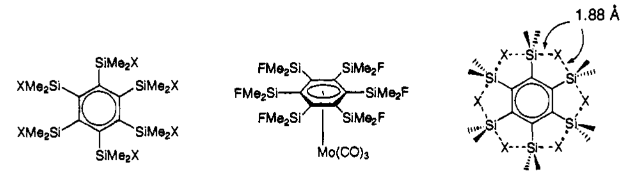


Figure 2. Temperature dependent ^{29}Si NMR spectra of hexakis(fluorodimethylsilyl)benzene in toluene-d_8.

Scheme 1



1 : X = F

3 : X = OMe

2

4

At low temperature (273 K), the ^{29}Si NMR of **1** shows a triplet (J_{SiF} = 127 Hz), indicating that all the silicon atoms interact with two fluorine atoms in accord with the solid-state structure. This triplet did not change to a doublet of doublets at the low-temperature limit; however, these signals transformed at higher temperatures to a septet (J_{SiF} = 43 Hz at 328 K) as shown in Figure 2. Correspondingly, all the ^{1}H and ^{13}C NMR signals which are triplets at 273 K become septets at 328 K. Noteworthy is the fact that chemical shifts in these NMR spectra did not change at all; only the coupling pattern changed.

This unusual dynamic behavior can be explained by a mechanism where, at low temperature, rotation of the silyl groups is frozen but fluorine atom transfer between vicinal silyl groups is rapid. This process corresponds to a cyclic network of intramolecular consecutive S_N2(Si) type Walden inversions which

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[1] Chemistry of Organosilicon Compound. 305.

[2] (a) Sakurai, H.; Ebata, K.; Kabuto, C.; Sekiguchi, A. *J. Am. Chem. Soc.* **1990**, *112*, 1799. (b) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 1464. (c) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7081. (d) Sekiguchi, A.; Ebata, K.; Terui, Y.; Sakurai, H. *Chem. Lett.* **1991**, 1417.

[3] (a) Siegel, J.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 7763. (b) Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569. (c) Schuster, I. I.: Weissensteiner, W.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 6661. (d) Kahr, B.; Biali, S. E.; Schaefer, W.; Buda, A. B.; Mislow, K. *J. Org. Chem.* **1987**, *52*, 3713. (e) Chance, J. M.; Kahr, B.; Buda, A. B.; Toscano, J. P.; Mislow, K. *J. Org. Chem.* **1988**, *53*, 3226.

[4] For recent reviews on pentacoordinate silicon compounds, see: (a) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*, Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Part 2; Chapter 20. (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. See also: (c) Tamao, K.; Hayashi, T.; Ito, Y. Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 2422. (d) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099.

[5] Compound **1**: colorless crystals; mp 175 °C; ^{1}H NMR (300 MHz, benzene-d_6, 298 K) δ 0.55 (septet, $^3J_{HF}$ = 3.3 Hz, 36 H); ^{13}C NMR (75.5 MHz, benzene-d_6, 298 K) δ 3.26 (septet, $^2J_{CF}$ = 7.0 Hz, Me), 152.5 (septet, $^2J_{CF}$ = 5.0 Hz, C_{ar}); ^{29}Si NMR (59.6 MHz, toluene-d_8, 328 K) δ 6.13 (septet, $^1J_{SiF}$ = 43 Hz); ^{19}F NMR (282.4 MHz, benzene-d_6, 298 K) δ −111.9 (s); ^{1}H NMR (300 MHz, toluene-d_8, 240 K) δ 0.46 (t, $^3J_{HF}$ = 9.3 Hz, 36 H); ^{13}C NMR (75.5 MHz, toluene-d_8, 240 K) δ 3.4–3.9 (m, $\nu_{1/2}$ = 40 Hz, Me), 152.5–152.7 (m, $\nu_{1/2}$ = 25 Hz, C_{ar}); ^{29}Si NMR (59.6 MHz, toluene-d_8, 240 K) δ 7.6 (t, $^1J_{SiF}$ = 127 Hz); ^{19}F NMR (282.4 MHz, toluene-d_8, 240 K) δ −113.8 (s); MS (70 eV) *m/z* (rel intensity) 534 (2.3, M^+), 519 (16.4), 73 (100); high-resolution MS *m/z* calcd for $C_{18}H_{36}F_6Si_6$ 534.1337, found 534.1334.

[6] Crystal data for **1** at −78 °C: a = 22.483(7) Å, b = 12.440(10) Å, c = 22.864(6) Å, β = 118.73(17)°, V = 5607.7(51) Å^3, monoclinic with space group $P2_1/a$, Z = 8, ρ = 1.27 g cm^{-3}. The structure was solved by the direct method. Two independent molecules reside in a unit cell. The fluorodimethylsilyl groups are arranged around the benzene ring in a gear-meshed form, and the opposite arrangement results in a crystallographic orientational disorder. The silicons were refined by splitting the populations of the orientation (0.7/0.3 and 0.6/0.4). The final R factor was 0.0995 (R_w = 0.1036) for 4934 reflections with $F_o > 3\sigma(F_o)$.

[7] Klebe, G. *J. Organomet. Chem.* **1985**, *293*, 147.

[8] Glidewell, C. *Inorg. Chim. Acta* **1975**, *12*, 219.

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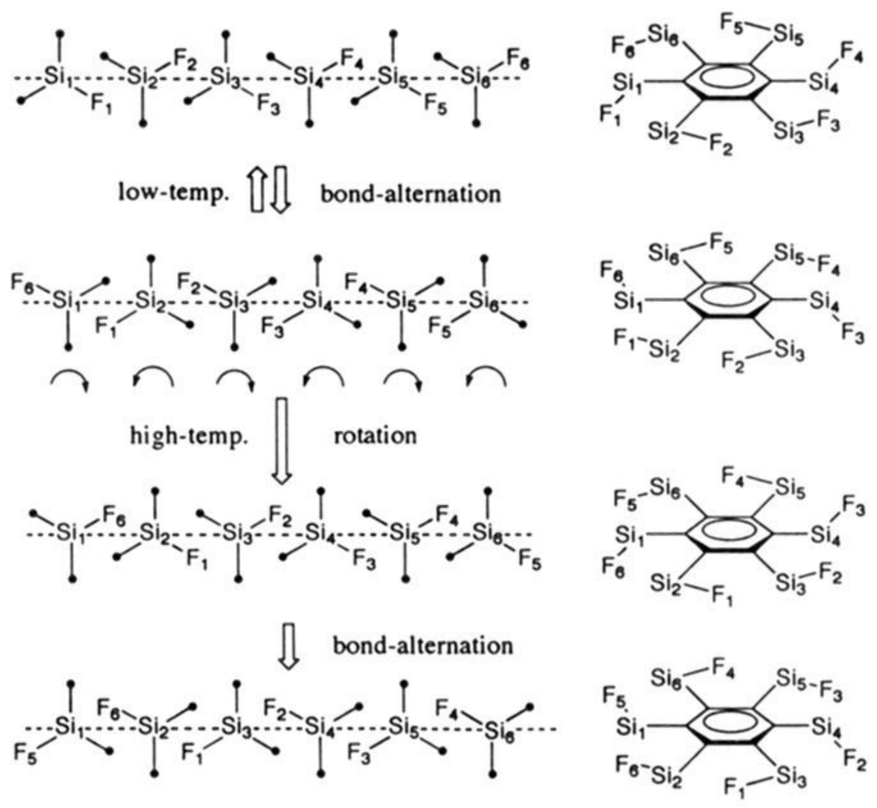

Figure 3. Merry-go-round degenerate fluorine migration.

are very rapid because each silicon atom already forms a quasi-pentacoordinate structure.[9] As a consequence, triplet signals are observed. From a symmetry perspective, Si–F bond alternation in the present study is analogous to the inversion mechanism studied by Chance *et al.*, for hexakis(dimethylamino)benzene, although the molecular mechanism of the exchange is quite different.[10]

Septet signals mean that silicon and other atoms interact with six fluorine atoms *equally* at high temperature. At high temperature, rotation of the silyl groups is allowed and all the fluorine atoms migrate throughout the ring by a combination of Si–F bond alternation and rotation. Although it is not proven in a strict sense, the gear-meshed motion is highly likely as the mechanism of rotation, since the molecule already takes the gear-meshed structure in the solid state. Fluorine atoms thus move like a merry-go-round (Figure 3).

The reaction of **1** and hexacarbonylmolybdenum gave complex **2**,[11] the ^{29}Si NMR spectrum of which showed only a triplet signal at –2.6 ppm (J_{SiF} = 147 Hz) in the temperature range 298–368 K. Rotation about the C_{ar}–Si bonds is hindered by the introduction of the bulky metal carbonyl moiety, and the "merry-go-round" is stopped. Si–F bond alternation remains a rapid process, unhindered by the steric bulk of the metal.

The quasi trigonal bipyramidal structures found for the silicon atoms of **1** are rather distorted from the ideal trigonal bipyramidal geometry. One of the reasons that **1** cannot take the ideal pentacoordinate structure must be the short Si–F bonds, since the perfectly planar D_{6h} structure of $C_6(SiMe_2X)_6$ (**4**) requires all Si–X bond lengths to be 1.88 Å, much longer than the Si–F. Therefore, if an electronegative group with an Si–X bond longer than the Si–F distance could be introduced, the D_{6h} structure might be realized. Hexakis(methoxydimethylsilyl)benzene (**3**) would be a candidate, but no spectral nor structural information has been given except for ^{1}H NMR data.[12] We have prepared compound **3** and examined the structure. Interestingly, the ^{29}Si NMR chemical shift of **3** appeared at the very high field of –64.2 ppm[13] in the region of pentacoordinate silicon.[14] The coupling constant $^1J_{SiC(Me)}$ of **3** was observed as 80 Hz in the ^{13}C NMR. The value is $^4/_3$ times larger than those of the other methoxysilanes, which are around 60 Hz.

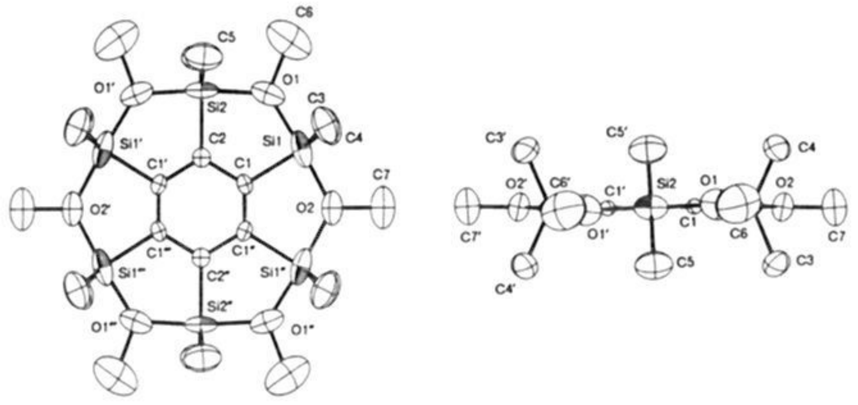

Figure 4. ORTEP drawings of hexakis(methoxydimethylsilyl)benzene: top and side views.

The molecular structure of **3** determined by the X-ray crystallographic method (Figure 4) is remarkable in that the molecular framework of **3** is perfectly planar with 6-fold symmetry.[15] Oxygen atoms are located in between two silicon atoms with a distance of 1.88 Å, the value exactly expected from the D_{6h} structure **4**. Each O–Si–O is arranged in a linear configuration. The other angles across the silicon atoms in the equatorial plane are 120°.

Acknowledgment. We are grateful for the financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No. 02102004).

Supplementary Material Available: Tables of X-ray experimental data, atomic parameters, anisotropic temperature factors, bond distances, and bond angles (21 pages); table of observed and calculated structure factors for **1** and **3** (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[9] The pentacoordinate structure is not the transition state but the intermediate with the energy minimum for silicon. Dewar, M. J. S.; Healey, E. *Organometallics* **1982**, *1*, 103.

[10] Chance *et al.*[3e] observed that barriers to pyramidal inversion of nitrogen atoms in hexakis(dialkylamino)benzenes were substantially lower than barriers to rotation about the C_{ar}–N bonds.

[11] Compound **2**: yellow crystals; mp 235 °C dec; ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.44 (t, $^3J_{HF}$ = 11 Hz, 18 H), 0.64 (t, $^3J_{HF}$ = 11 Hz, 18 H); ^{13}C NMR (75.5 MHz, C_6D_6, 298 K) δ 2.9–3.8 (m), 4.0–4.9 (m), 111.9–112.5 (m), 219.9; ^{29}Si NMR (59.6 MHz, C_6D_6, 298 K) δ –2.64 (t, $^1J_{SiF}$ = 147 Hz); ^{19}F NMR (282.4 MHz, C_6D_6, 298 K) δ –95.7; high-resolution MS *m/z* calcd for $C_{21}H_{36}F_6O_3MoSi_6$ 716.0240, found 716.0243.

[12] Fink, W. *Helv. Chim. Acta* **1974**, *57*, 1010.

[13] Compound **3**: colorless crystals; mp >250 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.29 (s, 36 H), 3.14 (s, 18 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 3.5, 47.8, 155.8; ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ –64.2; MS (20 eV) *m/z* (rel intensity) 606 (1.0, M$^+$), 591 (17), 397 (100).

[14] The ^{29}Si NMR signals of (methoxydimethylsilyl)benzene and 1,2-bis(methoxydimethylsilyl)benzene are at 8.4 and 8.8 ppm, respectively.

[15] Crystal data for **3** at 13 °C: a = 22.105(2) Å, b = 12.046(2) Å, c = 12.619(3) Å, V = 3360.5(10) Å^3, orthorhombic with space group *Cmca*, $Z = 4$, ρ = 1.20 g cm^{-3}. The structure was solved by direct methods, R = 0.099 and R_w = 0.087 for 1298 reflections with $F_o > 3\sigma(F_o)$. The molecule has a crystallographic 2-fold axis (through Si2 and C2) and a mirror plane (include O2 and C7).