Hexacoordinated silicon species: a possible model for reaction intermediates. 1. X-ray determination of the geometry in the solid state

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Hexacoordinated Silicon Species: A Possible Model for Reaction Intermediates. 1. X-ray Determination of the Geometry in the Solid State

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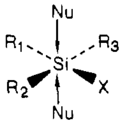
Summary: X-ray determination of the structure of bis(8-(dimethylamino)naphthyl)fluorosilane, bis(8-(dimethylamino)naphthyl)silane, and (2-((dimethylamino)methyl)phenyl)-(8-(dimethylamino)naphthyl)difluorosilane has shown hexacoordination to occur at the silicon atom. This result supports hexacoordinated silicon as a possible intermediate in the course of chemical reactions.

Hexacoordinated silicon species have frequently been proposed as intermediates or transition states in the course of chemical reactions.[1-3] The racemization of halosilanes induced by nucleophilic solvents has been shown to involve two molecules of nucleophilic catalyst and has been proposed to proceed via a hexacoordinated intermediate, 1.

The nucleophilic catalysis of nucleophilic substitutions at silicon is widely used in organic synthesis. The process was proposed to involve a reversible coordination of the nucleophilic catalyst (of which the fluoride ion is the most widely used) at silicon followed by nucleophilic attack of the reagent in the rate-determining step.

Such intermediates have been proposed for the activation of enoxysilanes by F⁻ leading to cross aldolizations or Michael reactions.[4] This has been strongly supported in the case of group transfer polymerization of methacrylates thanks to the migration of the silicon moiety along the living polymer without any exchange.[5]



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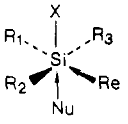

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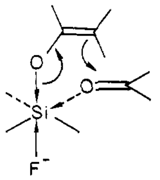

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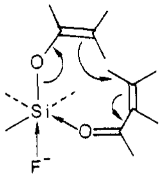

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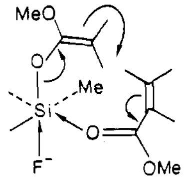

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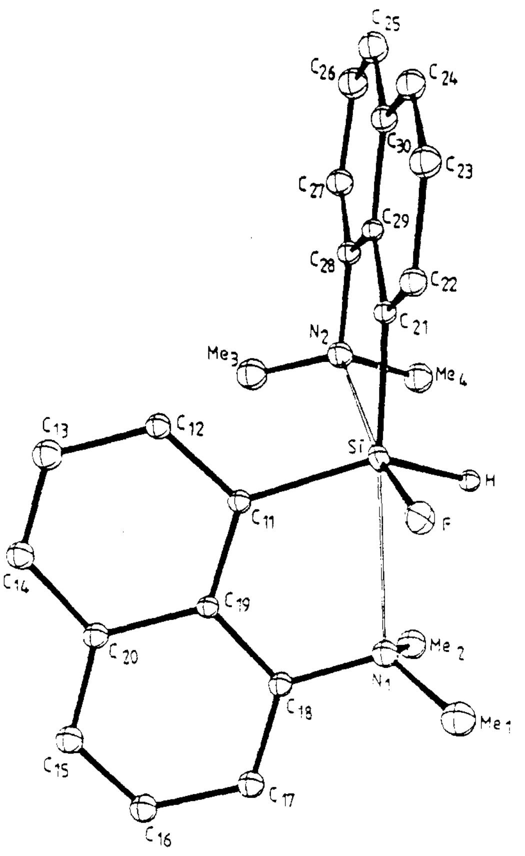

Figure 1. ORTEP drawing of the molecule of compound 6. Spheres are at the 10% probability level.

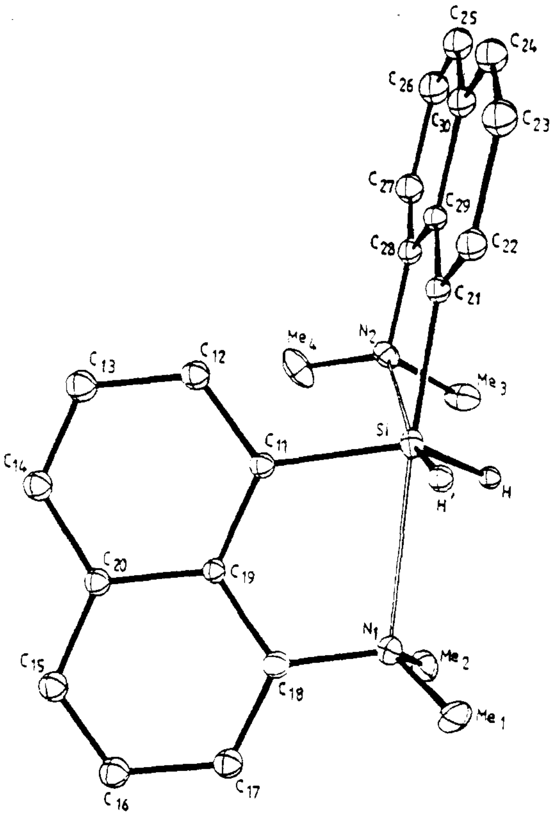

Figure 2. Perspective view of compound 7. Spheres enclose 10% of the electron density.

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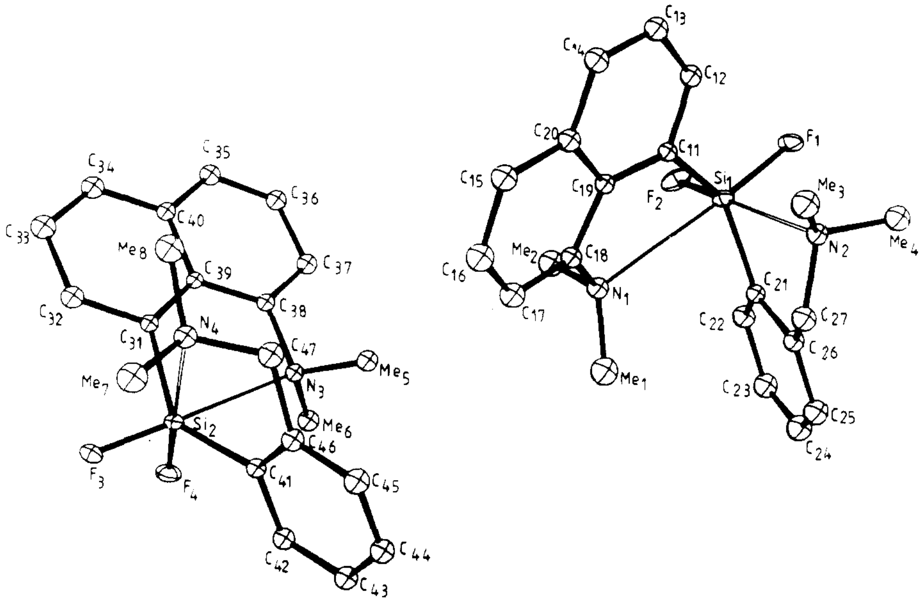

Figure 3. ORTEP drawing of the two conformations of compound 8 in the crystal. Spheres are at the 10% probability level.

In the course of studies on the formation and the reactivity of hypervalent species,[6] we have recently sought particularly to explore the conditions under which hexacoordinated silicon compounds may be formed. The possibility of an increase in the coordination number of silicon when it is not surrounded by electronegative groups is much debated,[7] and mechanistic studies of the substitution reactions of hexacoordinated silicon compounds favor the operation of dissociative processes.[8]

Following the concepts developed by Dunitz,[9] who demonstrated that the interactions between nucleophilic and electrophilic centers in the crystal are a good picture of transition states or intermediates of corresponding chemical reactions, we have studied molecular structures having possibly two favorable intramolecular coordinations at silicon.[10]

In this communication, we report the X-ray structures of bis(8-(dimethylamino)naphthyl)fluorosilane (6), bis(8-(dimethylamino)naphthyl)silane (7), and (2-((dimethylamino)methyl)phenyl)(8-(dimethylamino)naphthyl)difluorosilane (8). Compound 6 contains only one electronegative group (fluorine) and permits as close as possible a comparison with the postulated intermediates (1–5: three nonpolar groups, one fluorine group, and two leaving groups). Compound 7 does not exhibit any polar group. In the case of compound 8, with the ligand 2-((dimethylamino)methyl)phenyl, it is possible for one nitrogen atom to avoid interaction with the silicon atom.

The syntheses of compounds 6, 7, and 8 are reported in ref 11.

The X-ray structure of 6 shows (Figure 1) that the lone pair of both nitrogen atoms is directed toward the silicon giving a formally hexacoordinated complex.[12] Our results show the formation of two dative Si←N bonds having comparable lengths (2.680 (8) and 2.646 (8) Å) to those reported for pentacoordinated silicon derivatives[2b,13] (2.44–2.66 Å) and for some hexacoordinated silicon compounds which contain several polar groups.[14] We also observe that one of the coordinated nitrogen atoms is

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(11) **Synthesis of Bis(8-(dimethylamino)naphthyl)fluorosilane (6).** To 8-((dimethylamino)naphthyl)lithium [Jones, F. K.; Zinn, M. F.; Hauser, C. R. *J. Org. Chem.* **1963**, *28*, 663; ref 10] as a suspension in dry ether (90 cm^3) was added, dropwise at -30 °C, trimethoxysilane (2.5 g in 30 cm^3 of dry ether). The mixture was stirred overnight, and after usual workup (8-(dimethylamino)naphthyl)dimethoxysilane was isolated by fractional distillation (bp 120–124 °C); 2.9 g, 62%. To (8-(dimethylamino)naphthyl)dimethoxysilane (4.7 g) in solution in dry ether (20 cm^3) was added 1.7 g of boron trifluoride etherate dropwise, and the mixture was stirred for 15 min. After the usual workup, (8-(dimethylamino)naphthyl)difluorosilane was obtained by crystallization from hexane; 3 g, 70%. (8-(Dimethylamino)naphthyl)lithium (2 g) as a suspension in dry ether (50 cm^3) was added dropwise to (8-(dimethylamino)naphthyl)difluorosilane (3.2 g) in ethereal solution (50 cm^3). After being stirred for 30 min and usual workup, bis(8-(dimethylamino)naphthyl)fluorosilane was isolated by crystallization; mp 141–144 °C. Anal. Calcd for $C_{24}H_{25}N_2SiF$: C, 74.19; H, 6.48; N, 7.21; F, 4.89. Found: C, 74.38, H, 6.18; N, 6.98; F, 4.77. Mass: 388, $(M - 1)^+$; 387. NMR: ^{29}Si (TMS) −37.33 ppm (*J*(Si–H) - 285.45 Hz); ^{19}F ($CFCl_3$) −157.5 ppm (*J*(F–H) = 63.6 Hz); ^{1}H (TMS, C_7D_8) 2.61 and 2.26 (s, NMe_2), 5.88 (d, *J*(H–F) = 63.9 Hz, SiH), 6.6–8.4 ppm (m, 12 H, arom).

Synthesis of Bis(8-(dimethylamino)naphthyl)silane (7). To (8-(dimethylamino)naphthyl)lithium (4.5 g) as a suspension in dry ether (60 cm^3) was added dropwise tetrachlorosilane (1.1 cm^3 in 20 cm^3 of dry ether). After the mixture was stirred 1 h, $LiAlH_4$ (0.7 g) was added to the mixture. After the mixture was stirred overnight, toluene (40 cm^3) was added, the salts were filtered, and the solvent was evaporated. Bis(8-(dimethylamino)naphthyl)silane (7) was obtained by crystallization from hexane: mp 151–152 °C; 2.48 g, 53%. Anal. Calcd $C_{24}H_{26}N_2Si$: C, 77.79; H, 7.07; N, 7.56. Found: C, 76.5; H, 7.09; N, 7.69. Mass: 370, $(M - H)^+$ 369. IR (CCl_4, cm^{-1}): ν(Si–H) 2090, 2180. NMR: ^{29}Si (TMS) −39.8 ppm (t, *J*(Si–H) = 216.4Hz); ^{1}H (TMS, C_7D_8) 2.3 (s, 6 H, NMe_2), 5.3 (s, 2 H, SiH), 7.1–7.6 ppm (m, 12 H, arom).

Synthesis of (8-(Dimethylamino)naphthyl)(2-(dimethylamino)methyl)phenyl)difluorosilane (8). To a solution of (8-(dimethylamino)naphthyl)trifluorosilane in hexane (2.75 g in 50 cm^3) was added (2-(dimethylamino)methyl)phenyl)lithium (1.52 g) as the solid substance. After the mixture was stirred for 1 h, (8-(dimethylamino)naphthyl)(2-((dimethylamino)methyl)phenyl)difluorosilane (8) was obtained by crystallization from hexane: mp 91 °C, 4.4 g (67%). Anal. Calcd for $C_{21}H_{24}F_2N_2Si$: C, 68.1; H, 6.53; N, 7.56. Found: C, 68.09; H, 6.50; N, 6.32. NMR: ^{29}Si (TMS) −52.84 ppm (t, *J*(Si–F) - 273 Hz); ^{19}F ($CFCl_3$) −143 ppm (s); ^{1}H (TMS) 1.45 (s, 6 H, NMe_2), 2.25 (s, 6 H, NMe_2), 3.15 (s, 2 H, NCH_2–), 7.15–8.75 ppm (m, 10 H, arom).

Table I. Main Bond Lengths (Å) and Bond Angles (deg) in Compounds 6 and 7

6		7	
Si–H	1.55 (6)	Si–H	1.44 (5)
Si–F	1.628 (6)	Si–H′	1.54 (6)
Si–C(11)	1.878 (8)	Si–C(11)	1.890 (7)
Si–C(21)	1.881 (9)	Si–C(21)	1.898 (8)
Si···N(1)	2.680 (8)	Si···N(1)	2.610 (7)
Si···N(2)	2.646 (8)	Si···N(2)	2.800 (8)
F–Si–H	100.8 (24)	H–Si–H′	112.1 (31)
C(11)–Si–C(21)	109.7 (5)	C(11)–Si–C(21)	108.2 (3)
F–Si–C(11)	102.0 (3)	H′–Si–C(11)	104.2 (19)
F–Si–C(21)	99.1 (3)	H′–Si–C(21)	96.1 (20)
H–Si–C(11)	130.4 (22)	H–Si–C(11)	127.3 (21)
H–Si–C(21)	109.2 (22)	H–Si–C(21)	104.4 (21)
N(1)···Si–C(21)	175.7 (3)	N(1)···Si–C(21)	176.2 (3)
N(2)···Si–F	171.9 (3)	N(2)···Si–H′	168.2 (19)

Table II. Main Bond Lengths (Å) and Bond Angles (deg) in the Two Molecules of Compound 8

molecule 1		molecule 2	
Si(1)–F(1)	1.617 (6)	Si(2)–F(3)	1.604 (7)
Si(1)–F(2)	1.603 (7)	Si(2)–F(4)	1.603 (8)
Si(1)–C(11)	1.841 (11)	Si(2)–C(31)	1.870 (9)
Si(1)–C(21)	1.869 (10)	Si(2)–C(41)	1.873 (11)
Si(1)···N(1)	2.770 (10)	Si(2)···N(3)	2.665 (9)
Si(1)···N(2)	2.594 (10)	Si(2)···N(4)	2.806 (10)
F(1)–Si(1)–F(2)	96.5 (4)	F(3)–Si(2)–F(4)	98.3 (4)
C(11)–Si(1)–C(21)	135.5 (5)	C(31)–Si(2)–C(41)	136.0 (5)
F(1)–Si(1)–C(11)	104.5 (4)	F(3)–Si(2)–C(31)	103.4 (4)
F(1)–Si(1)–C(21)	108.5 (4)	F(3)–Si(2)–C(41)	103.0 (4)
F(2)–Si(1)–C(21)	101.8 (4)	F(4)–Si(2)–C(41)	103.9 (4)
F(2)–Si(1)–C(11)	103.3 (4)	F(4)–Si(2)–C(31)	106.3 (4)
N(1)···Si(1)–F(1)	175.5 (3)	N(3)···Si(2)–F(3)	175.8 (4)
N(2)···Si(1)–F(2)	174.8 (4)	N(4)···Si(2)–F(4)	174.8 (3)

opposite to the fluorine and orthogonal to the Si–H bond while the other is perpendicular to both functional groups.

The X-ray structure of **7** shows immediately that the shapes of the molecules of compounds **6** and **7** are the same (Table I; Figure 2), though the coordinates of the Si atom in each compound differ markedly. The striking feature of the molecule of compound **7** is the nonequivalence of the two hydrogen atoms: H is opposite to a naphthyl carbon atom and orthogonal to two nitrogen–silicon bonding interactions while H′ is opposite to one of the N···Si interactions and orthogonal to the other. The N···Si bondings are significantly different with the strongest interaction being opposite to an aryl carbon atom (Si···N(1) - 2.610 (7) Å, N(1)–Si–C(21) 176.2 (3)°) and the weakest (Si···N(2) - 2.800 (8) Å, N(2)–Si–H′ - 168.2 (19)°) being opposite to the atom H′.

Compound **8** exhibits two different conformations in the solid state. However, these conformations are very similar and correspond once again to two extra coordinations of a nitrogen atom opposite to one fluorine atom and perpendicular to the second one. The efficiency of the two types of ligand seems equivalent: the N···Si bond distance is larger for the (dimethylamino)naphthyl ligand in conformation 1 of compound **8** (2.77 (1) Å) whereas in conformation 2 it is the ((dimethylamino)methyl)phenyl ligand which exhibits the longest N···Si interaction (2.81 (1) Å). For compound **8**, the overall tetrahedral geometry of the diaryldifluorosilane is again retained although it is worth noting that the Ar–Si–Ar′ angles have been increased to 135.5 and 136.0 (5)° for each conformation.

On the whole the silicon atom largely maintains the basic tetrahedral geometry in spite of the two dative bonds with the nitrogen atom, which leads to a structure similar to the bicapped tetrahedron defined by Hoffmann and his collaborators:[15] this is the geometry of a tetrahedral silicon undergoing two nucleophilic coordinations.

In conclusion, following the general concept developed by Dunitz,[9] this work illustrates that the formation of hexacoordinate silicon compounds by nucleophilic addition of two ligands to a silicon atom bonded only to one electronegative group is possible, as we have proposed in the racemization of halosilanes induced by two molecules of solvent.[1] This process of inversion of the stereochemistry by nucleophilic coordination is different from the edge process recently reported.[16] Finally the structures **6**, **7**, and **8** support the possible existence of the hexacoordinate intermediates **1**–**5** which have been postulated to arise in reactions of organic synthesis using silicon.

Supplementary Material Available: Tables of crystal data, intensity collection, and refinement, atomic coordinates and thermal parameters for the non-H atoms, calculated atomic coordinates for the H atoms, bonds distances, and bond angles for **6**, tables of crystal data, intensity collection, and refinement, atomic coordinates and thermal parameters for the non-H atoms, anisotropic thermal parameters for six of the atoms, bond distances, bond angles, and calculated atomic coordinates for the H atoms for **7**, and tables of crystal data, intensity collection, and refinement, atomic coordinates and thermal parameters for both conformations, anisotropic thermal parameters for the Si and F atoms, calculated atomic coordinates for the H atoms, bond distances, and bond angles for **8** (20 pages); listings of structure factors amplitudes for **6**, **7**, and **8** (15 pages). Ordering information is given on any current masthead page.

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(12) **X-ray crystal analysis of 6**: monoclinic, space group $P2_1/c$; $a = 9.847$ (2), $b = 13.261$ (4), $c = 15.879$ (5) Å; $\beta = 98.82$ (2)°; $V = 2049$ Å^3; $Z = 4$, $d_{\mathrm{calcd}} = 1.259$, $d_{\mathrm{measd}} = 1.27$ (3) g cm^{-3}; μ(Mo Kα) = 0.97 cm^{-1}. A colorless platelike crystal (0.15 × 0.30 × 0.40 mm^3) was crystallized from hexane and sealed in a Lindeman glass capillary. A total of 1648 unique reflections were collected but only 844 could be measured ($F_o > 2.04\sigma(F_0)$) (CAD$_4$ diffractometer, Enraf-Nonius, graphite monochromator, Mo Kα radiation); direct methods, Due to the low number observed reflections only the silicon atom was refined anisotropically. The hydrogen atomic positions were determined by calculation (SHELX-76 program), and the hydrogen atoms were then taken in account in the refinement. The hydrogen atom bonded to silicon was located by a difference Fourier map. No constraint was applied to this hydrogen atom in the final refinement. Final residuals: $R = 0.054$, $R_w = 0.051$.

X-ray crystal structure of 7: monoclinic space group $P2_1/c$; $a = 9.958$ (2), $b = 13.060$ (3), $c = 16.153$ (3) Å; $\beta = 100.59$ (1)°; $V = 2065$ Å^3; $Z = 4$, $d_{\mathrm{calcd}} = 1.192$, $d_{\mathrm{measd}} = 1.19$ (2) g cm^{-3}; μ(Mo Kα) = 1.19 cm^{-1}. A colorless block (0.75 × 0.35 × 0.25mm^3) was crystallized from the solvent toluene–hexane (1:6) and sealed in a capillary. A total of 2042 unique reflections were collected and 1087 kept for the refinement of the structure ($F_o > 2.6\sigma(F_0)$). The silicon atom, the nitrogen atoms, and the methyl carbon atoms were refined anisotropically. The H atoms bonded to carbon atoms were taken in account in the refinement. The two hydrogen atoms bonded to silicon were easily located by a difference Fourier map. Final residuals: $R = 0.063$, $R_w = 0.063$.

X-ray crystal structure of 8: monoclinic, space group $P2_1/c$; $a = 9.699$ (4), $b = 16.500$ (6), $c = 24.445$ (11) Å; $\beta = 97.90$ (3)°; $V = 3875$ Å^3; $Z = 8$; $d_{\mathrm{calcd}} = 1.270$, $d_{\mathrm{measd}} = 1.26$ (2) g cm^{-3}; μ(Mo Kα) = 1.40 cm^{-1}. A colorless plate (0.45 × 0.45 × 0.08 mm^3) was crystallized from hexane and sealed in a capillary. A total of 3582 unique reflections were collected and 1429 kept for the refinement of the structure ($F_o > 2.2\sigma(F_o)$). The silicon atoms and the four fluorine atoms were refined anisotropically. The hydrogen atoms were taken into account in the refinement. Final residuals: $R = 0.059$, $R_w = 0.062$.

Full details of the structure determinations for **6**, **7**, and **8** are available as supplementary material.

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