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Pentacoordinate silicon compounds: stereochemical non-rigidity of chelates formed by intramolecular ring-closure. Crystal structure of 8-dimethylamino-1-trifluorosilylnaphthalene *

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Abstract

The application of dynamic NMR spectroscopy to the study of stereochemical non-rigidity in pentacoordinate chelated organosilicon compounds is described. It is shown that in the compounds $Me_2NCH(Me)C_6H_4SiXYZ$, non-dissociative ligand permutation at silicon can be distinguished unambiguously from processes associated with rupture of the chelate ring and nitrogen inversion. The crystal and molecular structure of 8-$Me_2NC_{10}H_6SiF_3$ has been determined. Pentacoordination of the silicon atom is confirmed, with the donor nitrogen atom and a fluorine atom occupying axial sites in an overall trigonal bipyramidal geometry. The N → Si separation is 2.3 Å (average of two distinct but closely related molecular conformations), which is less than the C^1–C^8 distance in the naphthalene nucleus, indicating a substantial bonding interaction. NMR studies of the dynamic behaviour of the Me_2N group, and where possible (^{19}F, ^1H) of the monodentate ligands in 8-dimethylamino-1-silylnaphthalene compounds, together with the results for the chelated benzylaminosilicon compounds, confirm that inversion of the absolute configuration at the silicon atom is not achieved by this process. The free energies of activation for non-dissociative ligand permutation at a silicon range from less than 7 kcal mol^{-1} [SiH_3, $Si(OR)_3$], which is below the limit of direct measurement, to 13 kcal mol^{-1} for $Me_2NCH(Me)C_6H_4SiF_3$; difunctional silicon chelate compounds (Cl, F, OR) display values from 9–12 kcal mol^{-1}. These are comparable with those determined for fluxional processes in acyclic pentacoordinate silicon compounds.

Key words: Silicon; Pentacoordinate silicon; Intramolecular coordination; Dynamic NMR; Pseudo-rotation; Crystal structure

1. Introduction

The stereochemical non-rigidity of pentacoordinate molecules and ions is now recognized to be a widespread phenomenon. The pioneering studies by Muetterties *et al.* [4] on fluorophosphoranes, based on the difference in chemical shift between fluorine atoms in axial and in equatorial sites, which may be observed in ^{19}F NMR spectra at low temperatures, were soon followed by similar observations of pentacoordinate fluorosilicate ions [5]. Although the silicon systems were found to be more prone to impurity-catalysed intermolecular exchange of fluoride ion, subsequently fully investigated by Janzen and Marat [6], the similarity in dynamic stereochemistry of analogous silicon and phosphorus compounds has since been amply confirmed. Damrauer and coworkers [7], Holmes and coworkers [8] and very recently Tamao *et al.* [9] have

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* See references 1–3.

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obtained dynamic ^{19}F NMR spectra over a wide temperature range from five-coordinate organofluorosilicates as salts with K(18-crown-6). Under these conditions ^{19}F–^{29}Si coupling is maintained over the whole range of temperature, showing that the interfering intermolecular processes are completely suppressed.

Other silicon systems which have been comprehensively studied from this point of view [10] include bicyclic pentacoordinate anions **A**. Inversion of the configuration of these ions is strongly dependent on the nature of Y, being favoured by electronegative substituents. It is thus most probably a regular process, although inversion by Si–O bond fission, followed by closure of the ring again cannot be unambiguously excluded. The free energies of activation for the fluxional processes of acyclic fluorosilicates [7–9] range from below 6–14 kcal mol^{-1}, and of the bicyclic anions from 16.8–28.6 kcal mol^{-1}. These values, and the studies of Holmes *et al.* [11] on the change of bis-(arenediolato)silicates **B** from trigonal bipyramidal to square pyramidal, strongly support the notion that stereochemical non-rigidity of pentacoordinate silicon compounds is actually subject to less restraint than that of their phosphorus analogues [12].

We have made extensive studies [2,13] of silyl derivatives of L^1, L^2 and L^3 (Fig. 1), in which intramolecular coordination by the dimethylamino group generally results in chelated pentacoordinate species which are models for the intermediates involved in nucleophilic displacement at silicon. The remaining monodentate ligands attached to silicon can be varied almost without restriction, and the opportunity is thus presented to study a wide range of compounds with respect to their stability and dynamic NMR behaviour. The ligands L^1, L^2 and L^3 were originally introduced by Van Koten and coworkers [14] in investigations of the stereochemistry and fluxionality of tin and other metal complexes [14,15].

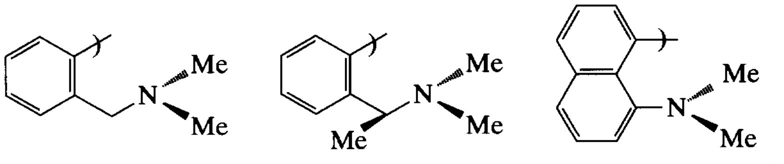
In previous papers [2,13] we have presented crystallographic and NMR evidence that in the silicon chelates the geometry about the pentacoordinate silicon atom is close to trigonal bipyramidal; that the donor nitrogen atom occupies an axial site, the chelate ring so formed spanning axial and equatorial sites; and that the atom or group which preferentially occupies the axial site opposite to the coordinated nitrogen atom is given by an apicophilicity series

Cl, OCOR > F ~ SR > OR, NR$_2$ > aryl > alkyl > H.

This series was established from observations on a number of bifunctional compounds in which fluorine was one of the ligands competing for the available apical site, and completed by structural data on hydrogenosilanes. The apicophilicity is thus determined by the ability of the bond *trans* to the donor atom to be stretched on electron donation to the silicon atom. The significance of the polarisability of this bond is illustrated [16] by the 15% increase in the Si–Cl distance for the pentacoordinate silicon atom in compound **C**, compared with the Si–Cl bond length for the corresponding tetracoordinate silicon compound. It has also been established that the stability of the chelate with respect to decoordination and inversion of the nitrogen atom is a function of the nature of the atom occupying the opposite apical site, and mostly parallels the apicophilicity series. There is however a notable exception to this generalisation, in that hydrogen, while showing a marked preference for equatorial sites, significantly enhances the acceptor properties of the silicon atom.

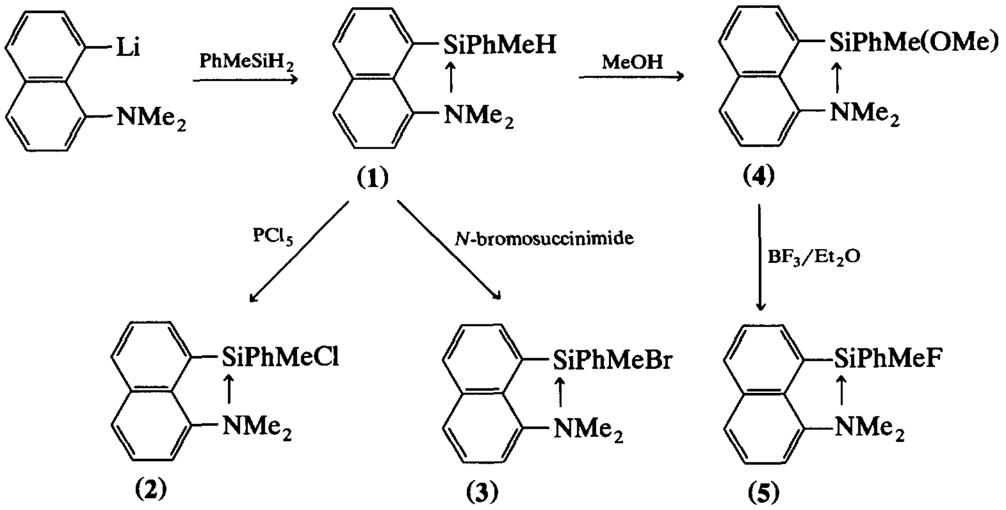
By dynamic ^{1}H NMR spectroscopy, the free energy of activation for inversion of the nitrogen atom, which may be taken as a measure of the stability of the chelate compound, has been evaluated for the derivatives of L^2 and for suitable derivatives of L^1. The values have been found to lie in the range 7–16 kcal mol^{-1}, and therefore overlap with the range of energies characterising fluxional processes at silicon.

Preliminary accounts of some cases for which fluxional exchange of ligands occurs more rapidly than inversion at the coordinated nitrogen atom, therefore being a property of the pentacoordinate complex, have already been given [2a–2c]. Further light on ligand permutation in five-coordinate chelates of silicon is provided by studies of derivatives of L^3. In such complexes, the rigidity of the naphthalene skeleton imposes a close approach of the potential donor nitrogen and acceptor silicon atoms.



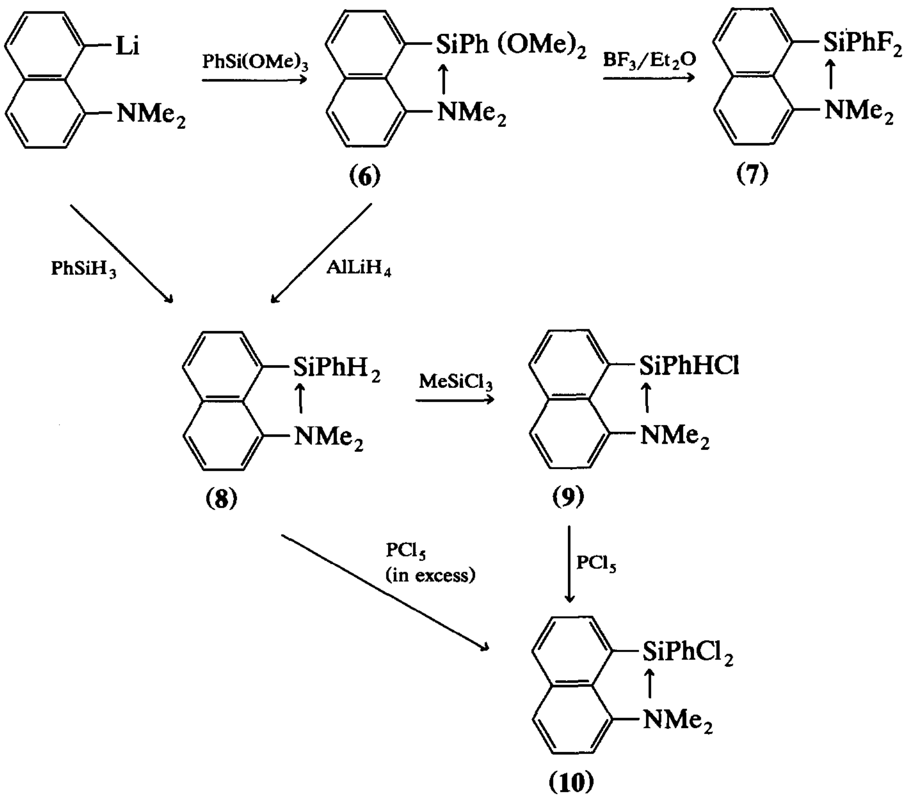
Ligand L^1 Ligand L^2 Ligand L^3

Fig. 1.

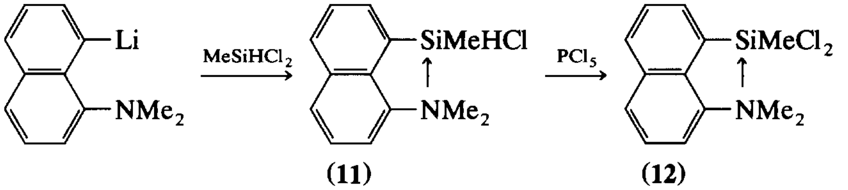


Scheme 1.

The significance of this interaction has already been demonstrated by X-ray crystallographic studies of (8-dimethylaminonaphthyl)phenylsilane, L^{3}SiPhH$_2$ [13e], and we report here an X-ray structure determination of (8-dimethylaminonaphthyl)trifluorosilane, L^{3}SiF$_3$. In this series of compounds, inversion at the nitrogen



Scheme 2.



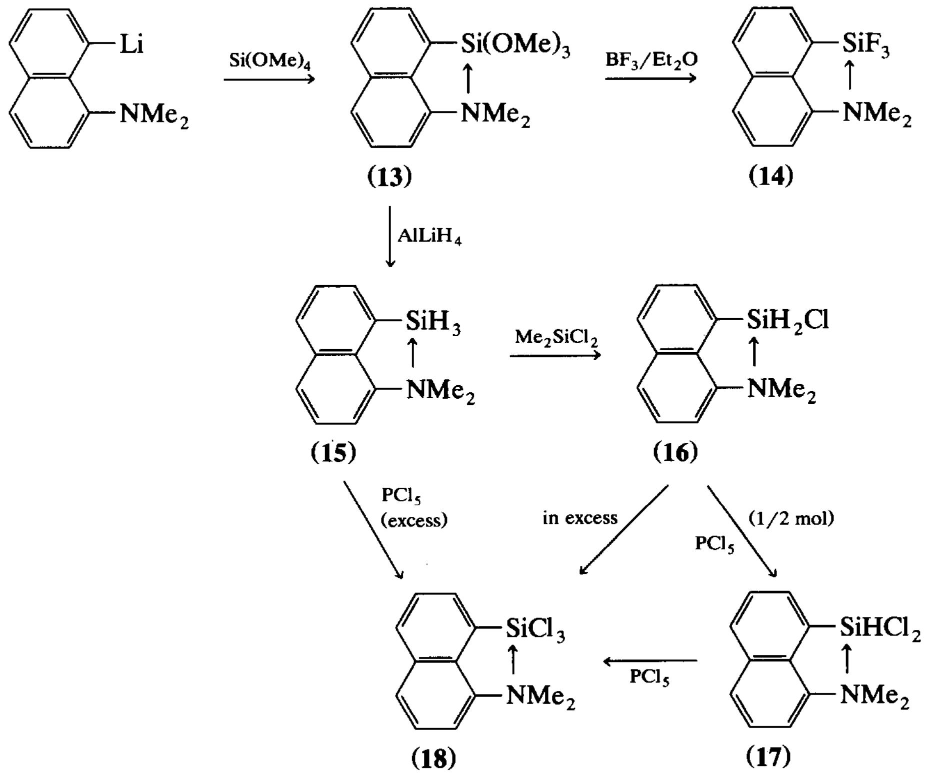
Scheme 3.

atom is strongly inhibited, providing a further opportunity for the study of dynamic processes at pentacoordinate silicon.

2. Experimental details

Organosilicon compounds were prepared by reaction with the lithium aminoaryl compound appropriate to each series [14,17]. Subsequent conversion of the functional groups on silicon to produce additional members of the series was carried out as shown in Schemes 1–4. All reactions were carried out under dry dinitrogen using vacuum line and Schlenk tube techniques. Yields and characterisation of compounds not hitherto reported are given below. Elemental analyses were performed by the Service de Microanalyse du CNRS. Mass spectra were obtained with a JEOL JMS D-100 instrument. ^1H NMR spectra given in Table 1 were recorded on a VARIAN HA 100 spectrometer at 100 MHz, or on a BRUKER 200 SY machine. ^{19}F NMR spectra were determined at 84,67 MHz on a VARIAN EM 390 spectrometer using $CFCl_3$ as the internal reference. ^{29}Si NMR spectra were obtained with a BRUKER 200 SY spectrometer using deuteriated solvents as locks; chemical shifts, reported in ppm, are referenced to TMS.

In order to determine whether diastereotopy was displayed by the NMe_2 group, and if so, to measure coalescence temperatures, it was necessary to cover a range of −100°C to +200°C in the ^1H NMR studies. Variable temperature studies were generally performed with dichloromethane-d_2 solutions when coalescence occurred at low temperatures, or with toluene solutions for coalescence in the range −100°C to



Scheme 4.

+100°C. When coalescence occurred above 100°C, *ortho*-dichlorobenzene solutions were required. Temperature calibration was carried out before and after each run.

Coalescence of the separate ^1H resonances resulting from diastereotopic NMe_2 groups could be determined visually with a precision of ±2°C. The coalescence of the distinct signals from fluorine atoms occupying axial and equatorial sites respectively was subject to an uncertainty of ±8°C, because of the very broad flat peak observed over a large temperature range before appearance of the expected singlet.

Free energies of activation for the processes resulting in coalescence of NMR signals were calculated from the Eyring equation [18].

2.1. *Preparation of silanes*

These were obtained by reaction of the lithium aminoaryl compound with the appropriate silane, or by reduction of the corresponding alkoxysilane with $LiAlH_4$ as described in ref. [13f].

2.1.1. $(8Me_2NC_{10}H_6)PhMeSiH$ *(1)*

From L^3Li (0.08 mol) and $PhMeSiH_2$ (0.08 mol, 10 g), colourless oil (16 g, 70%), bp 150°C 0.08 mm Hg. ^{29}Si NMR (toluene) δ: −23.3. IR (CCl_4): 2060 cm^{-1} (SiH, w); 2130 cm^{-1} (br). Anal. Found: C, 78.65; H, 7.82; N, 4.65. $C_{19}H_{21}NSi$ calc.: C, 78.35; H, 7.21; N, 4.81%.

2.1.2. $(8Me_2NC_{10}H_6)PhSiH_2$ *(8)*

From L^3Li (0.05 mol) and $PhSiH_3$ (0.05 mol, 5.4 g). See ref. [13f].

2.1.3. $(8Me_2NC_{10}H_6)SiH_3$ *(15)*

From $L^3Si(OMe)_3$ (0.05 mol, 14.5 g) and $AlLiH_4$ (0.05 mol, 1.9 g). See ref. [19].

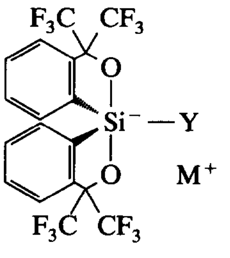
TABLE 1. ^1H NMR data for (8-dimethylamino naphthyl)silanes [a]

Compound	Temp. (°C)	NMe_2	Others
1	+20 [b]	2.08 and 2.34	0.54 (d, SiMe, J_{HH} = 4), 5.36 (q, SiH, J_{HH} = 4), 6.94–7.82 (m, 11H)
	+160 [c]	2.30 (broad)	
2	+20	1.54 and 2.42	0.94 (s, SiMe); 7.0–7.88 (10H); 8.63 (d, 1H ar, J_{HH} = 6)
	+155 [c]	1.96	
3	+20	1.38 and 2.34	0.4 (s, SiMe); 6.80–7.64 (10H); 8.18 (d, 1H ar, J_{HH} = 7)
	+110 [c]	2 broad singlets, similar position	
4	+20 [b]	1.46 and 2.15	0.60 (s, SiMe); 3.18 (s, Si OMe); 6.84–7.76 (10H); 8.56 (d, 1H, J_{HH} = 6)
	+180 [c]	2.06 (broad)	
5	+30	1.46 and 2.13 (2s)	0.68 (d, SiMe); 6.82–7.76 (10H); 8.54 (d, 1H ar, J_{HH} = 7)
	+200 [c]	2.04 (broad)	
6	+20	2.02	3.46 (s, Si OMe); 7.15–7.98 (10H); 8.46 (d, 1H ar, J_{HH} = 6)
	+100	1.52 and 2.42	3.38 and 3.50 (2s, $Si(OMe)_2$)
7	+20	2.22	7.2–8.10 (10H); 8.32 (d, 1H ar, J_{HH} = 7)
	−55	1.85 and 2.58	
8	+20	2.24	5.30 (s, SiH_2); 6.95–7.70 (m, 11H))
9	+20 [b]	1.90 and 2.42	5.92 (s, SiH); 6.96–7.94 (10H); 8.60 (d, 1H ar, J_{HH} = 7)
10	+20	2.10	7.16–8.06 (10H); 8.70 (d, 1H, J_{HH} = 7)
	−90	1.64 and 2.66	
11	+20	2.76 and 2.43	0.50 (d, SiMe, J_{HH} = 3); 5.36 (q, Si H, J_{HH} = 3); 7.10–7.90 (5H); 8.30 (d, 1H ar, J_{HH} = 6)
12	+20	2.72	1.20 (s, SiMe); 7.44–8.06 (6H)
	−85	2.52 and 2.96	
13	+20	2.56	3.54 (s, OMe, 9H); 7.32–7.10 (m, 5H); 8.15 (d, 1H ar, J_{HH} = 5)
14	+20	2.80	7.43–8.23 (m, 6H)
15	+30	2.58	4.44 (s, SiH_3), 7.24–7.96 (6H)
16	+30	2.72	5.40 (s, SiH_2); 7.42–8.04 (5H); 8.40 (d, 1H ar, J_{HH} = 7)
	−110	broad, similar position	
17	+30	2.66	5.83 (s, SiH); 7.13–7.73 (5H); 8.26 (d, 1H ar, J_{HH} = 7)
	−82 [b]	1.50 and 2.16	
18	+30 [b]	2.73	7.20–7.96 (5H), 8.45 (d, 1H ar, J_{HH} = 7)

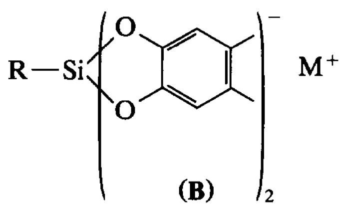
[a] δ in ppm relative to TMS: J in Hz: solvent; CD_2Cl_2 or CCl_4: all the NMe_2 signals are singlets. The resonance of the naphthyl proton *ortho* to silicon is low-field shifted when the silicon bears an electronegative substituent.

[b] Solvent: toluene-d_8.

[c] Solvent: *ortho*-dichlorobenzene.



(A)



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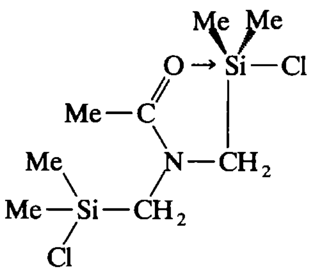


(C)

2.2. *Preparation of alkoxysilanes*

2.2.1. *$(8Me_2NC_{10}H_6)PhMeSi(OMe)$ (**4**)*

This was obtained from **1** (9.8 mmol, 2.85 g), by stirring in methanol (in an excess, 16 mmol, 0.5 ml) freshly distilled from sodium. The heterogeneous mixture became homogeneous after stirring for 15 h; the methanol was evaporated off, and **4** recovered by distillation *in vacuo* (2.06 g, 65%). Colourless oil, bp 137°C, 0.02 mmHg. ^{29}Si NMR (toluene) δ -11.84 (s). Anal. Found: C, 74.85; H, 6.95; N, 4.52. $C_{20}H_{23}NOSi$ calc.: C, 74.76; H, 7.16; N, 4.36%.

Other alkoxysilane derivatives were prepared from reaction of the lithium aminoaryl compound with the appropriate alkoxysilane in ether. The mixture was stirred at room temperature for 20 h and then hydrolysed with ice, and the ethereal layer rapidly separated and dried over sodium sulphate. After filtration the ether was removed *in vacuo*.

2.2.2. *$(8Me_2NC_{10}H_6)PhSi(OMe)_2$ (**6**)*

From L^3Li (0.06 mol) and $PhSi(OMe)_3$ (0.06 mol, 11.8 g). Colourless crystals from hexane (13.6 g, 68%) M.S. (EI): *m/z* 303 (M^+); 258 (M^+-OEt); 243 (M^+-OEt-Me). Anal. Found: C, 70.84; H, 6.88; N, 4.06. $C_{20}H_{23}NO_2Si$ calc.: C, 71.22; H, 6.82; N, 4.15%. ^{29}Si NMR (CD_2Cl_2) δ -38.1 (s).

2.2.3. *$(8Me_2NC_{10}H_6)Si(OMe)_3$ (**13**)*

From L^3Li (0.06 mol) and $Si(OMe)_4$ (0.06 mol, 9.1 g). Liquid (7.5 g, 60%), bp. 125°C, 0.1 mm Hg. Anal. Found: C, 61.52; H, 7.35; N, 4.63. $C_{15}H_{21}NO_3Si$ calc.: C, 61.85; H, 7.21; N, 4.81%. ^{29}Si NMR (CD_2Cl_2) δ -59.9.

2.3. *Preparation of chlorosilanes*

These compounds were obtained from the corresponding silane by reaction with PCl_5, which was found to be the most effective reagent. The mixture was stirred in CCl_4 under dinitrogen at ambient temperature. The monochlorinated silane was obtained after 5 min, the dichlorinated silane after 30 min, and the trichlorinated silane after 1 h, with 85% yield. The selective and quantitative monochlorination of di- or trihydrogensilanes was obtained more satisfactorily with $MeSiCl_3$, in C_6H_6, after 10 min [20].

2.3.1. *$(8Me_2NC_{10}H_6)PhMeSiCl$ (**2**)*

From **1** (2.8 mmol, 815 mg) and PCl_5 (1.4 mmol, 292 mg). Colourless crystals (770 mg, 85%). m.p. 148°C. MS (EI relative intensity): *m/z* 325 (M^+, 14) and 327; 324 (M^+-H, 46) and 326; 290 (M-Cl, 100); 275 (M^+-Me-Cl, 16).

2.3.2. *$(8Me_2NC_{10}H_6)PhSiHCl$ (**9**)*

From **8** (3.6 mmol, 1 g) and $MeSiCl_3$ (4 mmol, 598 mg) in C_6H_6 (1 g, 90% yield). MS (EI, relative intensity): *m/z* 311 (M^+, 47) and 313; 295 (M-Me-H, 27) and 297; 276 (M-Cl, 80); 234 (M-Ph, 100) and 236.

2.3.3. *$(8Me_2NC_{10}H_6)PhSiCl_2$ (**10**)*

From **8** (2.16 mmol, 600 mg) and PCl_5 (2.16 mmol, 450 mg) in CCl_4. Colourless oil (596, 80%). ^{29}Si NMR (CD_2Cl_2) δ -25.9 (s). MS (EI): *m/z* 345 (M^+, 19) and 347; 295 (M-Cl-Me, 17); 268 (M-Ph, 15); 170 (M-$SiPhCl_2$, 100).

2.3.4. *$(8Me_2NC_{10}H_6)MeSiHCl$ (**11**)*

From L^3Li (0.05 mol) and $MeSiHCl_2$ (0.05 mol, 5.75 g) in dry diethyl ether, at ambient temperature. After stirring for 4 h under nitrogen, the solution was filtered and the solvent evaporated *in vacuo*. Colourless crystals, mp 72°C (38% yield). MS (EI): *m/z* 249 (M^+) for $C_{13}H_{16}ClNSi$ calc.: M, 249.

2.3.5. *$(8Me_2NC_{10}H_6)MeSiCl_2$ (**12**)*

From **11** (8.03 mmol, 2 g) and PCl_5 (4.01 mmol, 834 mg). Colourless liquid (1.8 g, 80%). MS (EI, relative intensity): *m/z* 283 (M^+, 13) and 285; 248 (M-Cl, 12); 233 (M-Cl-Me, 14); 170(M-$SiMeCl_2$, 100).

2.3.6. *$(8Me_2NC_{10}H_6)SiH_2Cl$ (**16**)*

From **15** (2.48 mmol, 500 mg) and $MeSiCl_2$ (1.5 mol, 193 mg) in C_6H_6 (5 ml). Yellow powder (525 mg, 90%). MS (EI, relative intensity): *m/z* 235 (M^+, 32) and 237;

234 (M–H, 79) and 236; 219 (M–H–Me, 72); 185 (M–Cl–Me, 35).

2.3.7. $(8Me_2NC_{10}H_6)SiHCl_2$ (17)

From **15** (4.97 mmol, 1 g) and PCl_5 (4.97) mmol, 1.035 g) in CCl_4. Yellow powder (1.07 g, 80%). MS (EI, relative intensity): m/z 269 (M^+, 42) and 271; 253 (M–H–Me, 28) and 255; 234 (M–Cl, 49); 219 (M–Cl–Me, 33); 170 ($M-SiHCl_2$, 100).

2.3.8. $(8Me_2NC_{10}H_6)SiCl_3$ (18)

From **15** (4.97 mmol, 1 g) and PCl_5 (7.35 mmol, 1.55 g) in CCl_4. Colourless powder (1.2 g, 80%). MS (EI, relative intensity): m/z 303 (M^+, 3), 305 and 307; 268 (M–Cl, 5) and 270; 253 (M–Cl–Me, 5) and 255.

2.4. *Preparation of bromosilane*

2.4.1. $(8Me_2NC_{10}H_6)PhMeSiBr$ (3)

From **1** and *N*-bromosuccinimide. This compound, unstable at ambient temperature, was identified in CCl_4 solution by its ^1H NMR spectrum.

2.5. *Preparation of fluorosilanes*

Fluorosilanes were obtained from the corresponding alkoxysilanes by treatment with BF_3/Et_2O for a few minutes, following the procedure already described for **14** [13f].

2.5.1. $(8Me_2NC_{10}H_6)PhMeSiF$ (5)

From **4** (8.88 mmol, 2.85 g) and BF_3/Et_2O (2.95 mmol, 372 ml). Colourless oil (2 g, 73% yield), bp. 200°C 0.35 mm Hg. ^{19}F NMR (in *ortho*-dichlorobenzene) δ -137.6 (q, $J_{FH} = 7$ Hz). ^{29}Si NMR ($CDCl_3$) δ -12.47 ($J_{SiF} = 264.3$ Hz, $^3J_{FH} = 7.3$ Hz). MS (EI): m/z 309 (M^+); 294 (M^+–Me); 279 (M^+–2Me); 232 (M^+–Ph); 217 (M^+–Ph–Me). Anal. Found C, 73.18; H, 6.21; N, 4.16. $C_{19}H_{20}FNSi$ calc.: C, 73.78; H, 6.47; N, 4.53%.

2.5.2. $(8Me_2NC_{10}H_6)PhSiF_2$ (7)

From **6** (5.93 mmol, 2 g) and BF_3/Et_2O (3.95 mmol, 0.49 ml). Colourless crystals (1.48 g, 80%) m.p. 106.2°C (from hexane). ^{19}F NMR (CD_2Cl_2, 30°C) δ -144 (br.s) ppm; at -60°C δ -125.6 (d, $J_{FF} = 20$ Hz, F_{ax}) and -159.6 (d, F_{eq}) ppm. ^{29}Si NMR (CD_2Cl_2) δ -51.9 (t, $J_{SiF} = 264$ Hz). Anal. Found: C, 67.79; H, 5.48; N, 4.38; F, 10.91. $C_{18}H_{17}NSiF_2$ calc.: C, 69.01; H, 5.43; N, 4.47; F, 12.14%.

2.5.3. $(8Me_2NC_{10}H_6)SiF_3$ (14)

From **13** (0.017 mmol, 5.07 g) and BF_3/Et_2O (0.017 mmol, 2.13 ml). Fractional distillation *in vacuo* yielded **14** (3.73 g, 84%). Bp 105°C at 0.08 mm Hg. Mp 62°C (from hexane). See ref. [13f].

2.5.4. $(2Me_2NCHMe)C_6H_4SiF_3$

($= L^2SiF_3$) from $L^2Si(OEt)_3$ [13 g] (6 mmol, 2 g) and BF_3/Et_2O (6 mmol, 0.8 ml) in ether (20 ml). After 20 min stirring at room temperature, fractional distillation *in vacuo* yielded L^2SiF_3 as a colourless liquid (1 g, 67% yield), b.p. 155°C at 16 mm Hg. ^1H NMR (CCl_4, 30°C) δ 1.4 (d, 3H, ^3J 7 Hz, $CHCH_3$); 2.3 (s, 6H, NMe_2); 3.75 (q, 1H, $^3J = 7$ Hz, $CHCH_3$); 7.3 (m, 3H aromatic); 7.9 (m, 1H aromatic). MS (EI): m/z 233(M^+) for $C_{10}H_{14}F_3NSi$ calc.: M, 233.

2.5.5. $(2Me_2NCHMe)C_6H_4SiMeF_2$

($= L^2SiMeF_2$) 1 g, 61% yield, from $L^2SiMe(OEt)_2$ (7.1 mmol, 2 g) and BF_3/Et_2O (7.2 mmol, 0.9 ml) [13g]. ^{29}Si NMR (CD_2Cl_2) at 20°C δ -47.06 (t, $J_{Si-F} = 264.7$ Hz); at -100°C δ -53.5 (dd, $J_{Si-Feq} = 256.2$ Hz; $J_{Si-Fax} = 265.4$ Hz).

3. Crystallographic study

Single crystals of L^3SiF_3 were grown by slow cooling of a pentane solution under dinitrogen. Thick colourless plates were obtained. Preliminary Weissenberg photographs established a triclinic unit cell with space group $P1$ or $P\bar{1}$ and $Z = 4$. A small colourless parallelipiped of dimensions 0.4 mm × 0.4 mm × 0.2 mm was sealed inside a Lindeman glass capillary with the [001] direction parallel to the ϕ axis of the diffractometer.

3.1. *X-ray data collection*

Data were collected on a CAD-4 automated diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Lattice constants [$a = 11.915(2)$ Å, $b = 9.263(1)$, $c = 12.885(2)$ Å, $\alpha = 104.32(1)°$, $\beta = 119.32(1)°$, and $\gamma = 76.35(1)°$] were derived from a least-squares refinement of 24 reflections obtained in the range $12 < 2\theta < 23°$. The intensities of three standard reflections were monitored at intervals of 60 min; no significant change in these intensities occurred during data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. Of the 3076 unique reflections, only 1840 having $F > 3\sigma(F)$ were considered to be observed. No absorption corrections were made ($\mu = 1.98$ cm^{-1}).

3.2. *Structure determination and refinement*

Direct methods (1980 version of the MULTAN program and SHELXS-86 program) [21] failed to give a solution in the centrosymmetric space group $P\bar{1}$. Nevertheless four silicon atoms were readily located by using the non-centrosymmetric space group, in which refinement of the atomic positions allowed location of the fluorine atoms, the nitrogen atoms and eight of the carbon atoms. At this stage, the centrosymmetric space group was definitively adopted by displacing the origin of the unit cell. The remaining carbon atoms were located in two successive difference Fourier syntheses. The atomic scattering factors were taken from ref. [22]. After four cycles of least-squares refinement with isotropic thermal parameters to all atoms ($R = 0.139$), anisotropic thermal parameters were given to the fluorine, nitrogen and silicon atoms and refinement was resumed; convergence occurred to 0.083. An attempt to allocate anisotropic parameters to all atoms resulted in a temporary improvement in the R factor (0.067 after three cycles of least-squares refinement) but also in a dramatic increase in most of the δ/σ ratios, unreasonable bond distances and the generation of high numbers of correlation matrix elements greater than 0.5: 22, 72, 65 and 70 respectively, for each of the four cycles. Refinement with anisotropic thermal parameters for the Si, F and N atoms only was performed, the hydrogen atoms being positioned by calculation (SHELX 76 program) [23]. Two isotropic thermal parameters were attributed to the hydrogen atoms according to the group to which they were attached: (methyl or naphthyl) (Fig. 2). Refinement converged to an R value of 0.057 with $\rho = 0.44$ e^{-} Å^{-3}.

The final atomic coordinates are listed in Table 2. Important bond angles are listed in Table 3, and individual bond lengths in Table 4. Additional material, available from the Cambridge Crystallographic Data Centre, is comprised of a list of anisotropic thermal parameters and a full table of bond angles.

4. Results and discussion

Our studies of the application of dynamic NMR (DNMR) spectroscopy to the elucidation of the structure and behaviour of chelated organosilanes in solution make much use of the diastereotopy which may be induced in *gem* *N*-methyl groups on coordination to silicon, provided that at least one stereocentre is present (or is created) in the molecule. It is however important to be able to discriminate between the different processes which might, on the NMR timescale, lead to equivalence of the environments of the *N*-methyl groups, and hence to coalescence of the signals from these groups in the NMR spectrum. In particular, it is necessary to distinguish between the irregular mechanism (*i.e.* a change of coordination number is involved) where rapid fission and re-formation of the chelate ring allow inversion of the nitrogen atom (Scheme 5, $a \rightleftharpoons b \rightleftharpoons c$), and the regular mechanism by which ligand permutation (Scheme 5, $c \rightleftharpoons d$) takes place whilst pentacoordination is maintained. In fact, as will be shown below, inversion of configuration at the silicon atom, $c \rightleftharpoons d$ does not occur in the benzylamino systems studied, but a limited pseudorotation for compounds of structure $LSiRX_2$ can be discerned for all three ligands (Scheme 6, $e \rightleftharpoons f$). In order to study the dynamic processes involving all the ligands attached to the five-coordinate silicon atom, the integrity of the

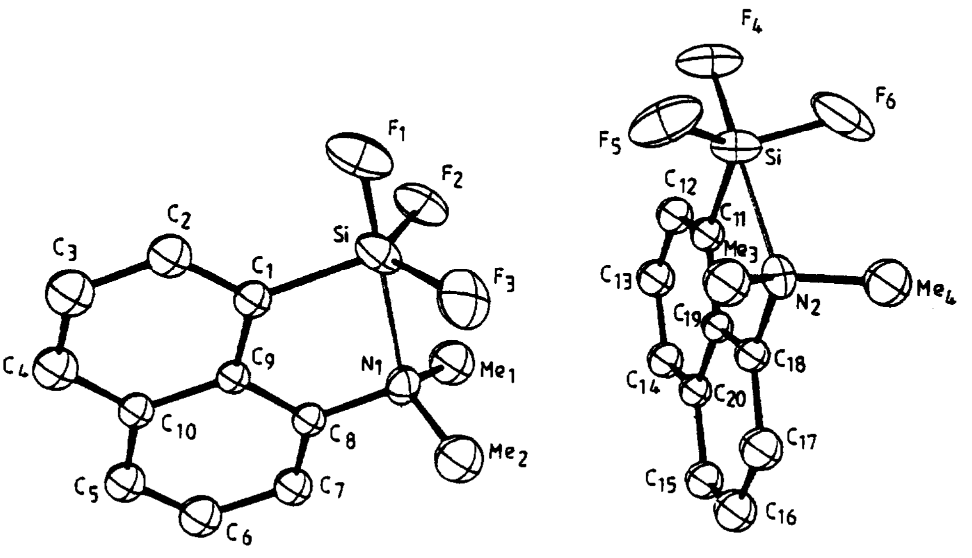


Fig. 2. ORTEP drawing of the two conformations of the molecule L^3SiF_3, **14**. The ellipsoids and spheres are at the 30% probability level.

TABLE 2. Fractional atomic parameters ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) for compound **14**; Esd's are in Parentheses

Atom	x	y	z	U_{iso}
Si(1)	7347(2)	2100(2)	2669(2)	[a]
F(1)	8074(5)	3272(4)	2554(4)	[a]
F(2)	7018(4)	3122(4)	3685(4)	[a]
F(3)	6149(4)	2117(5)	1387(3)	[a]
N(1)	6319(4)	389(5)	2827(4)	[a]
C(1)	8661(5)	536(6)	3035(5)	43(1)
C(2)	9832(6)	564(7)	3071(5)	58(2)
C(3)	10839(6)	−651(7)	3383(6)	66(2)
C(4)	10705(6)	−1868(7)	3697(5)	61(2)
C(5)	9342(6)	−3191(7)	4015(5)	57(2)
C(6)	8199(6)	−3224(7)	3977(6)	62(2)
C(7)	7158(6)	−2051(6)	3605(5)	54(2)
C(8)	7330(5)	−848(6)	3283(4)	40(1)
C(9)	8514(5)	−753(5)	3345(4)	36(1)
C(10)	9545(5)	−1955(6)	3696(4)	42(1)
Me(1)	5711(7)	1042(8)	3653(7)	77(2)
Me(2)	5301(7)	−179(9)	1624(6)	79(2)
Si(2)	3339(2)	6409(2)	1891(2)	[a]
F(4)	3989(5)	7553(5)	3124(4)	[a]
F(5)	4508(4)	6064(6)	1584(4)	[a]
F(6)	2215(5)	7604(4)	1164(4)	[a]
N(2)	2387(4)	4787(5)	147(4)	[a]
C(11)	3050(5)	5034(6)	2515(5)	43(1)
C(12)	3389(6)	5157(6)	3724(5)	54(2)
C(13)	3171(6)	4077(7)	4156(5)	60(2)
C(14)	2630(5)	2858(6)	3429(5)	53(2)
C(15)	1757(5)	1352(6)	1376(5)	54(2)
C(16)	1462(6)	1196(7)	198(6)	63(2)
C(17)	1656(6)	2295(7)	−248(6)	60(2)
C(18)	2161(5)	3554(6)	507(4)	41(1)
C(19)	2497(5)	3742(5)	1744(4)	36(1)
C(20)	2281(5)	2630(6)	2180(4)	41(1)
Me(3)	3218(6)	4234(8)	−466(6)	66(2)
Me(4)	1124(6)	5493(8)	−721(6)	70(2)

[a] The anisotropic thermal parameters for these atoms are in the supplementary material.

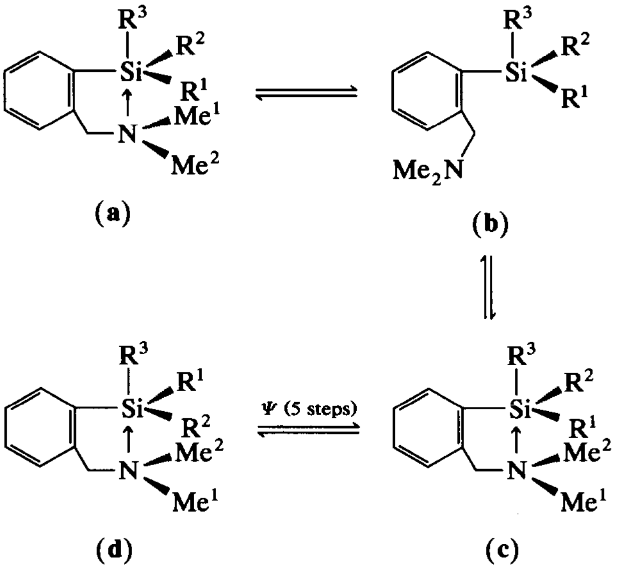
TABLE 3. Selected bond angles (deg) for compound **14**

F(1)–Si(1) ··· N(1)	179.2(2)	F(4)–Si(2) ··· N(2)	179.0(3)
F(1)–Si(1)–F(2)	97.1(3)	F(4)–Si(2)–F(5)	96.9(3)
F(1)–Si(1)–F(3)	96.7(3)	F(4)–Si(2)–F(6)	96.2(2)
F(1)–Si(1)–C(1)	98.8(3)	F(4)–Si(2)–C(11)	97.9(3)
N(1) ··· Si(1)–F(2)	83.6(2)	N(2) ··· Si(2)–F(5)	84.1(2)
N(1) ··· Si(1)–F(3)	83.4(2)	N(2) ··· Si(2)–F(6)	83.4(2)
N(1) ··· Si(1)–C(1)	80.5(3)	N(2) ··· Si(2)–C(11)	81.5(2)
C(1)–Si(1)–F(2)	120.1(2)	C(11)–Si(2)–F(5)	120.4(3)
F(2)–Si(1)–F(3)	112.1(2)	F(5)–Si(2)–F(6)	113.0(4)
F(3)–Si(1)–C(1)	122.6(2)	F(6)–Si(2)–C(11)	122.1(3)
Si(1) ··· N(1)–C(8)	104.9(4)	Si(2) ··· N(2)–C(18)	105.3(3)
Si(1) ··· N(1)–Me(1)	112.6(4)	Si(2) ··· N(2)–Me(3)	112.2(3)
Si(1) ··· N(1)–Me(2)	110.8(5)	Si(2) ··· N(2)–Me(4)	111.9(3)
C(8)–N(1)–Me(1)	111.0(5)	C(18)–N(2)–Me(3)	111.1(5)
C(8)–N(1)–Me(2)	108.7(4)	C(18)–N(2)–Me(4)	108.7(5)
Me(1)–N(1)–Me(2)	108.8(5)	Me(3)–N(2)–Me(4)	107.5(5)
Si(1)–C(1)–C(9)	119.7(5)	Si(2)–C(11)–C(19)	119.2(5)
C(1)–C(9)–C(8)	119.4(4)	C(11)–C(19)–C(18)	119.1(6)
C(9)–C(8)–N(1)	114.8(5)	C(19)–C(18)–N(2)	114.7(4)

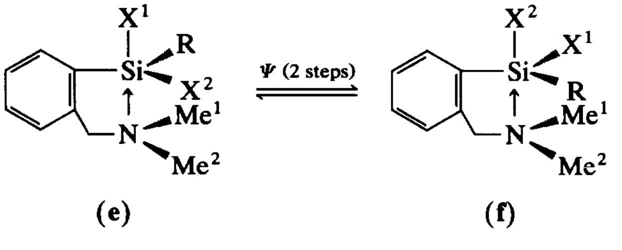
TABLE 4. Interatomic distances (Å) for the two conformations of compound **14** with Esd's in Parentheses

Si(1)–F(1)	1.612(6)	Si(2)–F(4)	1.612(4)
Si(1)–F(2)	1.574(5)	Si(2)–F(5)	1.571(7)
Si(1)–F(3)	1.568(4)	Si(2)–F(6)	1.575(4)
Si(1)–C(1)	1.822(5)	Si(2)–C(11)	1.836(7)
Si(1) ··· N(1)	2.318(6)	Si(2) ··· N(2)	2.287(4)
N(1)–C(8)	1.448(6)	N(2)–C(18)	1.457(9)
N(1)–Me(1)	1.501(11)	N(2)–Me(3)	1.481(10)
N(1)–Me(2)	1.486(7)	N(2)–Me(4)	1.481(7)
C(1)–C(2)	1.381(10)	C(11)–C(12)	1.386(9)
C(2)–C(3)	1.408(8)	C(12)–C(13)	1.385(11)
C(3)–C(4)	1.355(11)	C(13)–C(14)	1.340(8)
C(4)–C(10)	1.402(11)	C(14)–C(20)	1.423(9)
C(10)–C(5)	1.413(10)	C(20)–C(15)	1.405(7)
C(5)–C(6)	1.346(11)	C(15)–C(16)	1.357(10)
C(6)–C(7)	1.410(8)	C(16)–C(17)	1.396(12)
C(7)–C(8)	1.370(10)	C(17)–C(18)	1.366(7)
C(8)–C(9)	1.396(9)	C(18)–C(19)	1.415(8)
C(9)–C(1)	1.421(9)	C(19)–C(11)	1.412(7)
C(9)–C(10)	1.418(6)	C(19)–C(20)	1.413(9)

chelate ring must be established independently of those features of the spectrum related to the N → Si coordination.



Scheme 5. Irregular and regular mechanisms for *N*-methyl group equivalence. (Ψ = Berry pseudo-rotation or similar process.)



Scheme 6. Ligand permutation without inversion at silicon.

TABLE 5. Free energies of activation for pseudo-rotation at silicon in pentacoordinate chelated silanes

Compounds	ΔG *ª kcal mol^{-1}	T_c ᵇ	Ref.
L^3SiH_3	< 7	< −100	2b
L^2SiH_3	< 7	< −100	2b
$L^3Si(OMe)_3$	< 7	< −100	2c
$L^2Si(OMe)_3$	< 7	< −100	13g
L^3SiF_3 ª	12	+20	2c
L^2SiF_3 ª	13.1	+50	13g
L^1SiF_3 ª	11.7	0	13g
L^2SiMeF_2	9.4	−75	13g
$L^2SiPhCl_2$	11.1	−45	13g

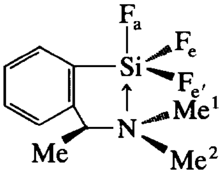
ª ΔG* was calculated from the ^{19}F NMR spectrum at the temperature just before appearance of the two distinct signals F_{eq} (to high field) and F_{ax} (to low field). $L^1 = 2\text{-}(Me_2NCH_2)C_6H_4\text{-}$. $L^2 = 2\text{-}(Me_2NCHMe)C_6H_4\text{-}$. $L^3 = 8\text{-}(Me_2N)C_{10}H_6\text{-}$.

ᵇ T_c is the coalescence temperature in °C.

4.1. The stereochemical non-rigidity of chelated benzylamino derivatives.

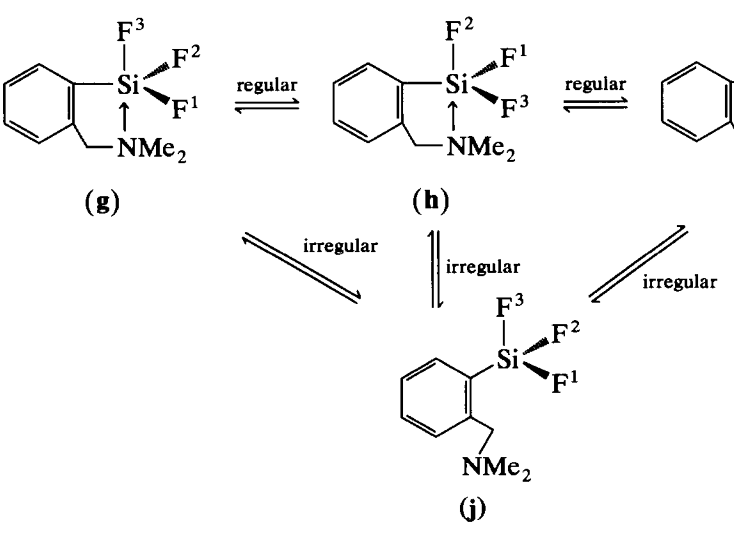
The clearest distinction between the dynamic behaviour of the NMe_2 and the ligands at Si can thus be made if each process can be studied in isolation. This is the case in fluorosilane derivatives of L^2 where the chirality at the benzyl carbon atom, which cannot invert, results in diastereotopy of the *N*-methyl groups when the nitrogen atom is coordinated and its inversion inhibited, whilst the situation of the fluorine atoms is revealed by ^{19}F (and ^{29}Si) NMR spectra. Although it might be expected that ^{1}H NMR spectra would also yield information on the site occupancy and fluxionality of hydrogen and organic groups attached to silicon, this is not often realised in practice, as will be detailed later.

It is well established [2a,13b,13f,24] that at the low-temperature limit, fluorine atoms occupying axial or equatorial sites around a silicon atom which has been rendered pentacoordinate by intramolecular coordination may readily be distinguished by the difference in their chemical shifts. As with acyclic pentacoordinate fluorosilicates [5,7–9], which adopt a trigonal bipyramidal structure, axial fluorine atoms resonate at lower fields than equatorial fluorine atoms. The low-temperature ^{19}F spectrum of L^1SiF_3 has been described previously [2a], and consists of a low-field triplet and a high-field doublet, the latter signal having twice the intensity of the former. That of L^2SiF_3, **D**, (at −50°C), is consistent with an analogous structure, but differs in the presence of two distinct signals for the two equatorial fluorine atoms [2a], which are diastereotopically related because of the chiral carbon atom. For both of these compounds, coalescence of the fluorine signals to singlets occurs on raising the temperature, at 0°C for L^1SiF_3 and at +50°C for L^2SiF_3. The NMR parameters lead to values of 11.7 kcal mol^{-1} and 13.1 kcal mol^{-1} respectively (Table 5) for the free energies of activation, for the processes leading to the equivalence of the fluorine atoms in the ^{19}F NMR spectra.



(D)

It is not possible to assign an unambiguous mechanism for this process in the case of L^1SiF_3. The observed coalescence could arise equally well from permutation of the fluorine atoms by a regular mechanism between sites in the trigonal bipyramid (Scheme 7, g $\rightleftharpoons$ h $\rightleftharpoons$ i, etc.) or by the irregular mechanism (g $\rightleftharpoons$ j $\rightleftharpoons$



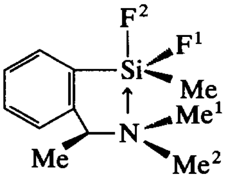
Scheme 7. Ligand permutation by regular and irregular mechanisms.

h, *etc.*). However, for compound L^2SiF_3 the diastereotopy of the *N*-methyl groups with respect to the chiral benzyl centre in the chelate, which is evident in the ^1H NMR spectrum up to 30°C, is eliminated at 50°C, but with a free energy of activation of 15.8 kcal mol^{-1}. This is significantly higher than the 13.1 kcal mol^{-1} obtained for the equivalence of the fluorine ligands in the ^{19}F NMR spectrum, and thus demonstrates that permutation of the fluorine atoms amongst the available sites is more rapid than the breaking of the coordinate link and inversion at the chelating nitrogen atom. This conclusion can be extended by analogy to identify the coalescence of the signals in the ^{19}F DNMR spectrum of L^1SiF_3 with the permutation of the ligands about the silicon atom. Furthermore, any process involving intermolecular fluorine exchange is ruled out by the persistence of $^{19}F-^{29}Si$ coupling up to the highest temperatures studied, above that of the fluorine coalescence.

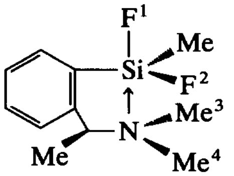
This conclusion is confirmed and amplified by the study of the DNMR ^1H, ^{19}F, and ^{29}Si spectra for L^2SiF_2Me. At the lowest temperatures the ^1H spectrum [2a,13g] displays four singlets for the methyl groups of the NMe_2 moieties, and two quartets for the lone benzylic hydrogen atom coupled to the adjacent methyl group. These signals are consistent with the existence of two diastereomeric chelates, **E** and **E′**, in which the silicon atom is pentacoordinate and chiral.

Accordingly, there are also four absorptions in the ^{19}F spectrum at −75°C, corresponding to one axial fluorine and one equatorial fluorine for each diastereomer [2a]. The ^{29}Si resonance consists of a doublet of doublets, since the coupling constants $^1J_{Si-Fax}$ and $^1J_{Si-Feq}$ are slightly different (265.4 Hz and 256.2 Hz respectively).

A first coalescence of the four *N*-methyl signals to two occurs consecutively in pairs at −80°C and −75°C, with free energies of activation of 9.4 kcal mol^{-1} and 9.5 kcal mol^{-1} respectively, for the two diastereomers. One diastereomer (probably **E′**) is thus slightly more stable than the other, but integration of the NMR signals does not show a significant difference in the populations. Coalescence of the two C*H*Me quartets to one (at −75°C), and of the four ^{19}F resonances to two (at −30°C) also give free energies of activation of 9.4 kcal mol^{-1} and 9.3 kcal mol^{-1} for the process involved. There is thus good agreement between the values obtained from the different probes. As in the case of L^2SiF_3, this process is one which equilibrates the fluorine atoms between axial and equatorial sites at a rate greater than the one which renders the *N*-methyl groups equivalent. The final coalescence of the *N*-methyl group resonances to a singlet, characteristic of a rapidly inverting nitrogen atom, occurs only at −25°C, with a free energy of activation of 11.8 kcal mol^{-1}.



(E)



(E′)

The ^{29}Si resonance at −100°C consists of only one doublet of doublets instead of the two expected for two diastereomers, because the coupling constants $^1J(Si-F_{ax})$ and $^1J(Si-F_{eq})$, at 265.4 Hz and 256.2 Hz, respectively, are only slightly different. It is significant however that the two fluorine atoms still give rise to separate resonances in the ^{19}F NMR spectrum, because they retain their diastereotopic relationship with respect to the chiral benzylic centre.

Although no direct observation of the process can be made for $L^2SiPhCl_2$, the fluxional behaviour of this molecule can be deduced from its ^1H dynamic NMR spectrum by analogy with the proton spectra of L^2SiF_2Me. Thus the limiting low-temperature ^1H spectrum of $L^2SiPhCl_2$ shows four *N*-methyl signals and two benzylic C*H*Me quartets. Coalescence of these signals to two and one respectively, leads to a value of 11.1 kcal mol^{-1} for the free energy of activation for permutation of the ligands at silicon. The final coalescence of the *N*-methyl signals to a singlet occurs at −17°C and corresponds to a value of 12.2 kcal mol^{-1} for inversion at the nitrogen atom.

However, $L^2SiPh(OMe)_2$, which might be expected to show behaviour similar to that of $L^2SiPhCl_2$, is not sufficiently strongly coordinated for any information to be obtained on the stereochemical non-rigidity of the chelate. Ring-opening and inversion at the nitrogen atom occur with a free energy of activation of less than 8 kcal mol^{-1}, and the ^1H signals from the methoxy groups reflect only the diastereotopy of these groups at all temperatures.

The case of the simple silanes is rather different. Chelation is favoured by hydrogen ligands despite the low electronegativity and preferential occupancy of equatorial sites. Thus for the trihydrogenosilane L^2SiH_3, the free energy of activation for nitrogen inversion is 10 kcal mol^{-1}. The ^1H NMR resonance of the SiH_3 group is a sharp singlet at all temperatures, indicating rapid permutation of hydrogen atoms between axial and equatorial sites even at low temperature, with a free energy of activation of less than 7 kcal mol^{-1}. An accidental identity of chemical shift between axial and equatorial hydrogen atoms cannot be ruled out, but appears unlikely in view of observations [25] on the acyclic anionic hydridosilicates, K^+

$[H_2Si(OR)_3]^-$, ($R = {}^iPr$ or ${}^sBu$). In these complexes hydrogen atoms occupying axial and equatorial sites can be distinguished by ^1H NMR spectroscopy, with chemical shifts of 4.38 ppm and 3.72 ppm, respectively.

The silanes L^2SiH_2R, (R = Me, Ph or Np) are similarly firmly chelated [13g], with $\Delta G^\#$ for nitrogen inversion in the range 9–10 kcal mol^{-1}. All three compounds show only one signal for the SiH resonances at ambient temperature; L^2SiH_2Np shows below −20°C only the two doublets expected for diastereotopic hydrogen atoms. The difference in chemical shifts between these two hydrogen atoms is quite small (0.10 ppm measured at 100 MHz), and in the other two compounds it is probably so small as to give rise to a singlet (when R = Ph) or quartet (when R = Me) only in the ^1H NMR spectrum over the whole temperature range studied. It is thus not possible to draw firm conclusions concerning the stereochemical non-rigidity of these chelates, although processes leading to the occupancy of an axial site by hydrogen would be expected to be subject to a considerable energy barrier. However, as with the fluorine atoms in L^2SiF_2Me, exchange leading to complete equivalence of the hydrogen atoms bound to silicon in these dihydrogenosilanes is precluded by the diastereotopy of the hydrogen atoms observed in the ^1H NMR spectrum of L^2SiH_2Np.

4.2. 8-Dimethylamino-1-silylnaphthalene compounds

4.2.1. The crystal structure of 8-dimethyamino-1-trifluorosilylnaphthalene L^3SiF_3, 14

The lattice contains two independent molecular conformations (Fig. 2) which differ only slightly, undoubtedly under the influence of crystal-packing forces. In both cases, the naphthalene nucleus and the nitrogen and silicon atoms attached directly to it, deviate little from planarity. The geometry about the silicon atom is close to trigonal bipyramidal with the $N–Si–F_{ax}$ axis accurately linear (Table 3). The $Si–F_{ax}$ bond is slightly longer than the $Si–F_{eq}$ bonds (Table 4) as is normal, but the silicon atom is displaced about 0.21 Å towards the axial fluorine atom with respect to the trigonal plane in each molecular conformation. The N–Si separation which averages 2.303 Å is relatively short, and is significantly smaller than that found previously [13e] for the compound L^3SiH_2Ph (2.584 Å). Therefore, it indicates a substantial bonding interaction.

This conclusion is reinforced by comparison with other *peri*-substituted naphthalene derivatives. The rigid geometry of the aromatic skeleton naturally forces substituents in *peri* positions into close proximity. Nevertheless, the sum of the contact radii of such groups, generally being greater than the $C_1–C_8$ separation in the idealized naphthalene skeleton with 120°C bond angles (*ca.* 2.45 Å), means that significant distortions consistent with repulsion between the substituents are usually found. For example, X-ray crystallographic data show [26] that in 1,8-dimethylnaphthalene the carbon atoms of the methyl groups are 2.93 Å apart. In 1,8-bis(dimethylamino)naphthalene [27], the nitrogen atoms are 2.79 Å apart, and in 1,8-bis(trimethylsilyl) naphthalene [28] the silicon atoms are 3.8 Å apart, a distance similar to that found [29] for the quaternary carbon atoms in 1,3,6,8-tetrakis(*t*-butyl)naphthalene. In addition, the *exo*cyclic bonds to these substituents are bent away from each other, and displaced to opposite sides of the naphthalene ring-plane, with similar, though less pronounced, distortion of the skeleton itself. However, in some other compounds, where donor-acceptor interactions between the *peri*-substituents are possible, significantly shorter distances than those quoted above are found, as in the series of compounds F, studied by Dunitz *et al.* [30]. N–C separations in these cases were found to lie in the range 2.52–2.62 Å which, together with other characteristic features of the geometry, demonstrated incipient nucleophilic addition to the carbonyl group.

The attractive interaction between the dimethylamino and silyl groups in the *peri*-positions in the naphthalene derivative L^3SiF_3, **14** is manifestly greater than that determined for the carbonyl compounds, given the inherently greater radius of a silicon atom. Indeed, the dimethylamino group is inclined towards the silicon atom, the Si–N distance being less than the $C_1–C_8$ separation in the naphthalene nucleus [31*].

4.2.2. The dynamic ^1H spectra of 8-dimethylamino-1-silylnaphthalene compounds

The free energies of activation for the equivalence of the *N*-methyl groups in 8-dimethylamino-1-silyl-

TABLE 6. Free energies of activation for NMe_2 equivalence of monofunctional and heterobifunctional silanes [a]

Compounds	ΔG^* kcal mol^{-1}	T_c
1 $L^3SiPhMeH$	22	+160
2 $L^3SiPhMeCl$	20	+130
3 $L^3SiPhMeBr$	> 19	> 110
4 $L^3SiPhMe(OMe)$	22	+175
5 $L^3SiPhMeF$	23	+200
9 $L^3SiPhHCl$	> 22	> 160
11 $L^3SiMeHCl$	22	+160

[a] $L^3 = 8\text{-}(Me_2N)C_{10}H_6\text{-}$. T_c = coalescence temperature in °C.

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* Reference number with an asterisk indicates a note in the list of references.

TABLE 7. Free energies of activation for NMe_2 equivalence of polyfunctional compounds [a]

Compounds	ΔG^* kcal mol^{-1}	T_c
6 $L^3SiPh(OMe)_2$	9	−84
7 L^3SiPhF_2	12	−26
10 $L^3SiPhCl_2$	11	−43
12 $L^3SiMeCl_2$	9	−75
17 L^3SiHCl_2	10.2	−62

[a] $L^3 = 8\text{-}(Me_2N)C_{10}H_6\text{-}$. T_c = coalescence temperature in °C.

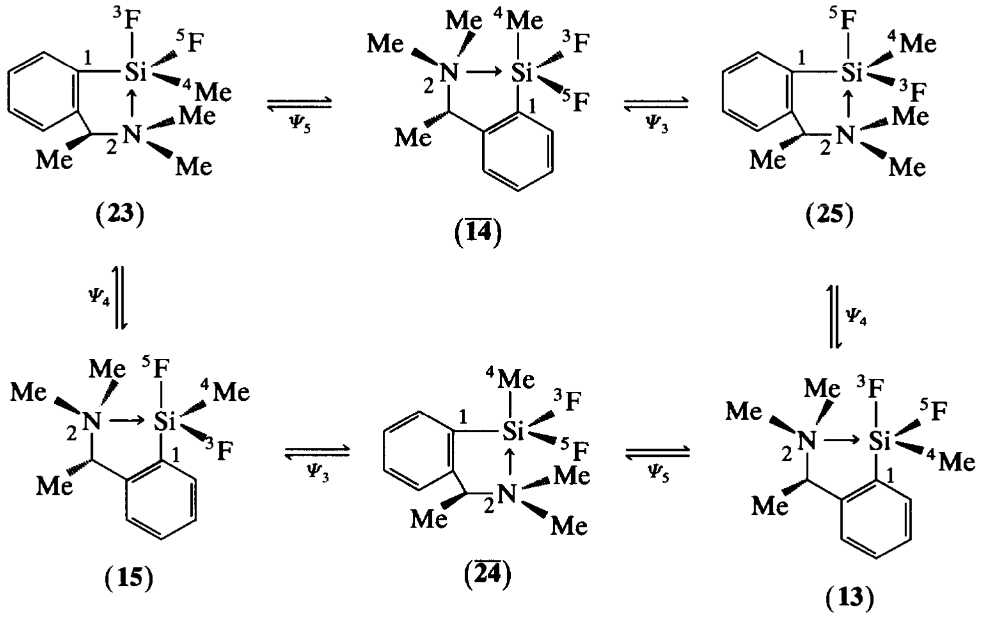
naphthalene compounds clearly fall into two groups (Tables 6 and 7). Those compounds for which the four-coordinate silicon atom is chiral (Table 6) always show non-equivalent methyl groups up to above 100°C, and where coalescence can be obtained and free energies of activation evaluated, barriers in excess of 20 kcal mol^{-1} are measured for equivalence of the *N*-methyl groups. These values, substantially greater than those for the benzylamino series, probably result from stabilisation with respect to rupture of the coordinate link and inversion as a consequence of the structural features discussed above.

By contrast, in the homobifunctional compounds (Table 7), diastereotopy of the *N*-methyl groups resulting from a dissymmetric configuration at a pentacoordinate silicon atom is eliminated *via* a process which has a free energy of activation of 12 kcal mol^{-1} or less. The trifluoro derivative also shows equilibration of the fluorine ligands amongst axial and equatorial sites with a similar energy barrier, and that for silyl and trialkoxy compounds is too small to be measured [less than 7 kcal mol^{-1}] (Table 5). These values are comparable to those found for the same substituents in the benzylamino series of compounds, and are fully consistent with a regular process of isomerization at the pentacoordinate silicon atom in both series of compounds. The appearance of separate resonances for methoxy groups occupying axial and equatorial sites in compound $L^3SiPh(OMe)_2$ represents the only case where we have been able to observe this distinction. Nevertheless it supports the contention that the single methoxy resonance seen in other polymethoxy compounds is diagnostic.

4.3. The nature of the fluxional processes in pentacoordinate chelates

The observation that in the ^{19}F spectrum of the difluorosilane L^2MeSiF_2 diastereotopy of the two fluorine atoms with respect to the asymmetric benzylic carbon atom is maintained at the fast exchange limit shows that, on the time-scale accessible to NMR measurements, inversion of absolute configuration of a four-coordinate silicon atom is not brought about by the formation of a five-coordinate chelate and its resulting fluxional behaviour. This is consistent with the findings of van Koten and Noltes [15a] on analogous tin compounds, who noted that the configurational stability of a chiral tin atom was greatly enhanced in these derivatives.

In order for inversion of a chiral tetrahedral centre to occur by conversion to a fluxional five-coordinate species *via* the Berry process (or equivalent mechanisms such as the turnstile rotation), it is necessary for

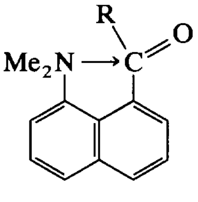


Scheme 8. Site exchange of acyclic ligands by pseudo-rotation in a pentacoordinate chelate without ring-opening.

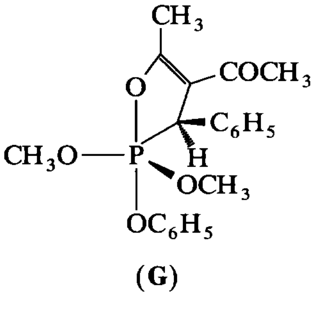
each of the five ligands to act as the "pivot" in the pseudo-rotation. In cyclic compounds this implies that the ring should at some time become di-equatorial, but such a conformation would obviously result in considerable ring strain. The intrinsic strength of the donor-acceptor interaction in the chelate compounds discussed, is difficult to assess accurately, but does not appear likely to exceed the 20 kcal mol^{-1} free energy of activation in the naphthalene series, and may well be only about 10 kcal mol^{-1} in the benzylamino series. It is likely that the strain energy involved in placing the chelate ring di-equatorial is in an excess of these values, not least since it must involve an increase in the C–Si–N angle from less than 90°C towards 120°. For this reason the donor-acceptor bond can be expected to break before the ring becomes di-equatorial, and inversion of the configuration of the silicon atom will thereby be precluded.

Equilibration of ligands between axial and equatorial sites in these trigonal bipyramid chelates by a fluxional process may, however, occur without ring fission. Successive conformations accessible in this way to L^2SiMeF_2 are shown in Scheme 8. It is evident that the fluorines may be distributed evenly between the available sites without becoming completely equivalent by exchange. The situation is analogous to that analysed in detail by Gorenstein and Westheimer [32] for the alkoxy-phosphorane **G**, in which the activation energy for exchange of methoxy groups between axial and equatorial sites was found to be 12 kcal mol^{-1} while the ring retained an apical-equatorial conformation. The activation energy to place the ring di-equatorial, resulting in complete equivalence of the methoxy groups was much greater at 21.8 kcal mol^{-1}.

The energy barriers for fluxional processes at silicon which have been determined in these studies, in the range from less than 7 kcal mol^{-1} to 13 kcal mol^{-1}, are similar to those found for the acyclic fluorosilicates. It is clear that stereochemical non-rigidity is a characteristic property of pentacoordinate silicon species, and should be seriously considered in all processes in which they may intervene.



(F)



(G)

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