Five-co-ordinated Silicon Compounds: Geometry of Formation by Intramolecular Co-ordination. Crystal Structure of 2-(Dimethylaminomethyl)phenyl-1-naphthylsilane†

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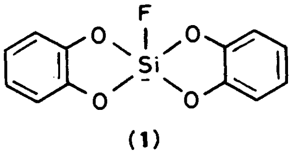
Studies of a wide range of intramolecularly five-co-ordinated silicon compounds with chelating nitrogen donors have been made, with a view to obtaining further information on the details of nucleophilic substitution reactions at silicon. The crystal structure of 2-(dimethylaminomethyl)-phenyl-1-naphthylsilane has been determined by single-crystal *X*-ray diffraction ($R = 0.074$ for 564 observed reflections). Crystals are tetragonal, space group $I\bar{4}$, with $Z = 8$ in a unit cell of dimensions $a = 21.845(5)$ and $c = 7.119(2)$ Å. The central silicon atom shows essentially trigonal-bipyramidal co-ordination, with the axial positions occupied by the naphthyl group and the donor nitrogen atom, and the two hydrogen atoms occupying equatorial positions. Comparison with other structures reported in the literature shows that this geometry, always with axial disposition of the donor atom, is generally adopted by molecules of this type. Silicon-29, ^{19}F, and ^{1}H n.m.r. spectroscopic data for similar compounds with varying substituents on the silicon atom show that the same geometry is adopted by these intramolecularly co-ordinated species in solution.

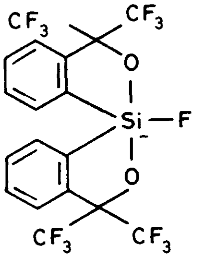
In recent years there has been a great increase in the number of five-co-ordinated structures known, both amongst Main Group and transition elements. Studies of such structures are significant from several points of view, notably (*i*) the existence of two limiting geometries, the square pyramid and the trigonal bipyramid, in neither of which are all the ligand sites equivalent; (*ii*) the prevalence of stereochemical non-rigidity, a consequence perhaps of the small difference in energy between the two geometries; and (*iii*) the relationship of five-co-ordinate structures to mechanisms for associative nucleophilic substitution at tetrahedral and square-planar centres, as well as for dissociative reactions of six-co-ordinate complexes.

Although hypervalent silicon compounds have been known since the beginning of the last century,[1] the systematic study of five-co-ordinate silicon species commenced only in the 1960s. Recent reviews of five-co-ordination, by Holmes,[2] and of five- and six-co-ordinate silicon structures, by Voronkov and co-workers,[3] are available. Holmes has, in particular, examined the relationship between the square-pyramidal and trigonal-bipyramidal geometries and has shown that structures intermediate between these two extremes may be observed. Such structures generally follow the local C_{2v} constraint connecting the square pyramid and the trigonal bipyramid *via* the Berry co-ordinate. Structures close to the square pyramid are found only in anionic systems such as (**1**) where two unsaturated five-membered rings are present, with identical atoms bound to the silicon in these rings.

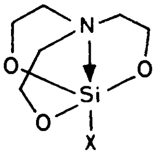
Geometries close to the trigonal bipyramid are far more common, and are adopted for example by silicates such as (**2**), in which the atoms bound to silicon in the rings are now different. These compounds have been employed in a series of structural studies by Martin and co-workers.[4] The silatranes (**3**) (2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane) which have been extensively studied by Voronkov and co-workers[3] are neutral compounds in which the geometry about the silicon atom is essentially trigonal bipyramidal, extension of the co-ordination resulting from intramolecular donation.



(**1**)



(**2**)



(**3**)

Our particular interest lies in the possible relationship of such five-co-ordinated species to the mechanism of nucleophilic substitution at silicon, in which the formation of five-co-ordinated intermediates is implicated.[5] It is thus important to discover the rules governing the formation and stability of these intermediates. Considerable variation in their behaviour can be expected, including the tendency to ligand permutation, as a function of the site preferences (axial or equatorial) of the different substituents.

For this purpose compounds of types (**1**), (**2**), and (**3**) are not the most suitable for study, for in general they carry only a single functional site, and the range of functions which may be introduced is relatively restricted. Structures more closely resembling the probable intermediates in nucleophilic sub-

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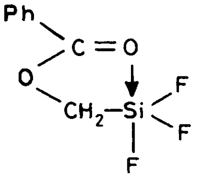
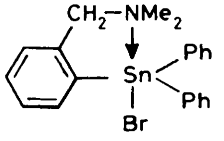
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: mmHg ≈ 13.6 × 9.8 Pa.

stitution at silicon are to be found in compounds such as (**4**) synthesized by Voronkov and co-workers,[6] and the tin derivative (**5**), studied by van Koten *et al.*[7]



(**4**)



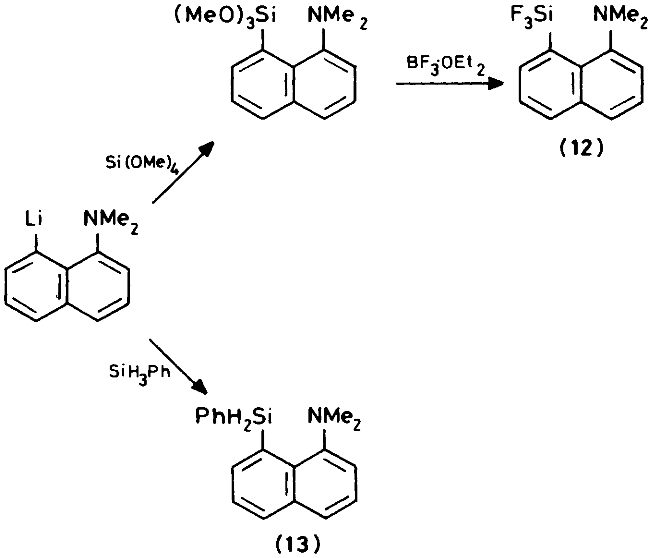
(**5**)

We decided to base our studies on the silicon analogues of (**5**), since it was expected that the stronger co-ordination of a nitrogen atom, compared to that of an oxygen atom, would facilitate the investigation of the effects induced by a larger range of substituents about the silicon atom. The types of compound studied are shown in Schemes 1—4, which outline the synthetic routes employed for the compounds discussed in this paper.

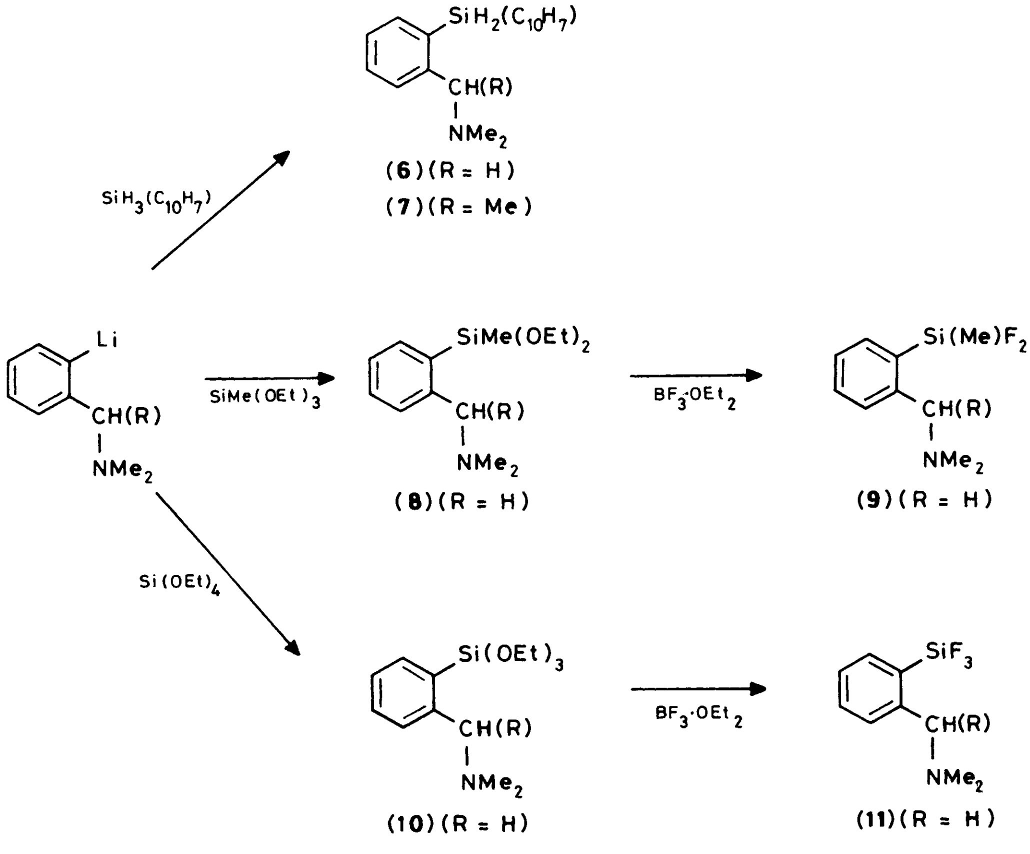
Experimental

Reactions were carried out under dry nitrogen. All melting points and boiling points are uncorrected. Elemental analyses were performed by the Centre de Microanalyse du C.N.R.S. Fluorine n.m.r. spectra were determined at 84.67 MHz on a Varian EM-390 spectrometer. Proton n.m.r. spectra were determined at 60 MHz by using a Varian EM-360 spectrometer or at 100 MHz with a Varian HA 100 spectrometer; silicon n.m.r. spectra were determined at 39.76 MHz with a Bruker WP 200 SY spectrometer; chemical shifts are reported relative to internal SiMe$_4$ as standard unless otherwise stated. Mass spectra were determined with a JEOL JMS-D 100 instrument.

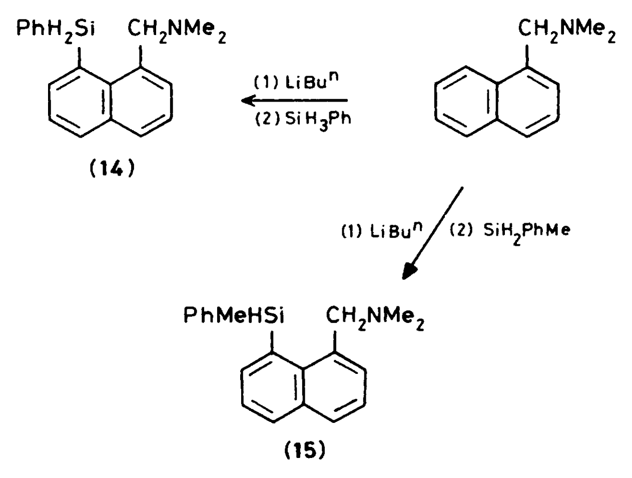
1-(Dimethylamino)ethylbenzene was obtained by methylation of 1-phenylethylamine with formic acid–formaldehyde by the method of Eschweiler and Clark.[8] 1-(Dimethylamino)-naphthalene was obtained by methylation of 1-naphthylamine with trimethyl phosphate.[9] 1-(Dimethylaminomethyl)naph-



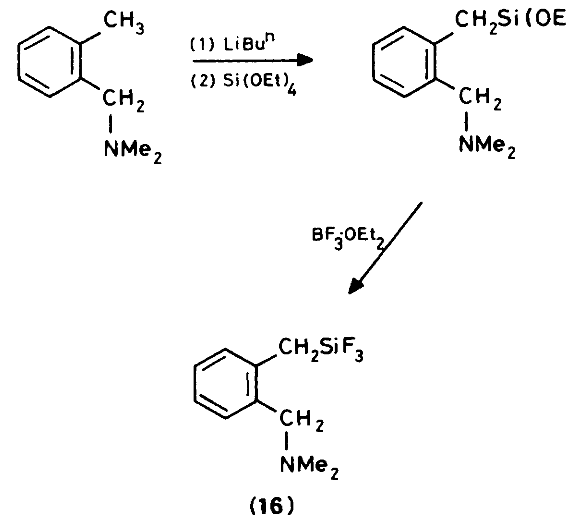
Scheme 2.



Scheme 1.



Scheme 3.



Scheme 4.

thalene was prepared by the reaction of 1-naphthylmagnesium bromide with dimethylaminomethyl 2-methylpropyl ether following the method of Robinson and Robinson.[10]

When necessary, solvents and reagents were dried prior to use; the other reagents were used as received (Aldrich, Janssen, Merck, or Fluka).

Crystal-structure Determinations.—Crystals of $SiH_2(C_{10}H_7)(C_6H_4CH_2NMe_2\text{-}o)$ (**6**) ($C_{10}H_7$ = 1-naphthyl) were obtained by two recrystallisations from pentane. Crystallisation of $SiH_2Ph(C_{10}H_6NMe_2\text{-}8)$ (**13**) and $SiHMePh(C_{10}H_6CH_2NMe_2\text{-}8)$ (**15**) was effected by cooling to −18 °C saturated solutions in pentane and hexane, respectively.

Crystal data for (**6**). $C_{19}H_{21}NSi$, $M = 291.5$, tetragonal, space group $I\bar{4}$ (S_4), $a = 21.845(5)$, $c = 7.119(2)$ Å, $U = 3\,397.2$ Å^3, $Z = 8$, $D_c = 1.140$ g cm^{-3}, $D_m = 1.13(1)$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 1.27$ cm^{-1}, $F(000) = 1\,248$. Systematic absences for hkl ($h + k + l$) = $2n + 1$, revealed a body centred unit cell. The presence of the reflections 00l for l = 2, 4, and 6 was consistent with several space groups ($I4$ and $I\bar{4}$, $Z = 8$, or five others with $Z = 16$ or $Z = 32$). The molecule was not expected to display any symmetry (a common plane for the naphthyl and phenyl groups is unlikely) and the space groups $I4$ and $I\bar{4}$ were tried to solve the structure; $I\bar{4}$ was finally revealed to be the correct space group.

Table 1. Fractional atomic co-ordinates (× 10^4) for compound (**6**) with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Si	7 058(2)	1 526(2)	3 797(8)
N	6 469(6)	2 401(6)	2 653(22)
C(1)	7 507(7)	860(7)	4 890(29)
C(2)	7 317(8)	672(8)	6 707(34)
C(3)	7 646(9)	202(8)	7 683(32)
C(4)	8 122(8)	−53(6)	6 907(27)
C(5)	8 877(8)	−185(9)	4 229(35)
C(6)	9 028(8)	−15(8)	2 546(36)
C(7)	8 750(9)	450(9)	1 417(35)
C(8)	8 215(7)	730(7)	2 219(29)
C(9)	8 025(6)	570(7)	4 049(26)
C(10)	8 355(8)	111(7)	5 039(27)
C(11)	6 531(6)	1 180(6)	2 033(21)
C(12)	6 446(8)	545(7)	2 040(28)
C(13)	6 012(9)	296(8)	702(34)
C(14)	5 713(9)	659(9)	−551(36)
C(15)	5 850(9)	1 306(9)	−626(35)
C(16)	6 243(7)	1 542(7)	767(28)
C(17)	6 366(7)	2 227(8)	710(29)
C(18)	5 879(7)	2 429(7)	3 720(31)
C(19)	6 802(8)	3 006(8)	2 809(30)
H(1)	6 672(49)	1 709(49)	5 392(184)
H(2)	7 547(46)	1 926(47)	3 161(168)

A small (0.10 × 0.12 × 0.20 mm) colourless columnar crystal of compound (**6**) was used for data collection. The h,k,l octant was collected in the 2θ—ω scan mode for $4 < 2\theta < 60°$ on a Nonius CAD-4 automated diffractometer equipped with a graphite monochromator, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å. A total of 2 165 reflections were collected and a few pairs were averaged to give a set of 2 154 unique reflections, of which 564 only were considered to be observed [$I > 2\sigma(I)$]. Monitoring of three standard intensities at intervals of 60 min showed no decomposition of the crystal. Usual Lorentz and polarization corrections were applied.

Solution and refinement of (**6**). The structure was solved by use of a 1980 version of the MULTAN program. The nitrogen and carbon atom positions were refined with isotropic thermal parameters whereas the silicon atom was refined anisotropically. The positions of the hydrogen atoms on silicon were calculated on the basis of a bond distance of 1.47 Å[*] and a symmetric disposition (*ca.* 120° angles) of these atoms with respect to the first carbon atom of the phenyl ring. After three cycles of least-squares refinement, the Si–H(2) distance remained at 1.48(9) Å and the H(1) atom moved out to 1.92(42) Å. New co-ordinates were adjusted for this atom and a final refinement gave reasonable positions for both atoms. The final full-matrix least-squares refinement agreement factors for 96 variables were $R = 0.074$ and $R' = 0.079$; $w = 0.4002/[\sigma^2(F) + 0.0136F^2]$. The final difference Fourier map showed no peak with a density greater than 0.36 e Å^{-3}. In view of the low number of observed reflections, no attempt was made to include the other hydrogen atoms in the refinement. The final atomic co-ordinates are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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[*] This value was chosen as an average between the value previously reported for molecule (**13**)[11] and other data from the literature (M. Schubert, K. Ackermann, and B. Wörle, *J. Am. Chem. Soc.*, 1982, **104**, 7378; E. A. V. Ebsworth, E. K. Murray, D. W. H. Rankin, and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1981, 1501).

Crystallographic information about compounds (**13**) *and* (**15**). The data collection for (**15**) was performed with graphite-monochromated Mo-K_α radiation on a Nonius CAD-4 automated diffractometer, leading to 739 observed intensities. An accurate set of 1 784 observed reflections was collected for compound (**13**) on a CAD-3 diffractometer[*] with Cu-K_α radiation. Other details of the crystal data, intensity measurements, and refinements are given in ref. 11 and its corresponding supplementary material.

Synthesis of 2-(*Dimethylaminomethyl*)*phenyl*-1-*naphthylsilane* (**6**).—2-(Dimethylaminomethyl)phenyl-lithium in ether [prepared[12] from (dimethylaminomethyl)benzene (3.65 g, 0.027 mol) in ether (50 cm^3) treated with n-butyl-lithium (0.025 mol in ether (100 cm^3))] was added dropwise to 1-naphthylsilane (4.0 g, 0.025 mol) in ether (50 cm^3) at 0 °C. The resulting mixture was stirred at room temperature for 24 h, then added to a mixture of crushed ice and ether. The ethereal layer was separated, washed with water, and dried over sodium sulphate. After removing the ether, 2-(*dimethylaminomethyl*)*phenyl*-1-*naphthylsilane* (**6**) (5.8 g, 80%) was obtained by distillation, b.p. 170 °C at 0.15 mmHg; m.p. 59 °C (from pentane) (Found: C, 78.6; H, 7.25; N, 4.7; Si, 9.65%; M^+, 291. $\mathrm{C_{19}H_{21}NSi}$ requires C, 78.3; H, 7.3; N, 4.8; Si, 9.6%; M, 291); $\delta_{\mathrm{H}}(\mathrm{CCl_4})$ 2.1 [6 H, s, $\mathrm{N(CH_3)_2}$], 3.50 (2 H, s, $\mathrm{CH_2N}$), 5.20 (2 H, s, $\mathrm{SiH_2}$), and 6.80—8.20 (11 H, br, aromatic); $\delta_{\mathrm{Si}}(\mathrm{CDCl_3})$ −47.25.

Synthesis of 2-[1-(*Dimethylamino*)*ethyl*]*phenyl*-1-*naphthylsilane* (**7**).—n-Butyl-lithium (0.030 mol) in ether (30 cm^3) was added to 1-(dimethylamino)ethylbenzene (4.6 g, 0.031 mol) in ether (30 cm^3). After stirring for 48 h at room temperature, the resulting solution of 2-[1-(dimethylamino)ethyl]phenyl-lithium[13] was added dropwise to a solution of 1-naphthylsilane (4.7 g, 0.030 mol) in ether (50 cm^3) at 0 °C. The mixture was stirred at room temperature for 24 h, then added to ice–water, and the ethereal layer separated. This ether layer was again washed with water, dried over sodium sulphate, and concentrated. 2-[1-(*Dimethylamino*)*ethyl*]*phenyl*-1-*naphthylsilane* (**7**) (5.5 g, 60%) was recovered by distillation, b.p. 175 °C at 0.1 mmHg (Found: C, 78.6; H, 7.9; N, 4.45. $\mathrm{C_{20}H_{23}NSi}$ requires C, 78.6; H, 7.6; N, 4.6%); $\delta_{\mathrm{H}}(\mathrm{CCl_4}$, 30 °C) 1.3 (3 H, d, $\mathrm{CHC}H_3$), 2.05 [6 H, s, $\mathrm{N(CH_3)_2}$], 3.7 (1 H, q, $\mathrm{C}H\mathrm{CH_3}$), 5.05 (2 H, s, $\mathrm{SiH_2}$), and 6.70—8.10 (11 H, br, aromatic); $\delta_{\mathrm{H}}(\mathrm{CD_2Cl_2}$, −100 °C) 2.00 (3 H, s, N–$\mathrm{CH_3}$), 2.40 (3 H, s, N–$\mathrm{CH_3}$), 5.02 and 5.12 [2 H, 2 d, J(A–B) 3 Hz, $\mathrm{SiH_2}$]; $\delta_{\mathrm{Si}}(\mathrm{CD_2Cl_2})$ −52.80.

Synthesis of 2-(*Dimethylaminomethyl*)*phenyldi*(*fluoro*)*methylsilane* (**9**).—2-(Dimethylaminomethyl)phenyl-lithium (0.1 mol) in ether, prepared as above, was added dropwise to triethoxy(methyl)silane (17.8 g, 0.1 mol) in ether (50 cm^3). The mixture was stirred for 24 h at 0 °C, and then poured into ice–water. The ethereal layer was rapidly separated, dried over magnesium sulphate, and the ether removed. 2-(*Dimethylaminomethyl*)*phenyldi*(*ethoxy*)*methylsilane* (**8**) (13.35 g, 50%) was recovered by distillation, b.p. 90 °C at 0.02 mmHg; $\delta_{\mathrm{H}}(\mathrm{CCl_4})$ 3.73 (4 H, q, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.33 (2 H, s, $\mathrm{CH_2N}$), 2.16 [6 H, s, $\mathrm{N(CH_3)_2}$], 1.23 (6 H, t, $\mathrm{OCH_2C}H_3$), and 0.28 (3 H, $\mathrm{SiCH_3}$); $\delta_{\mathrm{Si}}(\mathrm{CDCl_3})$ −18.19. Boron trifluoride etherate (1.56 g, 0.011 mol) in ether (5 cm^3) was added to a solution of the diethoxysilane (**8**) (4.27 g, 0.16 mol) in ether (3 cm^3). The mixture was stirred for 10 min, and the ether removed. 2-(*Dimethylaminomethyl*)*phenyldi*(*fluoro*)*methylsilane* (**9**) (2.75 g, 80%) was obtained by distillation, b.p. 162 °C at 18 mmHg (Found: C, 55.5; H, 7.1; F, 17.0; N, 6.4%; M^+, 215. $\mathrm{C_{10}H_{15}F_2NSi}$ requires C, 55.8; H, 7.0; F, 17.7; N, 6.5%; M, 215); $\delta_{\mathrm{H}}(\mathrm{CD_2Cl_2}$, 30 °C) 3.58 (2 H, s, $\mathrm{CH_2N}$), 2.25 [6 H, s, $\mathrm{N(CH_3)_2}$], 0.40 (3 H, t, $\mathrm{SiCH_3}$); (−95 °C) 2.24 (3 H, s, N–$\mathrm{CH_3}$), 2.45 (3 H, s, N–$\mathrm{CH_3}$), 3.56 and 3.90 [2 H, 2 d, J(A–B) 15 Hz, $\mathrm{CH_2N}$]; $\delta_{\mathrm{F}}(\mathrm{CD_2Cl_2}$, standard $\mathrm{CFCl_3}$, 30 °C) −137 (q, $\mathrm{CH_3}$-$\mathrm{SiF_2}$); (−95 °C) −111 (br s, $\mathrm{F_{ax}}$), −154.6 (d, $\mathrm{F_{eq}}$); $\delta_{\mathrm{Si}}(\mathrm{CDCl_3}$, 30 °C) −40.82 (t, $\mathrm{SiF_2}$); (−90 °C) −52.53 [t, J(Si–F) 260.9 Hz].

Synthesis of 2-(*Dimethylaminomethyl*)*phenyltri*(*fluoro*)*silane* (**11**).—2-(Dimethylaminomethyl)phenyl-lithium (0.16 mol) in ether, prepared as above, was added dropwise to tetraethoxysilane (33.3 g, 0.16 mol) in ether (100 cm^3) at 0 °C. The mixture was stirred for 24 h and the ether removed. The residue was extracted with pentane, the solution filtered and the pentane distilled, followed by 2-(*dimethylaminomethyl*)*phenyltri*(*ethoxy*)*silane* (**10**) (23.8 g, 50%), b.p. 115 °C at 0.05 mmHg (Found: C, 60.8; H, 10.0; N, 4.45. $\mathrm{C_{15}H_{27}NO_3Si}$ requires C, 60.6; H, 9.1; N, 4.7%); $\delta_{\mathrm{H}}(\mathrm{CCl_4})$ 3.88 (6 H, q, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.55 (2 H, s, $\mathrm{CH_2N}$), 2.23 [6 H, s, $\mathrm{N(CH_3)_2}$], 2.22 (9 H, t, $\mathrm{OCH_2C}H_3$); $\delta_{\mathrm{Si}}(\mathrm{CDCl_3})$ −57.17. Boron trifluoride etherate (2.38 g, 0.0168 mol) in ether (5 cm^3) was added to a solution of the triethoxysilane (**10**) (5.0 g, 0.0168 mol) in ether (5 cm^3). The mixture was stirred for 10 min and the ether removed. 2-(*Dimethylaminomethyl*)*phenyltri*(*fluoro*)*silane* (**11**) (3.13 g, 85%) was obtained by distillation, b.p. 135 °C at 15 mmHg, m.p. 84 °C (from hexane) (Found: C, 49.20; H, 5.50; F, 26.40; N, 6.10. $\mathrm{C_9H_{12}F_3NSi}$ requires C, 49.3; H, 5.5; F, 26.0; N, 6.4%); $\delta_{\mathrm{H}}(\mathrm{CCl_4})$ 3.72 (2 H, s, $\mathrm{CH_2N}$), 2.48 [6 H, s, $\mathrm{N(CH_3)_2}$]; $\delta_{\mathrm{F}}(\mathrm{CD_2Cl_2}$, standard $\mathrm{CFCl_3}$, 30 °C) −142.5 (s, $\mathrm{SiF_3}$); (−42 °C) −148 [d, 2 $\mathrm{F_{eq}}$, J(F–F) 42 Hz], −128 [t, $\mathrm{F_{ax}}$ J(F–F) 40.5 Hz]; $\delta_{\mathrm{Si}}(\mathrm{CDCl_3}$, −30 °C), −102.2 [q, J(Si–F) 233 Hz, $\mathrm{SiF_3}$]; (−60 °C) −104.8 [d, $J(\mathrm{Si–F_{ax}})$ 235 Hz].

Synthesis of [8-(*Dimethylamino*)-1-*naphthyl*]*trifluorosilane* (**12**).—A suspension of yellow 8-(dimethylamino)-1-naphthyl-lithium (0.048 mol) [prepared from the 1:1 reaction of 1-(dimethylamino)naphthalene with n-butyl-lithium in ether] was added to tetraethoxysilane (10.0 g, 0.048 mol) in ether (50 cm^3). After stirring at room temperature for 20 h, the mixture was refluxed for 2 h, filtered, and the ether removed in vacuum. Distillation afforded [8-(dimethylamino)-1-naphthyl]triethoxysilane (9.6 g, 60%), b.p. 125 °C at 0.05 mmHg. The triethoxysilane (2.3 g, 0.007 mol) in hexane (15 cm^3) was mixed with boron trifluoride etherate (0.007 mol, 0.86 cm^3). The mixture was stirred for 15 min, the hexane removed, and [8-(*dimethylamino*)-1-*naphthyl*]*trifluorosilane* (**12**) (1.5 g, 84%), b.p. 105 °C at 0.08 mmHg, recovered by fractional distillation, m.p. 62 °C (from hexane) (Found: C, 56.30; H, 4.8; F, 22.15; N, 5.40%; M^+, 255. $\mathrm{C_{12}H_{12}F_3NSi}$ requires C, 56.5; H, 4.7; F, 22.3; N, 5.5%; M, 255); $\delta_{\mathrm{H}}(\mathrm{CD_2Cl_2})$ 5.85 [6 H, s, $\mathrm{N(CH_3)_2}$]; $\delta_{\mathrm{F}}(\mathrm{CD_2Cl_2}$, 80 °C) −140.7 (s); (−60 °C) −142.9 [2 $\mathrm{F_{eq}}$, d, J(F–F) 46 Hz], −130 [$\mathrm{F_{ax}}$, t, J(F–F) 46 Hz]; $\delta_{\mathrm{Si}}(\mathrm{CDCl_3}$, 60 °C) 96.0 [q, $\mathrm{SiF_3}$, J(SiF) 236 Hz]; (−60 °C) −98.9 [q, J(Si–F) 233 Hz].

Synthesis of [8-(*Dimethylamino*)-1-*naphthyl*]*phenylsilane* (**13**).—8-(Dimethylamino)-1-naphthyl-lithium (0.05 mol) in ether (50 cm^3) prepared as above was added to phenylsilane (5.4 g, 0.05 mol) in ether (50 cm^3). The mixture was stirred at room temperature for 24 h and under reflux for 1 h. It was then poured into ice–water, the ethereal layer rapidly separated, and dried over sodium sulphate. After filtration, the ether was removed in vacuum, and [8-(*dimethylamino*)-1-*naphthyl*]*phenylsilane* (**13**) (5.7 g, 41%), b.p. 155 °C at 0.1 mmHg distilled, m.p. 84 °C (from hexane) (Found: C, 77.95; H, 7.0; N, 5.2. $\mathrm{C_{18}H_{19}NSi}$ requires C, 78.0; H, 6.85; N, 5.05%); $\delta_{\mathrm{H}}(\mathrm{CCl_4})$ 2.24 [6 H, s, $\mathrm{N(CH_3)_2}$], 5.30 (2 H, s, $\mathrm{SiH_2}$), 6.95—7.70 (11 H, br, aromatic).

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Synthesis of [8-(Dimethylaminomethyl)-1-naphthyl]phenylsilane (**14**).—8-(Dimethylaminomethyl)-1-naphthyl-lithium in ether [obtained from 1-(dimethylaminomethyl)naphthalene (18.5 g, 0.1 mol) in ether (100 cm^3) and n-butyl-lithium (0.095 mol) in ether (110 cm^3)] was added to phenylsilane (12 g, 0.11 mol) in ether (100 cm^3). The mixture was stirred at room temperature for 48 h, and the solution separated from precipitated solids. The solids were washed with hexane, and the extract added to the ethereal solution. The combined extracts were rapidly washed with water, the separated organic layer dried over sodium sulphate, and the solvents removed in vacuum. *[8-(Dimethylaminomethyl)-1-naphthyl]phenylsilane* (**14**) (16.8 g, 60%), b.p. 190—192 °C at 0.1 mmHg was isolated by fractional distillation, m.p. 53 °C (from hexane) (Found: C, 77.0; H, 7.1; N, 4.8. $C_{19}H_{21}NSi$ requires C, 78.3; H, 7.2; N, 4.8%); $\delta_H(CCl_4)$ 1.95 [6 H, s, $N(CH_3)_2$], 3.95 (2 H, s, CH_2N), 4.9 (2 H, s, SiH_2), 7.1—7.9 (11 H, br, aromatic).

Synthesis of [8-(dimethylaminomethyl)-1-naphthyl]methyl(phenyl)silane (**15**).—8-(Dimethylaminomethyl)-1-naphthyl-lithium (0.055 mol) in ether (150 cm^3) (obtained as above) was added dropwise to a solution of methylphenylsilane (8.5 g, 0.07 mol) in ether (70 cm^3). The mixture was stirred for 16 h, then poured on crushed ice, the ether layer rapidly separated and dried over magnesium sulphate. After removal of the ether in vacuum, the residual oil was dissolved in a small quantity of acetone from which by the addition of pentane crystals of *[8-(dimethylaminomethyl)-1-naphthyl]methyl(phenyl)silane* (**15**) (4.8 g, 29%) were obtained, m.p. 81 °C (Found: C, 78.65; H, 7.80; N, 4.60. $C_{20}H_{23}NSi$ requires C, 78.7; H, 7.5; N, 4.6%); $\delta_H(CD_2Cl_2)$ 0.65 [3 H, d, $^3J(HSiCH_3)$ 3.5 Hz], 1.95 [6 H, s, $N(CH_3)_2$], 3.7 [1 H, d, ^2J(H-H) 12 Hz, CH_2N], 4.25 (1 H, d, ^2J(H-H) 12 Hz, CH_2N), 5.1 [1 H, q, $^3J(HSiCH_3)$ 3.5 Hz], and 7.15—7.90 (11 H, br, aromatic).

Synthesis of 2-(Dimethylaminomethyl)benzyltri(fluoro)silane (**16**).—2-(Dimethylaminomethyl)benzyl-lithium [from 2-(dimethylaminomethyl)toluene (17.9 g, 0.120 mol) and n-butyl-lithium (0.114 mol) in ether][15] was added dropwise to a solution of tetraethoxysilane (29.00 g, 0.140 mol) in ether (100 cm^3) at 0 °C. The mixture was stirred for 48 h at room temperature, filtered, and the ether removed in vacuum. The residue was extracted with pentane, filtered again, and the pentane removed. *2-(Dimethylaminomethyl)benzyltri(ethoxy)silane* (18.0 g, 50%) was recovered by distillation, b.p. 120 °C at 1 mmHg (Found: C, 61.8; H, 9.2; N, 4.65; Si, 9.0. $C_{16}H_{29}NO_3Si$ requires C, 61.7; H, 9.3; N, 4.5; Si, 9.0%); $\delta_H(CCl_4)$ 1.15 (9 H, t, OCH_2CH_3), 2.20 [6 H, s, $N(CH_3)_2$], 2.35 (2 H, s, CH_2Si), 3.40 (2 H, s, CH_2N), 3.70 (6 H, q, OCH_2CH_3), and 7.05 (4 H, br, aromatic). Boron trifluoride etherate (0.0167 mol) in ether (5 cm^3) was added slowly to a solution of the triethoxysilane (4.0 g, 0.0128 mol) in ether (5 cm^3). After stirring for 15 min, the ether was removed and the residue fractionally distilled to give *2-(dimethylaminomethyl)benzyltri(fluoro)silane* (**16**) (2.0 g, 67%), b.p. 105 °C at 18 mmHg (Found: M^+, 233. $C_{10}H_{14}F_3NSi$ requires M, 233); $\delta_H(CCl_4)$ 2.20 [6 H, s, $N(CH_3)_2$], 2.5 [2 H, q, ^3J(H-F) 3 Hz, CH_2SiF_3], 3.45 (2 H, s, CH_2N); $\delta_F(CD_2Cl_2$, standard $CFCl_3$, 30 °C) −138 (s); (−126 °C) −147 (2 F_{ax}, br, s), −113 (F_{eq}, br, s).

Results and Discussion

Molecular Geometry.—The crystal structure of compound (**6**) is shown in Figure 1 together with the atomic numbering. Figure 2 is a stereoscopic representation with the same orientation. Selected bond lengths and angles for compounds (**6**), (**13**), and (**15**) are given in Table 2.

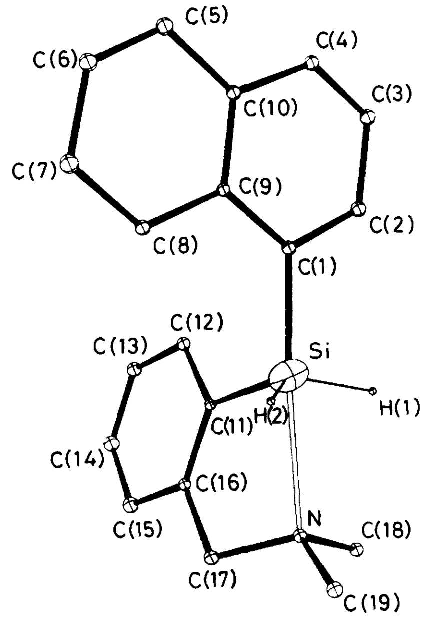


Figure 1. ORTEP drawing of the molecule of compound (**6**), showing the numbering of the atoms. The thermal ellipsoid of the silicon atom encloses 30% of the electron density. The spheres of the other atoms are at the 4% probability level and the H atoms are of arbitrary size

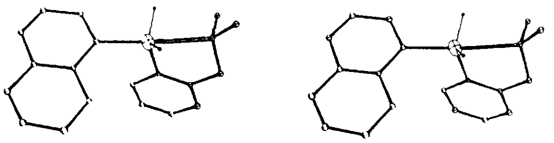


Figure 2. Stereoscopic view of the molecule of compound (**6**)

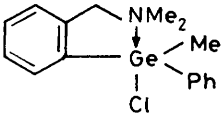
Table 2. Comparison of main structural features of compounds (**6**), (**13**), and (**15**) (R = aryl); distances in Å, angles in degrees

	(**6**)	(**13**)[11]	(**15**)[11]
Si-N	2.44(1)	2.584(3)	2.66(1)
Si-H	1.45(11); 1.47(11)	1.44(2)	Not located
Si-R_{ax}	1.92(2)	1.893(4)	1.91(1)
Si-R_{eq}	1.86(2)	1.881(4)	1.88(1)
Si-Me			1.90(2)
R_{ax}-Si-N	175.6(8)	178.7(1)	166.8(6)
R_{eq}-Si-N	76.6(6)	76.0(1)	80.8(5)
Me-Si-N			83.1(5)
R_{ax}-Si-H	101.5(50)	104.1(8)	
R_{eq}-Si-H	107.5(50)	111.9(8)	
R_{ax}-Si-R_{eq}	106.3(3)	105.2(2)	104.3(6)

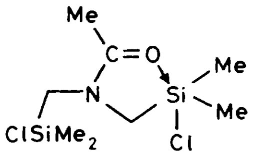
The geometry about silicon in each compound is that of a somewhat distorted trigonal bipyramid, with the chelating nitrogen atom in an axial position. The cyclic systems thus formed span equatorial and axial sites. A marked preference for this conformation is displayed by five-membered rings, where the axial–equatorial angle of 90° minimises ring strain.[16,17] Although the six-membered ring is more flexible, the axial–equatorial disposition has been observed also with similar compounds of tin.[15] The five-membered chelate rings are essentially planar, but the six-membered ring in compound (**15**) is significantly folded about the silicon–methylene group axis, with the nitrogen atom *ca.* 1.2 Å above the plane of the other five ring atoms.

The second axial site in compound (**6**) is occupied by the naphthyl group, and in compounds (**13**) and (**15**) by the phenyl group. Equatorial sites are occupied by the two hydrogen atoms [(**6**) and (**13**)] or by a hydrogen atom and methyl group [(**15**)]. Some remnant of the tetrahedral geometry is retained, in that the silicon atom is in each case displaced from the equatorial plane, towards the axial aryl group and away from the co-ordinated nitrogen atom, as is shown for example by the angles R_{ax}–Si–R_{eq}, R_{ax}–Si–H(1), and R_{ax}–Si–H(2) [(**6**), (R = aryl) Table 2; mean value 103(4)°]. The angle N–Si–R_{eq} is consequently substantially less than 90°.

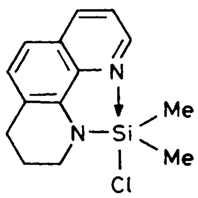
Previous *X*-ray crystallographic data for compounds (**4**)[6] and (**5**),[7] and the related compounds (**17**),[18] (**18**),[19] and (**19**)[20] for example, in which five-co-ordination is observed as a consequence of intramolecular co-ordination by a suitably positioned oxygen- or nitrogen-donor ligand, have also shown a preference for the trigonal-bipyramidal configuration.



(**17**)



(**18**)



(**19**)

In all cases the axial positions are occupied by the donor atom and a halogen atom, which are thus *trans* to each other. The donor–metal and metal–halogen distances for these compounds are shown in Table 3, together with the sum of the van der Waals radii[21] and typical metal–halogen distances respectively. The donor–acceptor distances are significantly longer than the normal single-bonded distances for each pair of elements, but short enough to indicate a substantial bonding interaction. For compound (**19**) the covalently bound nitrogen in the more saturated ring is situated at 1.77 Å from the silicon atom, whereas the donor nitrogen atom is at 2.03 Å. which may be compared with the sum of the van der Waals radii of 3.6 Å. Metal–halogen distances for the axial substituents especially are greater than those measured in four covalent species of otherwise similar composition. A direct comparison can be made in compound (**18**) where the Si–Cl distance for the four-co-ordinate silicon atom is 2.05 Å, and for the five-co-ordinate silicon atom, 2.35 Å.*

It thus appears to be a general rule that co-ordination to a metal atom in these systems occurs uniquely at a face of the original tetrahedral molecule, and preferentially *trans* to the most polarisable bond. In support of this conclusion, it may be noted that Britton and Dunitz,[22] in a survey of some 250 structures of tetravalent tin compounds in the solid state, where intermolecular interactions and incipient five-co-ordination are common, showed that overwhelmingly the geometry of these interactions tended towards trigonal-bipyramidal co-ordination at the tin atom. In a similar survey of a smaller number of organosilicon compounds Klebe[23] showed that the preferred geometry of such interactions was identical to that found for the tin compounds.

Table 3. Comparison of interatomic distances (Å)

Compound	E ⟶ M[a]	van der Waals sum	M–X[b]	MX_4[c]
(**4**)	2.01	3.5	1.60	1.54
(**5**)	2.51	3.85	2.63	2.44
(**17**)	2.48	3.7	2.33	2.08
(**18**)	1.92	3.6	2.35	2.01
(**19**)	2.03	3.6	2.27	2.01

[a] E ⟶ M = experimental distance between electron-donor ligand and central atom (Si, Ge, or Sn). [b] Experimental bond length between M and axial X atom (X = F, Cl, or Br). [c] MX_4 = metal–halogen bond length in comparable homoleptic tetrahedral molecule. Data from E. A. V. Ebsworth, in 'Volatile Silicon Compounds,' Pergamon Press, Oxford, 1963, p. 54.

In view of our aim of relating the information derived from structural studies of five-co-ordinated silicon to the elucidation of the mechanisms of nucleophilic substitution reactions in solution, it is necessary to establish that these structures, which can be determined with a high degree of precision in the solid state, are also those most commonly present in solution. For this purpose n.m.r. spectroscopy has provided much information, encompassing many more compounds than the few which provide structures suitable for *X*-ray analysis.

Confirmation that co-ordination of a potential chelating ligand to a silicon atom has occurred in solution is most directly provided by ^{29}Si n.m.r. spectroscopy. An increase in co-ordination number from four to five is normally accompanied by a substantial upfield shift in the position of the ^{29}Si resonance,[24] and we have observed this behaviour in a wide range of compounds. Table 4 lists the chemical shifts of a representative selection of the compounds we have studied, containing potential chelating ligands, compared with the shifts of similar compounds lacking the donor group. Compound (**11**) for example absorbs at δ −102.27 at 30 °C, whereas trifluoro(phenyl)silane absorbs at −72.86; compound (**4**) was observed by Voronkov and co-workers[6] to absorb at δ −94.8 compared with the absorption of (chloromethyl)trifluorosilane at δ −23.5. Only in cases where the three substituents on the silicon atom other than the chelating ligand are comprised solely of alkyl and alkoxy groups does co-ordination apparently fail to take place.

However, although evidence for co-ordination can be obtained from these measurements, no information on the geometry of the resulting five-co-ordinate species can be deduced. Such information may however be derived in many instances from the n.m.r. absorptions of appropriate substituent groups on the silicon atom, notably from the ^{19}F absorptions of Si–F groups, and from ^{1}H absorptions of the groups adjacent to the co-ordinating nitrogen atom [$-CH_3$, $-CH_2-$, $-CH(CH_3)-$].

Extensive studies by Voronkov and co-workers[25] of compounds such as (**4**), have shown that the ^{19}F n.m.r. spectra are entirely consistent with the *X*-ray structures. At ambient temperatures a single resonance is observed, δ −136.56 p.p.m., which however displays satellites due to ^{19}F–^{29}Si spin–spin

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* This disparity is considerably greater than that usually observed for identical substituents in equatorial and axial positions respectively in molecular species such as PCl_5 (2.02 and 2.14 Å). So great an elongation on co-ordination as that found above is not however always displayed (R. Holmes, 'Pentaco-ordinated Phosphorus,' American Chemical Society, Washington D.C., 1980, vols. 1 and 2, and refs. therein).

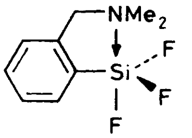
Table 4. ^{29}Si n.m.r. chemical shifts of five-co-ordinate silanes *versus* corresponding four-co-ordinate silanes (δ p.p.m., $CDCl_3$, 30 °C)

Compound[a]	δ(^{29}Si)	Compound	δ(^{29}Si)	Δδ
(**11**) SiF_3L^1	−102.27	SiF_3Ph	−72.86	−29.41
(**9**) $SiMeF_2L^1$	−36.13	$SiMeF_2Ph$	− 8.58	−44.61
(**16**) SiF_3L^5	−100.48	$SiF_3(CH_2Ph)$	−64.07	−36.41[b]
(**13**) SiH_2PhL^3	−44.10	$SiH_2Ph(C_{10}H_7)$	−35.63	−8.47
(**14**) SiH_2PhL^4	−55.52	$SiH_2Ph(C_{10}H_7)$	−35.63	−19.89
(**15**) $SiHMePhL^4$	−25.84	$SiHMePh(C_{10}H_7)$	−19.81	−6.03
(**6**) $SiH_2(C_{10}H_7)L^1$	−47.25	$SiH_2(C_{10}H_7)Ph$	−35.63	−11.62
(**7**) $SiH_2(C_{10}H_7)L^2$	−52.80	$SiH_2(C_{10}H_7)Ph$	−35.63	−17.17
(**10**) $Si(OEt)_3L^1$	−57.17	$Si(OEt)_3Ph$	−57.76	+0.59
(**8**) $SiMe(OEt)_2L^1$	−18.19	$SiMe(OEt)_2Ph$	−17.94	−0.25
$SiMe_3L^1$	−4.89	$SiMe_3Ph$	−4.11	−0.78
(**4**) $SiF_3(CH_2OCOPh)$	−94.8[c]	$SiF_3(CH_2Cl)$	−71.3	−23.5
$Si(OMe)_2PhL^3$	−38.16	$Si(OMe)_2Ph(C_{10}H_7)$	−27.6	−10.56

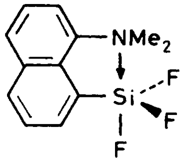
[a] L^1 = 2-(Dimethylaminomethyl)phenyl; L^2 = 2-[1-(dimethylamino)ethyl]phenyl; L^3 = (8-dimethylamino)-1-naphthyl; L^4 = (8-dimethylaminomethyl)-1-naphthyl; L^5 = 2-(dimethylaminomethyl)benzyl; $C_{10}H_7$ = 1-naphthyl. [b] Temperature = −30 °C. [c] See ref. 6.

coupling, showing that the fluorine atoms are not undergoing intermolecular exchange at a rapid rate compared with the n.m.r. time-scale. Lowering the temperature to −100 °C results in the ^{19}F resonance of (**4**) splitting into two separate signals, a triplet (δ −127.43 p.p.m.; relative intensity 1), and a doublet (δ −140.69 p.p.m.; relative intensity 2). The spectrum thus indicates the presence of one axial (downfield signal) and two equatorial (upfield signal) fluorine atoms with trigonal-bipyramidal geometry about the silicon atom.

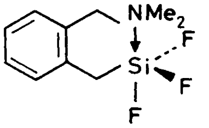
Precisely analogous ^{19}F spectra have been observed for compounds (**11**), (**12**), and (**16**), which give at 30 °C [(**11**) and (**16**)] and 80 °C [(**12**)] the single sharp lines of averaged resonances at δ −142.5, −138, and −140.7 p.p.m. respectively. For each compound, on lowering the temperature, the characteristic pattern of a low-field triplet (relative intensity 1) and high-field doublet (relative intensity 2), indicative of the presence of an axial and two equatorial fluorine atoms respectively, appears. We therefore conclude that these compounds have in solution the configurations shown, analogous to that established by *X*-ray analysis for compound (**4**).[6] The axial co-ordination of the nitrogen donor atom, and the axial–equatorial attachment of the resulting chelate ring is thus confirmed, whether a five- or a six-membered ring is formed.



(**11**)

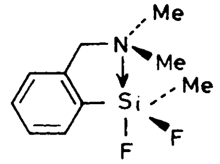


(**12**)



(**16**)

The methyldifluorosilane (**9**) also has a low-temperature ^{19}F n.m.r. spectrum in which axial (δ −111 p.p.m.) and equatorial (δ −154.6 p.p.m.) fluorine atoms can be discerned. In this case no ^2J(F–F) coupling is observed, but this is not unusual as axial–equatorial coupling constants are often very small.[26] The co-ordinated form of this molecule therefore has in solution the same configuration as compound (**11**). *X*-Ray analysis[27] has recently confirmed that this geometry is also adopted by the molecule in the solid state. In this form the methyl groups bonded to the co-ordinated nitrogen atom are rendered diastereotopic, and the ^1H n.m.r. spectrum can also be interpreted to provide further confirmation that co-ordination has occurred, with the geometry indicated. At the temperatures at which the fluorine resonances are split, two singlets of equal intensity are seen in the ^1H n.m.r. spectrum at δ 2.24 and δ 2.45 p.p.m.

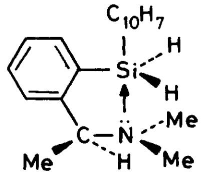


(**9**)

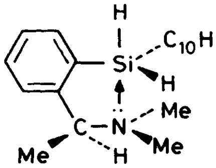
The observation of diastereotopic NMe_2 groups in the ^1H n.m.r. spectrum enabled us to demonstrate[28] the occurrence of internal co-ordination in a series of chiral or prochiral derivatives containing the (dimethylaminomethyl)phenyl ligand. In these early experiments, only one signal from the $-NMe_2$ group persisted at all temperatures not only when the hydrocarbyl or alkoxy groups were the sole remaining substituents on the silicon atom, but also when hydrogen was present too, for example in compounds (**6**) and $SiH_2Me(C_6H_4CH_2NMe_2$-*o*). As co-ordination was not expected to be favoured in the absence of electronegative substituents on the silicon atom, the apparent lack of co-ordination in these hydrogenosilanes was not surprising. However subsequent determination of the ^{29}Si chemical shifts[29] of these compounds clearly showed that extension of co-ordination at the silicon atom was taking place, and these observations led us to synthesize compound (**13**) in which co-ordination is imposed by the molecular structure, and to determine the crystal structure. ^{29}Si N.m.r. cannot furnish information on the geometry of the co-ordinated species, but having established the existence of co-ordination in this way, ^1H n.m.r. spectra may then be interpreted to give information on the most probable structure.

Compound (**13**) shows little change in its ^1H n.m.r. spectrum with temperature; at 30 °C δ(NMe_2) = 2.24 p.p.m.; and at

-100 °C, 2.10 p.p.m. consistent therefore with the structure found in the solid state, where the molecule has a plane of symmetry perpendicular to the $-NMe_2$ group. Similarly the single ^1H absorption from the $-NMe_2$ group observed at all temperatures for compound (**6**) is consistent with the chelated structure (Figure 1). In view of the small number of examples of hypervalent silicon hydrides, a wider investigation of the possibility of the extension of co-ordination in these species was desirable, and we therefore sought models in which additional proof of the geometry of co-ordination could be obtained, particularly where the compounds in question were not crystalline, and structures could not be determined by diffraction methods. Compound (**7**) is one such complex in which the benzylic carbon atom is itself chiral. In this system co-ordination of the nitrogen atom to the silicon renders the $-NMe_2$ moiety diastereotopic, whatever the configuration of the remaining substituents about the silicon atom. In the n.m.r. spectrum the absorptions of the two methyl groups appear as separate singlets at -75 °C, δ 2.0 and 2.4 p.p.m. respectively. At low temperature the Si–H absorptions appear as two doublets: δ 5.02 and 5.12 p.p.m. [^2J(H–H) 3 Hz]. A single diastereoisomer is thus formed with the same configuration of the groups about the silicon atom as found for compound (**6**). Had co-ordination occurred with an analogous disposition of the groups about silicon as was previously described for the difluorosilane (**9**),[27] then two diastereoisomers would have been detected for compound (**7**).



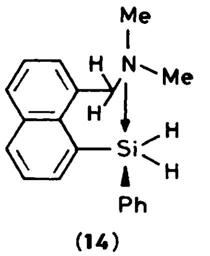
(**7**) (observed structure)



(**7**) (not formed)

An examination of the ^1H n.m.r. behaviour of compounds (**14**) and (**15**) also provides detailed information on the geometry of ring closure of the six-membered chelates. For both compounds the $-NMe_2$ group absorptions, which appear as a sharp singlet at room temperature, split into two as the temperature is lowered, indicating that co-ordination of the nitrogen atom occurs in such a way that the methyl groups become diastereotopic.

For compound (**15**) in which the four-co-ordinate silicon atom is in any case chiral, the benzylic protons are diastereotopic at room temperature [δ 3.70 and 4.25 p.p.m. respectively; ^2J(H–H) 12 Hz]. This persists down to the temperature at which the $-NMe_2$ group absorption splits (-95 °C; δ 2.2 and 1.75 p.p.m. respectively). By contrast, the benzylic protons of compound (**14**) are indistinguishable in the room-temperature ^1H n.m.r. spectrum by reason of the lack of chirality of the four-co-ordinate silicon atom in the compound.



(**14**)

Chirality of the molecule as a whole apparently develops on co-ordination of the nitrogen atom to the silicon atom with the formation of the six-membered ring, for as the $-NMe_2$ absorptions split at -73 °C (δ 2.20 and 1.70 p.p.m.), so do those of the benzylic protons (δ 4.62 and 3.45 p.p.m., J 16 Hz) and the SiH_2 group (δ 4.86 and 4.76 p.p.m.). The behaviour of these two compounds in solution is thus compatible with the chelated structure for (**15**) found in the crystal, and an analogous structure for (**14**), in which the chirality of the molecule is a consequence of the non-planar conformation of the six-membered chelate ring.

The geometry about the silicon atom in these two compounds in solution thus appears to be essentially trigonal bipyramidal, with axial entry of the nitrogen atom, and equatorial hydrogen atoms. The axial entry of the nitrogen in the formation of the six-membered chelate ring was also noted for compound (**16**).

Conclusions

From these studies we may conclude that intramolecular co-ordination by a donor nitrogen atom may occur with relative facility for the majority of functional silicon compounds. Only in cases where the sole substituents on the silicon are drawn from alkoxy and hydrocarbon groups does molecular co-ordination apparently fail to take place under any conditions. Axial entry of the donor atom with approximately trigonal-bipyramidal geometry about the five-co-ordinate silicon atom appears to be general, whether a five- or a six-membered chelate ring is formed, and irrespective of the presence or not of electronegative substituents on the silicon.

Acknowledgements

F. C. thanks Professor E. R. Corey, University of Missouri, St. Louis, for helpful hints concerning the determination of the space group of crystal (**6**).

References

1 J. L. Gay-Lussac and L. J. Thénard, *Mémoires de Physique et de Chimie de la Société d'Arceuil*, 1809, **2**, 317; J. Davy, *Philos. Trans.*, 1812, **2**, 352; *Liebigs Ann. Chem.*, 1813, **86**, 178.
2 R. R. Holmes, in 'Progress in Inorganic Chemistry,' ed. S. J. Lippard, Wiley-Interscience, New York, 1984, vol. 34, p. 119.
3 S. N. Tandura, M. G. Voronkov, and N. V. Alekseev, *Top. Curr. Chem.*, 1986, **131**, 99.
4 W. H. Stevenson III, S. Wilson, J. C. Martin, and W. B. Farnham, *J. Am. Chem. Soc.*, 1985, **107**, 6340.
5 R. J. P. Corriu and C. Guérin, *Adv. Organomet. Chem.*, 1982, **20**, 265; R. J. P. Corriu, C. Guérin, and J. J. E. Moreau, *Top. Stereochem.*, 1984, **15**, 43.
6 M. G. Voronkov, Yu. L. Frolov, Y. M. Dyakov, N. N. Chipanina, L. I. Gubanova, G. A. Gavrilova, I. V. Klyba, and T. N. Aklamentova, *J. Organomet. Chem.*, 1980, **201**, 165; E. A. Zel'bst, V. E. Shklover, Yu. T. Struchkov, Yu. L. Frolou, A. A. Kashaev, L. I. Gubanoua, V. M. Dyakov, and M. G. Voronkov, *Zh. Strukt. Khim.*, 1981, **22**, 82.
7 G. van Koten, J. G. Noltes, and A. L. Spek, *J. Organomet. Chem.*, 1976, **118**, 183.
8 M. L. Moore, 'Organic Reactions,' ed. R. Adams, Wiley, New York, 1949, vol. 5, p. 301.
9 A. I. Vogel, in 'Practical Organic Chemistry,' 3rd edn., Longmans, London, 1956, p. 573.
10 G. M. Robinson and R. Robinson, *J. Chem. Soc.*, 1923, **123**, 532.
11 C. Brelière, F. Carré, R. J. P. Corriu, M. Poirier, and G. Royo, *Organometallics*, 1986, **5**, 388.
12 F. N. Jones, M. F. Zinn, and C. R. Hauser, *J. Org. Chem.*, 1963, **28**, 663; G. van Koten, A. J. Lewink, and J. G. Noltes, *J. Organomet. Chem.*, 1975, **84**, 117.
13 G. van Koten, J. T. B. M. Jastrzebski, J. G. Noltes, W. M. G. F. Pontenagel, J. Kroon, and A. L. Spek, *J. Am. Chem. Soc.*, 1978, **100**, 5021.

14 J. T. B. M. Jastrzebski, C. T. Knapp, and G. van Koten, *J. Organomet. Chem.*, 1983, **255**, 287.

15 G. van Koten, J. T. B. M. Jastrzebski, J. G. Noltes, G. S. Verhoekx, A. L. Spek, and J. Kroon, *J. Chem. Soc., Dalton Trans.*, 1980, 1352.

16 K. Mislow, *Acc. Chem. Res.*, 1970, **3**, 321.

17 S. Trippett, *Pure Appl. Chem.*, 1974, **40**, 495.

18 C. Brelière, F. Carré, R. J. P. Corriu, A. de Saxcé, M. Poirier, and G. Royo, *J. Organomet. Chem.*, 1981, **205**, C1.

19 K. D. Onan, A. T. McPhail, C. Yoder, and R. W. Hillyard, *J. Chem. Soc., Chem. Commun.*, 1978, 209.

20 G. Klebe, J. W. Bats, and K. Hensen, *J. Chem. Soc., Dalton Trans.*, 1985, 1.

21 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

22 D. Britton and J. D. Dunitz, *J. Am. Chem. Soc.*, 1981, **103**, 2971.

23 G. Klebe, *J. Organomet. Chem.*, 1985, **293**, 147.

24 J. A. Cella, J. D. Cargioli, and E. A. Williams, *J. Organomet. Chem.*, 1980, **186**, 13; R. K. Harris, J. Jones, and Soon Ng, *J. Magn. Reson.*, 1978, **30**, 521; H. Marsmann, 'NMR Basic Principles and Progress,' Springer-Verlag, Berlin, 1981, vol. 17, p. 229.

25 A. J. Albanov, L. I. Gubanova, M. F. Larin, V. A. Pestunovich, and M. G. Voronkov, *J. Organomet. Chem.*, 1983, **244**, 5.

26 R. Damrauer and S. E. Danahey, *Organometallics*, 1986, **5**, 1490.

27 G. Klebe, *J. Organomet. Chem.*, 1987, **332**, 35.

28 R. J. P. Corriu, G. Royo, and A. de Saxcé, *J. Chem. Soc., Chem. Commun.*, 1980, 892.

29 B. J. Helmer, R. West, R. J. P. Corriu, M. Poirier, G. Royo, and A. de Saxcé, *J. Organomet. Chem.*, 1983, **251**, 295.

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