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Pentacoordinated silicon compounds. Intramolecular ring closure, site preferences of substituents and the stability of the resulting chelates

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Abstract

Dynamic NMR studies have been made of chelation in 2-(dimethylaminomethyl)phenylsilanes and 2-[1-(dimethylamino)ethyl]phenylsilanes with a wide range of substituents on the silicon atom. Temperature-dependent ^{19}F spectra of compounds of the type $Me_2NCH_2C_6H_4SiMeFX$ in which the geometry about the silicon atom is trigonal bipyramidal with the donor nitrogen atom axial, have established the preference of the substituent X for the axial site *trans* to the donor nitrogen atom, relative to that of the fluorine atom. Combined with other structural data this leads to te apicophilicity series: H < alkyl < aryl < OR,NR_2 < F ≈ SR < Cl,OCOR. It is concluded that the apicophilicity is closely correlated with the ability of the bond *trans* to the donor atom to be stretched by electron donation to the central atom.

The stability of the chelates has been investigated by dynamic ^1H NMR spectroscopy of the potentially diastereotopic NMe_2 groups. When the ligand that occupies the site *trans* to the donor nitrogen atom is electronegative, the stability is largely determined by the nature of that ligand, and increases with the apicophilicity. Intramolecular coordination is barely detectable in the case of an alkoxy group. Compounds containing only alkyl and aryl substituents in addition to the bidentate ligand are also not chelated, but dihydrogeno-alkyl (or -aryl) derivatives, in which the hydrogen atoms occupy the equatorial sites, and trihydrogeno derivatives, are relatively strongly coordinated.

Introduction

We previously [1] discussed the geometry of the interaction involved in intramolecular coordination by a suitably placed donor atom, especially nitrogen, that results in an increase of the coordination number of a silicon atom from four to five.

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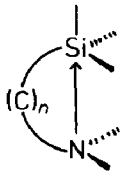
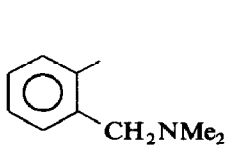


n = 3 or 4

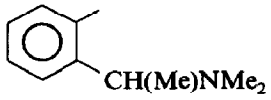
Fig. 1.

It was shown that the donor atom always occupied an axial site in an approximately trigonal bipyramidal geometry, with the chelate ring spanning equatorial and axial positions, irrespective of whether a five-membered or a six-membered ring was formed (Fig. 1). We now consider in more detail the question of the site preferences of the remaining substituents around the central atom (which may be expressed [2] in the form of an "apicophilicity series"), and the way in which the stability of the hypervalent species formed is related to the nature and positioning of these substituents.

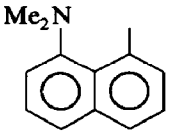
The compounds we have examined are silyl derivatives of the chelating ligands L^1, L^2, and L^3, discussed earlier [1]. The presence of these ligands permits the synthesis of compounds containing a wide range of substituents, both functional and non-functional, that satisfy the fundamental tetracovalency of the silicon atom.



L¹



L²



L³

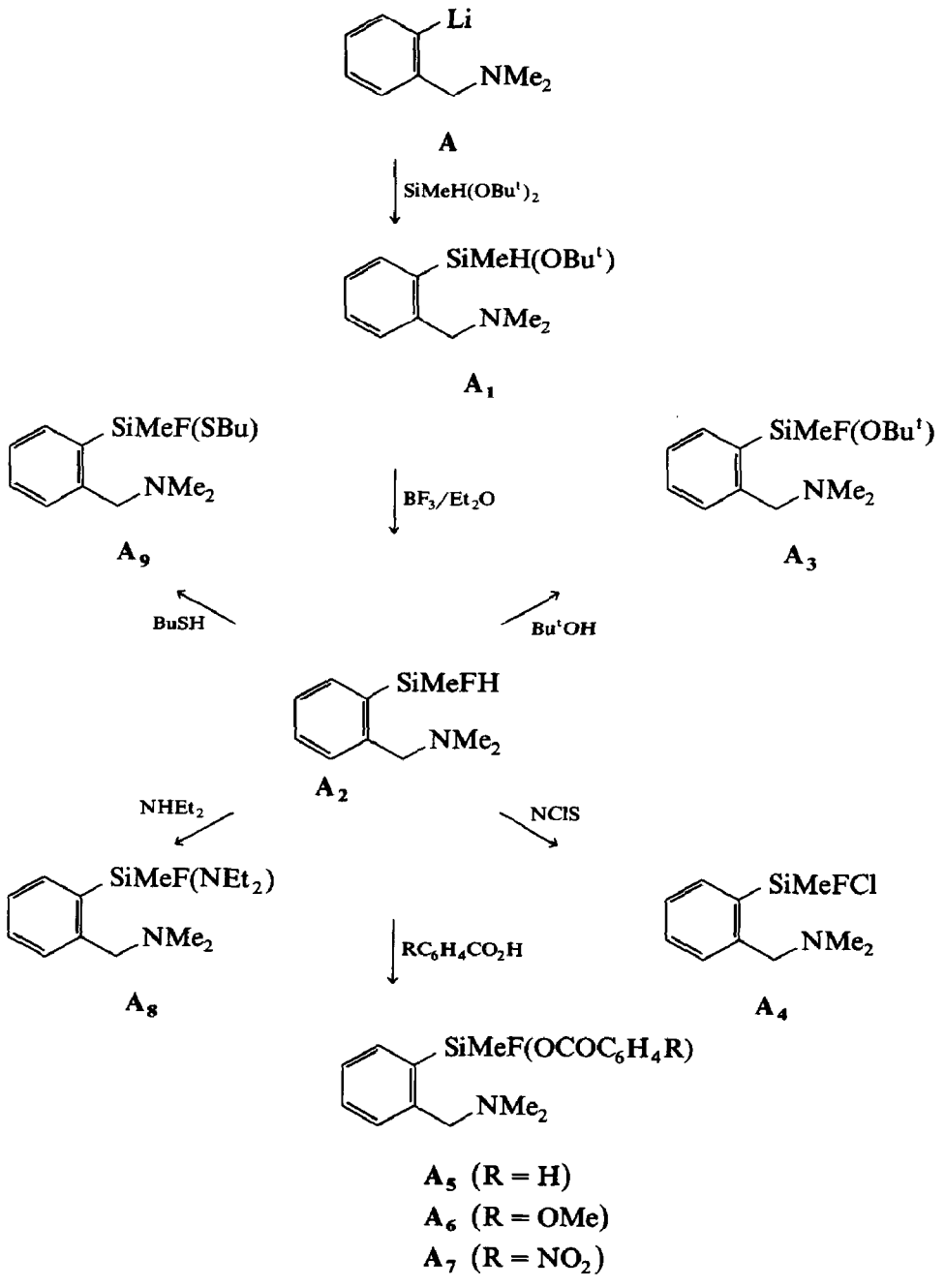
The structures of only a few such compounds have been determined by X-ray diffraction studies, which provided unambiguous information about molecular topology and bond lengths [3]. More comprehensive data have been provided by NMR studies, particularly involving ^1H, ^{19}F, and ^{29}Si spectra. The temperature-dependent dynamic NMR spectra may be used to provide a measure of the stability of the intramolecular coordination and the nature of the isomerisation processes that may occur as a result of the fission and reformation of this bond, whilst the limiting low temperature spectra indicate the most stable configuration of each chelate. In certain cases, the regular permutational isomerisation of the pentacoordinate species can also be studied.

Preliminary accounts of part of the results discussed here have appeared [4].

Results

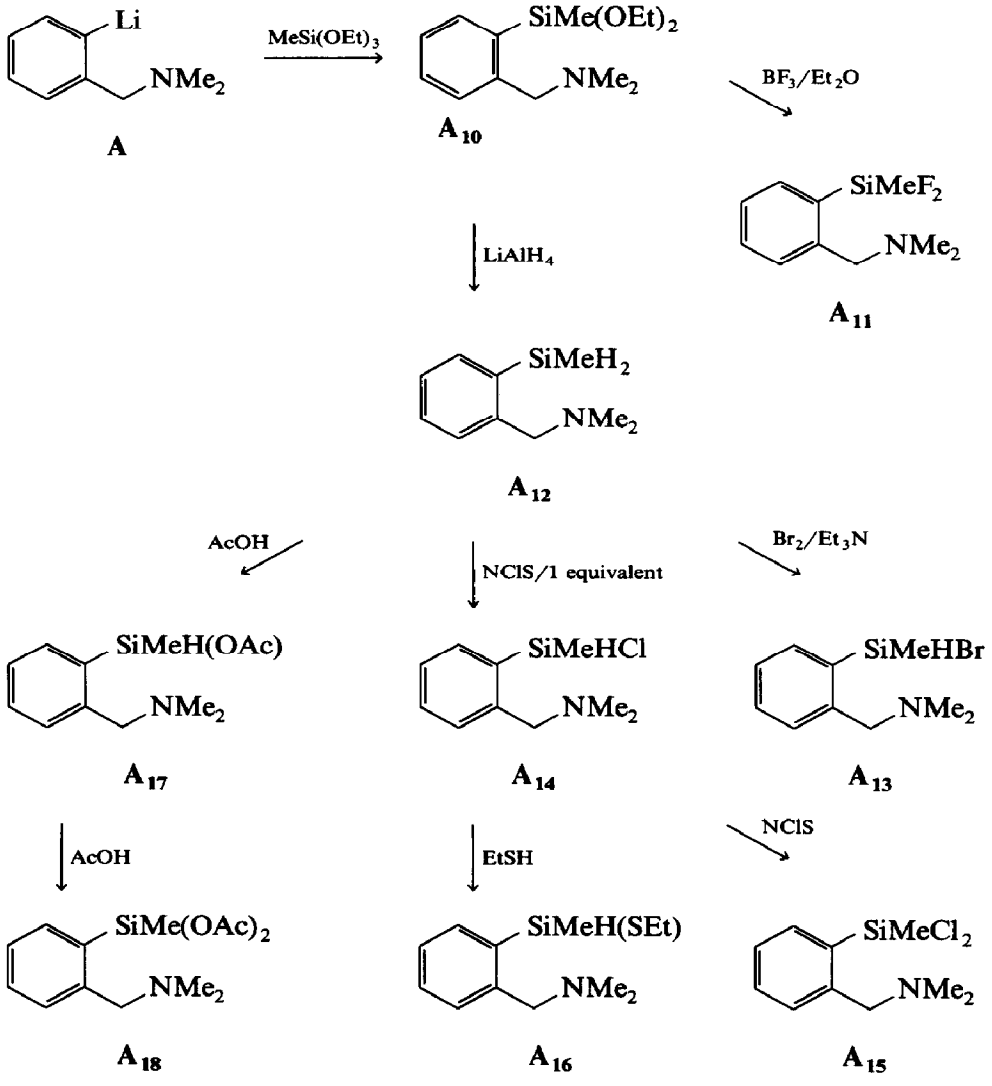
Starting materials were prepared by standard routes, as outlined in Schemes 1–6. ^1H NMR data are given in Tables 1 and 2, and ^{19}F NMR data in Table 3.

Fluorination by boron trifluoride etherate of the butoxy derivative $\mathbf{A_1}$ gave some 20% of the difluoro compound $Me_2NCH_2C_6H_4SiMeF_2$ ($\mathbf{A_{11}}$), presumably as the result of disproportionation, in addition to the desired fluorosilane, $\mathbf{A_2}$. As the latter



Scheme 1

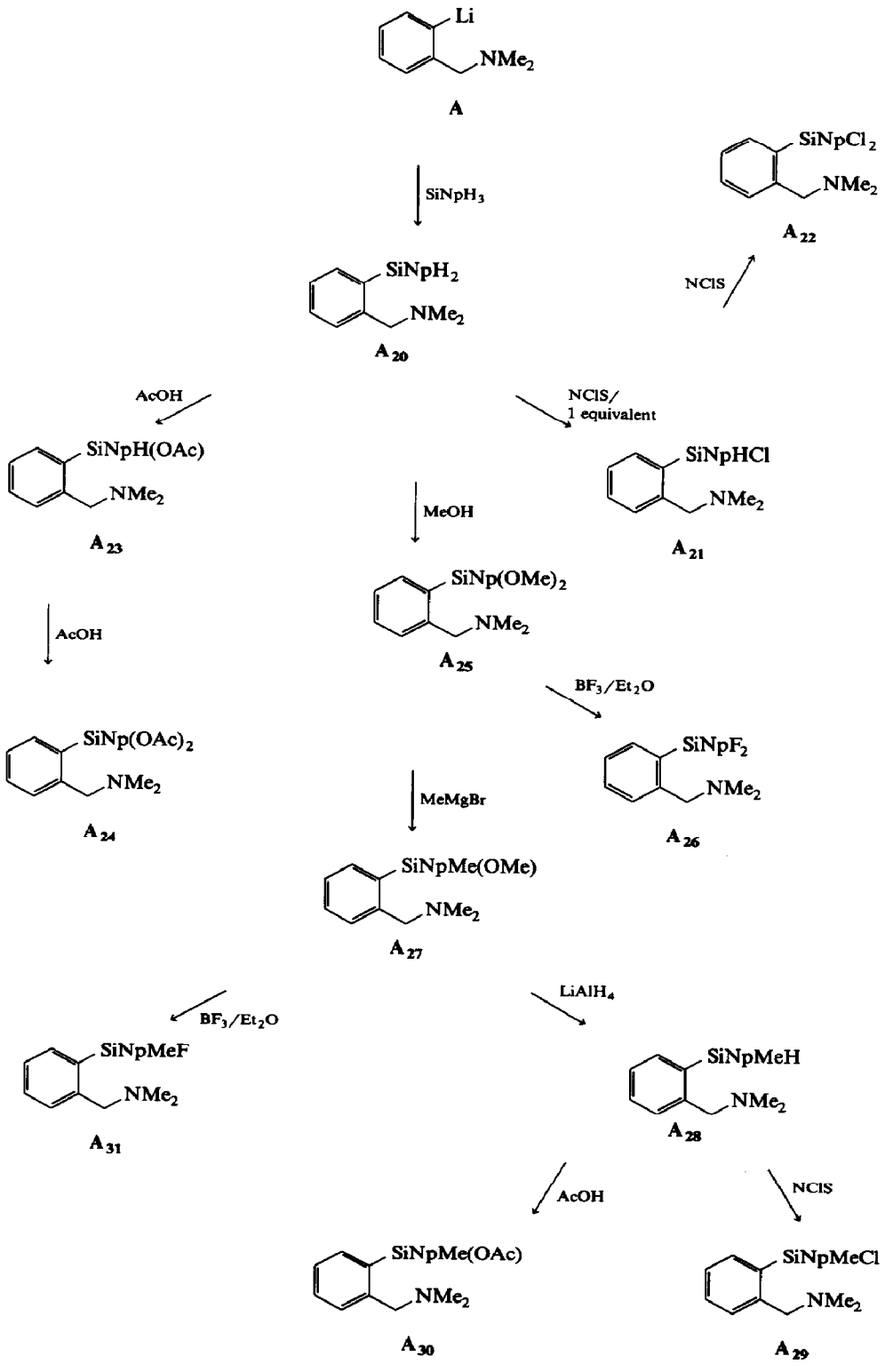
compound was the source of the remaining members of the series A_3–A_9, by further substitution they were also contaminated by A_{11}. In fact it seems that in most of these cases additional disproportionation of A_2 or of the product had occurred during the reaction, since the proportion of A_{11} in the product increased further. Such disproportionation is relatively common amongst fluorosilanes, and a similar



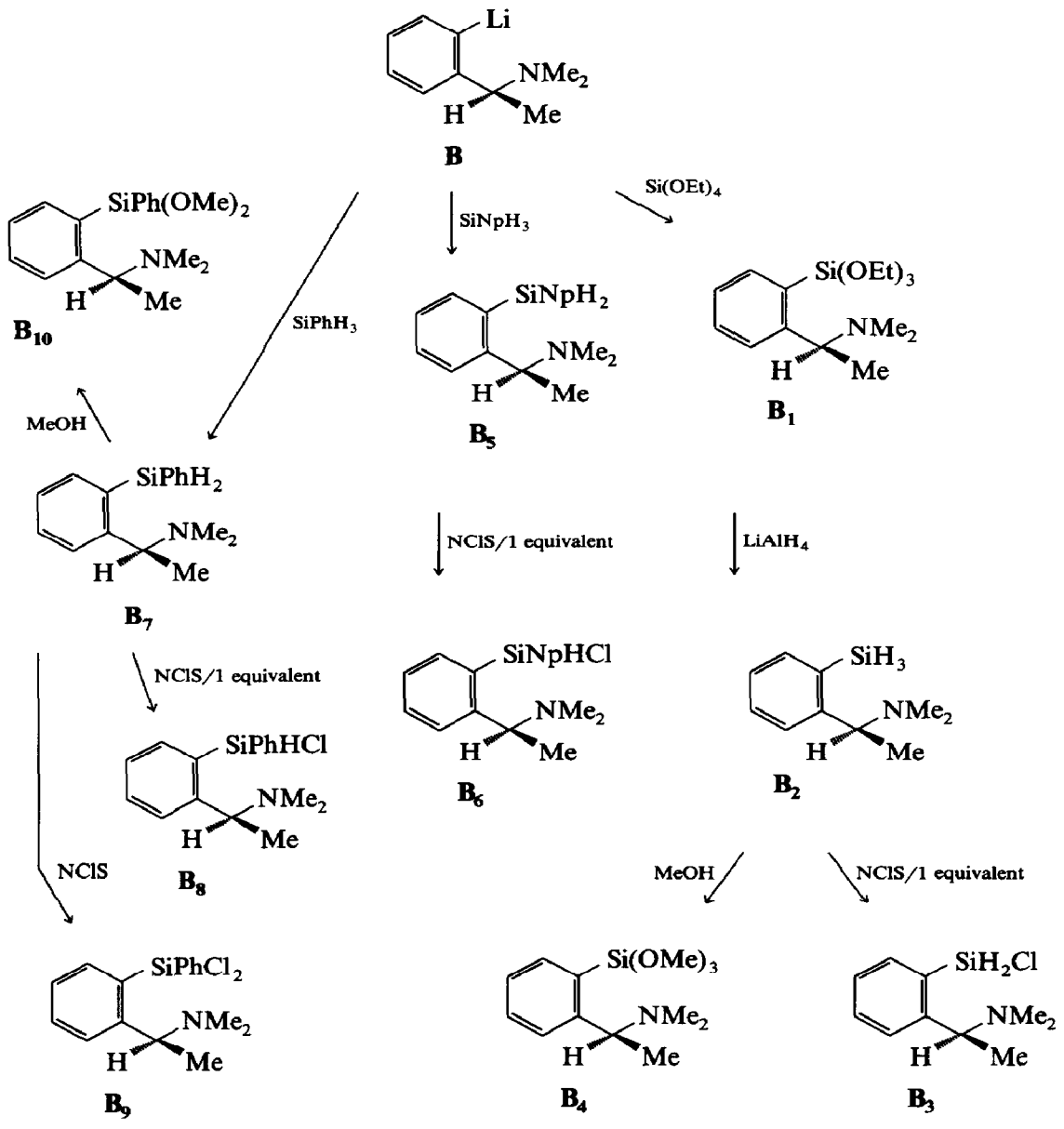
Scheme 2

redistribution reaction is the source of **1**, involving interaction of the trichloro- and trifluoro-silyltetrahydrophenanthrolines [5]. However the most important feature for our purposes, the shift of the ^{19}F NMR resonance of the desired compound on variation of the temperature, could always be observed unambiguously. (The difluoro compound, which was fully characterised, in fact functioned as an internal marker for these spectra at the lower temperatures).

Characteristic ^{1}H NMR spectra are shown in Fig. 2 for compound $\mathbf{A}_{14}$ at 30 °C and −50 °C. They are very similar to the published [6] spectra for the tin derivative **2** at 123 °C and 10 °C. They show in particular the single resonance for the NMe_2 groups at the higher temperatures, which is resolved into two separate singlets at the lower temperatures, and the AB quartet for the resonances of the methylene ($-CH_2N<$) protons due to the chirality of the silicon (and tin) atoms when


Li
NMe2
A
SiNpH3
SiNpH2
NMe2
A20
SiNpCl2
NMe2
A22
NClS
AcOH
SiNpH(OAc)
NMe2
A23
NClS/
1 equivalent
SiNpHCl
NMe2
A21
MeOH
SiNp(OMe)2
NMe2
A25
AcOH
SiNp(OAc)2
NMe2
A24
BF3/Et2O
SiNpF2
NMe2
A26
MeMgBr
SiNpMe(OMe)
NMe2
A27
BF3/Et2O
SiNpMeF
NMe2
A31
LiAlH4
SiNpMeH
NMe2
A28
AcOH
NClS
SiNpMe(OAc)
NMe2
A30
SiNpMeCl
NMe2
A29

Scheme 3

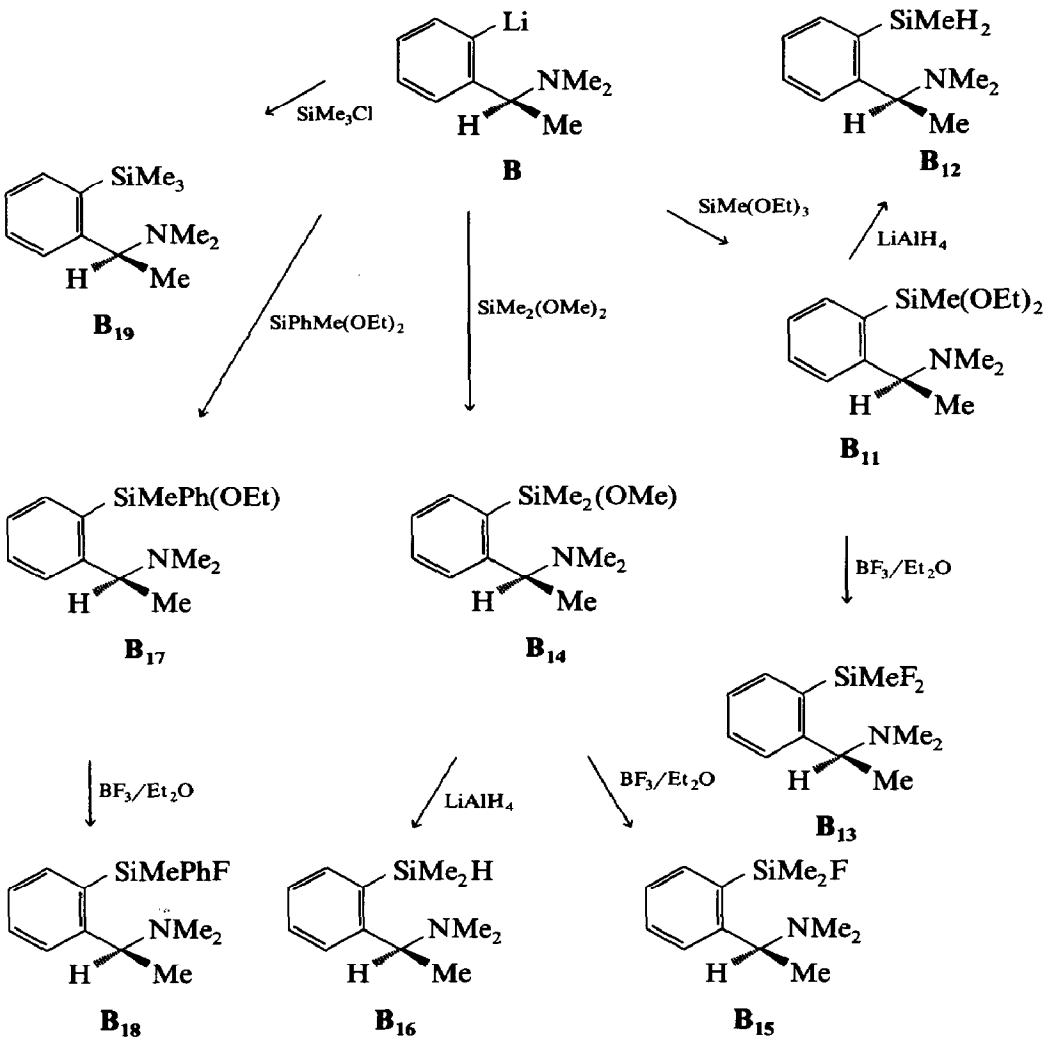


Scheme 4

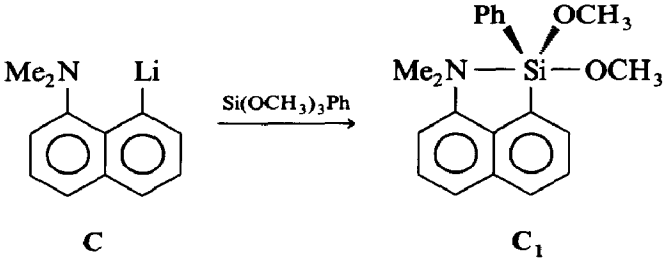
four-coordinate as well as five-coordinate. Coalescence temperatures for the Me_2N resonances, and the free energies of activation at these temperatures for the equivalence process, $\Delta G^{\ddagger}_{(TC)}$, derived by means of the Eyring equation, are given in Tables 4–7.

Discussion

The data obtained provide much information about the case of formation of the N→Si bond and the structure of the resulting chelates. Given the preference of the



Scheme 5



Scheme 6

donor atom to occupy an axial site, the question of the apicophilicity of the remaining substituents (excluding the bond to the carbon atom of the chelating ligand) can be considered in terms of the competition among these substituents for the opposite axial site.

Table 1

^{1}H NMR data for 2-(dimethylaminomethyl)phenylsilanes (δ ppm/TMS; J Hz)

Compound [a]	Temp., °C	$\delta N(CH_3)_2$	δNCH_2-	δ Other
A_1 $L^1SiMeH(OBu^t)$	30 [b]	2.20 (s)	3.32, 3.62 (2d) J(H,H) 12	0.3 (d, SiMe) J(H,H) 3 4.3 [s,$OC(CH_3)_3$] 5.0 (q, SiH) J(H,H) 3 7.0–7.9 (4H,ar)
A_2 $L^1SiMeFH$	30	2.20 (s)	3.53 (s)	0.26 (d of d,SiMe) J(H,H) 3 J(H,F) 7 4.56 (d of q,SiH) J(H,H) 3 J(H,F) 7 6.9–7.4 (3H,ar) 7.8 (1H,ar)
	−90	2.23, 2.33 (2s)	3.62, 3.77 (2d) J(H,H) 13	
A_3 $L^1SiMeF(OBu^t)$	30	2.13 (s)	3.26, 3.73 (2d) J(H,H) 12	0,36 (d,SiMe) J(H,F) 7 1.30 [s,$OC(CH_3)_3$] 6.8–7.6 (4H,ar)
	−100	1.90, 2.10 (2s)		
A_4 $L^1SiMeFCl$	30	2.28 (s)	3.53 (s)	0.73 (d, SiMe) J(H,F)5 7.0–8.1 (4H,ar)
	−60	2.22, 2.36 (2s)		
A_5 $L^1SiMeF(OCOC_6H_5)$	30	2.20 (s)	3.63 (s)	0.64 (d, SiMe) J(H,F) 5 7.0–8.2 (9H,ar)
A_6 $L^1SiMeF(OCOC_6H_4OMe)$	30	2.13 (s)	3.50 (s)	0.5 (d, SiMe) 3.80 (s, OMe) 6.8–8.1 (8H,ar)
A_7 $L^1SiMeF(OCOC_6H_4NO_2)$	30 [c]	2.46 (s)	3.66 (s)	0.68 (d, SiMe) J(H,F) 5 7.1–8.3 (8H,ar)
A_{10} $L^1SiMe(OEt)_2$	30	2.16 (s)	3.5 (s)	0.28 (s,SiMe) 1.23 (t,OCH_2CH_3) 3.63 (q,OCH_2CH_3) 7.1–7.9 (4H,ar)
A_{11} L^1SiMeF_2	30	2.25 (s)	3.58 (s)	0.40 (t,SiMe) J(H,F) 6 7.0–7.5 (3H,ar) 7.9 (1H,ar)
	−110	2.24, 2.45 (2s)	3.56, 3.83 (2d) J(H,H) 13	

(*continued*)

Table 1 (continued)

Compound [a]	Temp., °C	$\delta N(CH_3)_2$	δNCH_2-	δ Other
A_{12} L^1SiMeH_2	30	2.30 (s)	3.50 (s)	0.40 (t,$SiCH_3$) J(H,H) 4 4.40 (q,SiH_2) J(H,H) 4 7.0–7.5 (3H,ar) 7.9 (1H,ar)
A_{13} $L^1SiMeHBr$	30	2.43 (s)	3.86 (s)	0.86 (d,SiMe) J(H,H) 3 5.4 (q,SiH) J(H,H) 3 7.0–8.4 (4H,ar)
	−20	2.43 2.36 (2s)		
A_{14} $L^1SiMeHCl$	30 [b]	2.25 (s)	3.50 3.70 (2d) J(H,H) 15	0.83 (d,SiMe) J(H,H) 3 5.3 (q,SiH) J(H,H) 3 7.0–7.7 (3H,ar) 8.3 (1H,ar)
	−50	2.4 2.5 (2s)	3.80 3.93 (2d) J(H,H) 15	
A_{15} $L^1SiMeCl_2$ [d]	30	2.22 (s)	3.6 (s)	1.0 (s, SiMe) 7.0–8.2 (3H,ar) 8.5 (1H,ar)
	−70	2.22 (br)		
A_{16} $L^1SiMeH(SEt)$	30	2.13 (s)	3.23 3.71 (2d) J(H,H) 12	0.5 (d,SiMe) J(H,H) 3 1.2 (t,SCH_2CH_3) J(H,H) 7 2.4 (q,SCH_2CH_3) 4.9 (q,SiH) J(H,H) 3 7.0–8.6 (4H,ar)
A_{17} $L^1SiMeH(OAc)$	30	2.23 (s)	3.6 (m,br)	0.3 (d,SiMe) J(H,H) 3 2.0 (s,OCOMe) 4.7 (q,SiH) J(H,H) 3 7.0–7.4 (3H,ar) 7.75 (1H,ar)
A_{18} $L^1SiMe(OAc)_2$ [d]	30	1.7 (s)	3.3 (s)	0.3 (s,SiMe) 1.9 [s,$(OOCCH_3)_2$] 6.8–7.6 (4H,ar)
A_{20} L^1SiNpH_2	30	2.1 (s)	3.50 (s)	5.10 (s,SiH_2) 7.0–8.0 (11H,ar)
A_{21} $L^1SiNpHCl$	30	1.7 (s)	3.32 (s)	6.0 (s,SiH) 7.0–8.5 (11H,ar)
	−10	1.20 1.85 (2s)		

(*continued*)

Table 1 (continued)

Compound [a]	Temp., °C	$\delta N(CH_3)_2$	δNCH_2-	δ Other
A_{22} $L^1SiNpCl_2$	30	1.67 (s)	3.54 (s)	7.0–8.8 (11H,ar)
	−65	1.46 (2s) 2.50	3.32 (2d) 4.23 J(H,H) 15	
A_{23} $L^1SiNpH(OAc)$	30 [c]	1.7 (s)	3.33 (2d) 3.58 J(H,H) 15	1.9 [s,OOC(CH_3)] 5.9 (s,SiH) 7.0–8.6 (11H,ar)
	−30 [c]	1.32 (2s) 2.22		
A_{24} $L^1SiNp(OAc)_2$	30 [c]	1.63 (s)	3.32 s)	2.0 [s,($OOCCH_3$)$_2$] 7.0–8.6 (11H,ar)
A_{25} $L^1SiNp(OMe)_2$	30 [c]	1.66 (s)	3.33 (s)	3.5 [s,($OMe)_2$] 7.2–8.4 (11H,ar)
A_{26} L^1SiNpF_2	30	1.8 (s)	3.5 (s)	7.1–8.4 (11H,ar)
A_{27} $L^1SiNpMe(OMe)$	30 [b]	1.7 (s)	3.1 (s)	0.73 (s,SiMe) 3.3 (s,SiOMe) 7.1–8.1 (11H,ar)
A_{28} $L^1SiNpMeH$	30 [b]	1.8 (s)	3.3 (s)	0.6 (d,SiMe) J(H,H) 3 5.3 (q,SiH) J(H,H) 3 7.1–8.1 (11H,ar)
A_{29} $L^1SiNpMeCl$	30 [b]	1.5 (s)	2.80 (2d) 3.10 J(H,H) 12	0.96 (s,SiMe) 7.0–8.5 (11H,ar)
	−40	1.55 (2s) 1.70	3.25 (2d) 3.40 J(H,H) 12	
A_{30} $L^1SiNpMe(OAc)$	30	2.1 (s)	3.5 (s)	0.7 (s,SiMe) 2.4 [s,OOC(CH_3)] 7.0–8.3 (11H,ar)
A_{31} $L^1SiNpMeF$	30	1.53 (s)	3.1 (s)	0.86 (d,SiMe) J(H,F) 7 7.0–8.3 (11H,ar)
	−80	1.0 (2s) 1.96		

[a] L^1 = 2-(Me_2NCH_2)C_6H_4. Solvent: CD_2Cl_2. [b] Solvent: CCl_4. [c] Solvent: $CDCl_3$. [d] The previously reported [4a] NMR data at low temperature proved to be incorrect. The value of $\Delta G^{\ddagger}$ for these compounds (cf. Table 6) is probably in the region of 9 kcal mol^{-1}.

In acyclic and in chelated five-coordinate silicon species (as in the analogous phosphorus compounds [7]), the limiting low temperature ^{19}F NMR spectra of di- and tri-fluoro derivatives clearly distinguish fluorine atoms in axial sites (low field) from those in equatorial sites (high field) in the trigonal bipyramid [8]. The temperature-dependent ^{19}F NMR spectra of bifunctional fluorosilanes $L^1SiMeFX$ (A_3–A_9) thus serve to establish the apicophilicity of X relative to fluorine by the direction of the shift of the fluorine resonance at low temperatures. A shift to lower

(continued on p. 13)

Table 2

^{1}H NMR data for 2-[1-(dimethylamino)ethyl]phenylsilanes (δ ppm/TMS; J Hz)

Compound [a]	Temp., °C	δ $N(CH_3)_2$	δ $NCHCH_3$	δ $NCHCH_3$	δ Other
B_1 $L^2Si(OEt)_3$	30	2.15 (s)	1.25 (m) (12H) overlaps with $(OCH_2CH_3)_3$	3.45 (q) J(H,H) 7	3.85 (q, OCH_2CH_3)$_3$ J(H,H) 7 7.0–7.8 (4H,ar)
	−110	2.05 (br)			
B_2 L^2SiH_3	30	2.10 (s) J(H,H) 7	1.35 (d) J(H,H) 7	3.60 (q) J(H,H) 7	4.10 (s,SiH_3) 6.9–7.4 (3H,ar) 7.7 (1H,ar)
	−100	1.85 2.24 (2s)			
B_3 L^2SiH_2Cl [b]	+100	1.65 (s)			
	30	1.95 2.35 (2s)	1.35 (d) J(H,H) 7	3.75 (q) J(H,H) 7	4.65 4.85 (2d, SiH_2) J(H,H) 8 6.7–7.3 (3H,ar) 7.8 (1H,ar)
B_4 $L^2Si(OMe)_3$	30	2.15 (s)	1.20 (d) J(H,H) 7	3.35 (q) J(H,H) 7	3.6 [s,$Si(OCH_3)_3$] 6.9–7.8 (4H,ar)
	−110	1.95 2.14 (2s)			
B_5 L^2SiNpH_2	30	2.05 (s)	1.3 (d) J(H,H) 7	3.7 (q) J(H,H) 7	5.05 (s, SiH_2) 6.7–8.1 (11H,ar)
	−100	2.00 2.40 (2s)			5.02 5.12 (2d, SiH_2) J(H,H) 3
B_6 $L^2SiNpHCl$ (2 diastereomers)	30	1.60 1.70 (2s)	1.20 1.25 (2d) J(H,H) 7	3.70 3.90 (2q) J(H,H) 7	5.85 6.10 (2s,SiH) 7.0–8.6 (11H,ar)
	−25	1.20 2.30 1.70 2.10 (4s)			
B_7 L^2SiPhH_2	30	2.0 (s)	1.30 (d) J(H,H) 7	3.65 (q) J(H,H) 7	4.65 (s,SiH_2) 6.8–7.5 (9H,ar)
	−100	1.84 2.34 (2s)			
B_8 $L^2SiPhHCl$ (2 diastereomers)	30	1.70 1.85 (2s)	1.25 1.30 (2d) J(H,H) 7	3.65 3.85 (2q) J(H,H) 7	5.40 5.55 (2s,SiH) 6.7–8.4 (9H,ar)
	−40	1.25 2.40 1.90 2.05 (4s)			

(*continued*)

Table 2 (continued)

Compound [a]	Temp., °C	δ $N(CH_3)_2$	δ $NCHCH_3$	δ $NCHCH_3$	δ Other
B_9 $L^2SiPhCl_2$	30	1.65 (s)	1.30 (d) J(H,H) 7	4.05 (q) J(H,H) 7	7.40 (8H,ar) 8.40 (1H,ar)
	−90	2.0 [c] 2.44 1.25 1.98 (4s)		3.98 4.42 (2q)	
B_{10} $L^2SiPh(OMe)_2$	30	1.75 (s)	1.05 (d) J(H,H) 7	3.20 (m) 3.70 7H overlaps with $(OCH_3)_2$	6.8–7.6 (8H,ar) 7.9 (1H,ar)
	−110	1.75 (br)			
B_{11} $L^2SiMe(OEt)_2$	30	2.15 (s)	1.25 (m) (9H) overlaps with $(OCH_2CH_3)_2$	3.40 (m) 4.10 5H overlaps with OCH_2CH_3	0.30 (s,$SiCH_3$) 6.90–7.80 (4H,ar)
B_{12} L^2SiMeH_2	30	2.10 (s)	1.30 (s) J(H,H) 7	3.65 (q) J(H,H) 7	0.25 (t,SiMe) J(H,H) 4 4.25 (q,SiH_2) J(H,H) 4 7.20 (3H,ar) 7.60 (1H,ar)
	−100	1.80 2.25 (2s)			
B_{13} L^2SiMeF_2	30	2.15 (s)	1.35 (d) J(H,H) 7	3.75 (q) J(H,H) 7	0.35 (t,SiMe) J(H,F) 6 7.20 (3H,ar) 7.80 (1H,ar)
	−100	1.75 [c] 2.05 2.35 2.50 (4s)		3.80 4.05 (2q)	
B_{14} L^2SiMe_2OMe	30	2.10 (s)	1.20 (d) J(H,H) 7	3.4 (q) J(H,H) 7	0.35 [s,$Si(CH_3)_2$] 3.3 (s,$SiOCH_3$) 6.9–7.5 (4H,ar)
	−100	2.20 (br)			0.42 0.47 [2s,$Si(CH_3)_2$]
B_{15} L^2SiMe_2F	30	2.10 (s)	1.25 (d) J(H,H) 7	3.65 (q) J(H,H) 7	0.35 [d,$Si(CH_3)_2$] J(H,F) 8 7.4 (3H,ar) 7.7 (1H,ar)
	−100	1.70 2.35 (2s)			
B_{16} L^2SiMe_2H	30	2.10 (s)	1.30 (d) J(H,H) 7	3.50 (q) J(H,H) 7	0.30 [d,$Si(CH_3)_2$] J(H,H) 4 4.40 (m,SiH) J(H,H) 4 6.9–7.6 (4H,ar)
	−100	2.10 (br)			

(*continued*)

Table 2 (continued)

Compound [a]	Temp., °C	δ $N(CH_3)_2$	δ $NCHCH_3$	δ $NCHCH_3$	δ Other
B_{17} $L^2SiMePhOEt$ (2 diastereomers)	30	1.80 (s)	0.9–1.3 (6H,m) overlaps with OCH_2CH_3	3.1–3.9 (3H,m) overlaps with OCH_2CH_3	0.65 (s,$SiCH_3$) 6.80–7.80 (9H,ar)
B_{18} $L^2SiMePhF$ (2 diastereomers)	30	1.70 (s)	1.15 (d) J(H,H) 7	3.45 (2q) 3.75 J(H,H) 7	0.60 0.62 2d,SiMe, J(H,F) 8 7.0–7.6 (8H,ar) 7.9 (1H,ar)
	−100	1.50 1.65 (br)			
B_{19} L^2SiMe_3	30	2.15 (s)	1.25 (d) J(H,H) 7	3.30 (q) J(H,H) 7	0.30 [s,$Si(CH_3)_3$] 6.9–7.6 (4H,ar)
	−110	2.10 (s)			

[a] L^2 = 2-[$Me_2NCH(CH_3)$]C_6H_4. Solvent: CCl_4 (T = +30 °C), CD_2Cl_2 (T < 30 °C). [b] Solvent: $C_6D_5CD_3$. [c] Two diastereomers at low temperature.

field on cooling indicates preferential occupation by fluorine of an axial site, and a shift to higher field, occupation of an equatorial site.

The data in Table 3 show that fluorine is more apicophilic than hydrogen, alkoxy or dialkylamino, but less apicophilic than chlorine. Thioalkoxy seems to be of comparable apicophilicity to fluorine. Where X = benzoyloxy, both topomers can be

Table 3

^{19}F NMR data [a] for bifunctional fluorosilanes (δ ppm/$CFCl_3$; J/Hz)

Compound [b]	δ (F) at +30 °C	δ (F) at −90 °C
A_2 $L^1SiMeFH$	−134.5 [d of q, ^2J(F,H) 81] [^3J(F,H) 7.5]	−122.5 (d of q, F_{ax})
A_3 $L^1SiMeF(OBu^t)$	−129.3 [q, ^3J(F,H) 7.5]	−119.4 (br, F_{ax})
A_4 $L^1SiMeFCl$	−136.0 [q, ^3J(F,H) 6]	−142.0 (br, F_{eq})
A_5 $L^1SiMeF(OCOC_6H_5)$	−144.5 [q, ^3J(F,H) 7]	−156.3 (s, F_{eq}, 73%) −115.2 (s, F_{ax}, 27%)
A_6 $L^1SiMeF(OCOC_6H_4NO_2)$	−150.0 (br)	−156 (br, F_{eq}, 86%) −113 (br, F_{ax}, 14%)
A_7 $L^1SiMeF(OCOC_6H_4OMe)$	−142.7 (q, ^3J(F,H) 6)	−156.6 (br, F_{eq}, 64%) −116.0 (br, F_{ax}, 36%)
A_8 $L^1SiMeF(NEt_2)$	−130.7 [q, ^3J(F,H) 6]	−118 (br, F_{ax})
A_9 $L^1SiMeF(SBu)$	−131.8 (br)	−128.0 (br, F_{ax})
A_{11} L^1SiMeF_2	−137.0 [q, ^3J(F,H) 7]	−154.6 [d,F_{eq}, J(F,F) 15] −111 (br, F_{ax})
B_{13} L^2SiMeF_2	−130.7 (s) 2 diastereotopic F −137.9 (s)	−150.0 (s,F_{eq}) −108.3 (s,F_{ax}) 2 diastereomers −159.5 (s,F_{eq}) at −75 °C −114.5 (s,F_{ax})

[a] Solvent: CD_2Cl_2 [b] L^1 = 2-[Me_2NCH_2]C_6H_4. L^2 = 2-[$Me_2NCH(CH_3)$]C_6H_4.

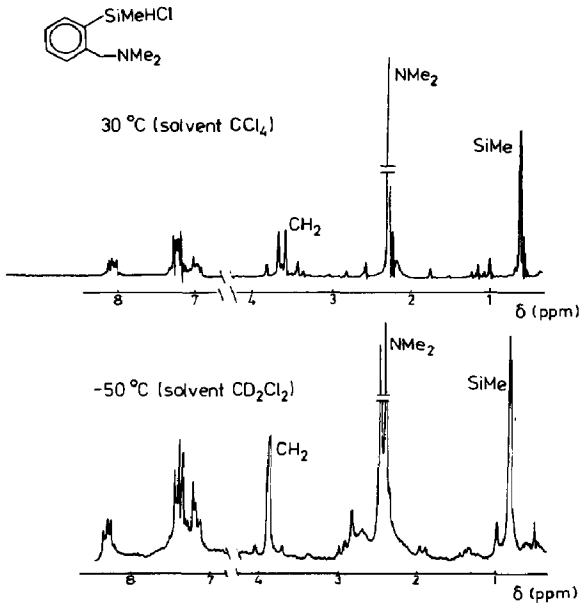
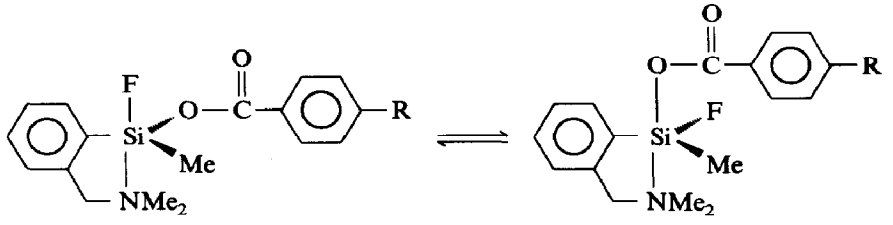


Fig. 2. The ^{1}H NMR spectra of A_{14}.

seen to be present at −95 °C. Although that with F equatorial always predominates, the precise position of the equilibrium is sensitive to substitution in the *para* position of the benzoyloxy moiety, an electron-withdrawing group causing an increase in the proportion of the topomer having the benzoyloxy group in the axial position as a result of increasing the apicophilicity of the group (equation 1).



(1)

Table 4

Free energies of activation ($\Delta G^{\ddagger}$) for NMe_2 equivalence of monofunctional compounds

Compound [a]	$\Delta G^{\ddagger}$, kcal mol^{-1}	T_c, °C
A_{28} $L^1SiNpMeH$	not measurable [b]	–
A_{31} $L^1SiNpMeF$	10,3	−65
A_{30} $L^1SiNpMe(OAc)$	12,0	−35
A_{29} $L^1SiNpMeCl$	12,3	−35 [c]
B_{16} L^2SiMe_2H	not measurable [b]	–
B_{15} L^2SiMe_2F	9.7	−70
$B_{18}L^2SiMePhF$	10	−73

[a] L^1 = 2-$(Me_2NCH_2)C_6H_4$; L^2 = 2-$[Me_2NCH(CH_3)]C_6H_4$. [b] Singlet NMe_2 down to lowest temperatures attainable (−100 °C). [c] Solvent: CCl_4.

Table 5

Free energies of activation ($\Delta G^{\ddagger}$) for NMe_2 equivalence of chelated hydrogenosilanes bearing one other functional group

Compound [a]	$\Delta G^{\ddagger}$ kcal mol^{-1}		T_c, °C
A_1 $L^1SiMeH(OBu^t)$	not measurable [b]		–
A_{16} $L^1SiMeH(SEt)$	10.8		−65
A_2 $L^1SiMeHF$	11.5		−52
A_{17} $L^1SiMeH(OAc)$	11.7		−46
A_{14} $L^1SiMeHCl$	12.3		−40
A_{21} $L^1SiNpHCl$	13		+1 [c]
A_{23} $L^1SiNpH(OAc)$	13		+16 [d]
A_{13} $L^1SiMeHBr$	13.8		−10
B_8 $L^2SiPhHCl$	13.4 14.3	2 diastereomers	+10
B_6 $L^2SiNpHCl$	13.6 14.1	2 diastereomers	+12

[a] $L^1 = 2\text{-}(Me_2NCH_2)C_6H_4$; $L^2 = 2\text{-}[Me_2NCH(CH_3)]C_6H_4$. [b] Singlet NMe_2 down to lowest temperatures attainable (−100 °C). [c] Solvent: CCl_4. [d] Solvent: $CDCl_3$.

Table 6

Free energies of activation ($\Delta G^{\ddagger}$) for equivalence of NMe_2 groups in bifunctional compounds

Compound [a]	$\Delta G^{\ddagger}$, kcal mol^{-1}	T_c, °C
A_{10} $L^1SiMe(OEt)_2$	not measurable [b]	–
A_{20} L^1SiNpH_2	see text	–
A_{11} L^1SiMeF_2	8.8	−90
A_2 $L^1SiMe(OMe)F$	9	−90
A_{22} $L^1SiNpCl_2$	10.6	−50 [c]
A_4 $L^1SiMeFCl$	11.8	−40 [d]
B_{10} $L^2SiPh(OMe)_2$	< 8 [e]	< −110
B_{12} L^2SiMeH_2	9	−86
B_{13} L^2SiMeF_2	9.4 [f] 11.8 [g]	−75 −25
B_5 L^2SiNpH_2	9.7	−72
B_7 L^2SiPhH_2	10.0	−65
B_9 $L^2SiPhCl_2$	11.1 [f] 12.2 [g]	−45 −17

[a] $L^1 = 2\text{-}(Me_2NCH_2)C_6H_4$; $L^2 = 2\text{-}[Me_2NCH(CH_3)]C_6H_4$. [b] Singlet NMe_2 down to lowest temperatures attainable (−100 °C). [c] Solvent: $CCl_4 + CDCl_3$. [d] Solvent: $CCl_4 + CD_2Cl_2$. [e] Significant broadening at this temperature. [f] With respect to chiral Si centre. [g] With respect to chiral C centre.

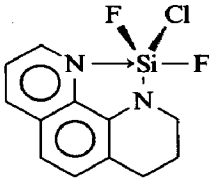
Table 7

Free energies of activation ($\Delta G^{\ddagger}$) for equivalence of NMe_2 groups in trifunctional compounds

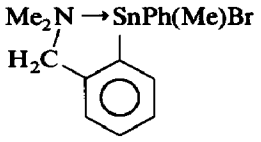
Compound	$\Delta G^{\ddagger}$, kcal mol^{-1}	T_c, °C
B_4 $L^2Si(OMe)_3$	7.6	−110
B_2 L^2SiH_3	10	−66
B_3 L^2SiH_2Cl	16.7	+60
B_{19} L^2SiMe_3	not measurable [a]	–

[a] Singlet NMe_2 down to lowest temperatures attainable (−100 °C).

Other structural data permit the ordering of the less apicophilic substituents on the silicon atom. The ^1H NMR spectrum of compound C_1 at $-100\,^\circ C$, showing the *N*-methyl and *O*-methyl groups to be diastereotopic, shows that the configuration about the silicon atom is that depicted, and thus that methoxy is more apicophilic than phenyl [9]. Similarly the structures established by X-ray diffraction for the



1



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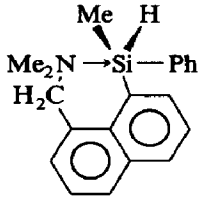

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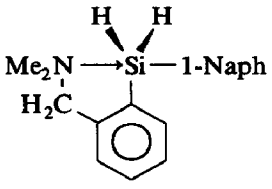
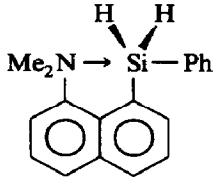


A_{20}

hydrogenosilanes A_{20} [1] and C_2 [10] show in turn that aryl groups are more apicophilic than hydrogen, and the structure of **3** [10] finally places methyl below phenyl. The relative positions of hydrogen and the organic groups in the series are supported by the NMR data to be discussed below, and lead to the extended apicophilicity series for substituents on the silicon atom in these intramolecularly coordinated compound:

$$H < \text{alkyl} < \text{aryl} < OR, NR_2 < F \approx SR < Cl, OCOR$$

Whilst this order is no doubt broadly applicable, variations in detail may be expected in certain cases; for example fluorine appears to be more apicophilic than chlorine in compound **1** [5]. This may in part be due to the fact that a nitrogen

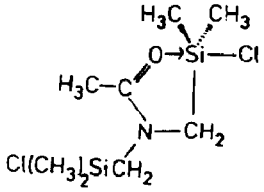


C_2

atom, with a lone pair, rather than a carbon atom, is bonded to silicon in an equatorial position but it also indicates that the factors which determine the relative positions of fluorine and chlorine are finely balanced. In phosphoranes, fluorine is the more apicophilic, and, at least in acyclic compounds, it is generally accepted that the electronegativity is the dominant factor [11], though recent theoretical studies have suggested that fluorine is more electrophilic than chlorine only when the remaining substituents are also of high electronegativity [12]. In the silicon compounds the order of apicophilicity seems rather to reflect the ability of the *trans*

apical bond in these chelates to be stretched under the influence of the donor nitrogen atom.

The pronounced effect of coordination on the length of the *trans* axial bond is strikingly illustrated in compound **4** [13], where the Si–Cl distance for the four-coor-



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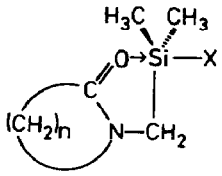
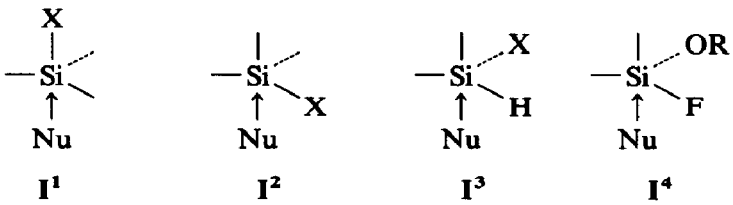


5 $n = 3$; X=F
6 $n = 4$; X=Cl

dinate silicon atom is 2.05 Å, and for the five-coordinate one, 2.35 Å. A similar feature is evident in other five-coordinate complexes containing Si–Cl or Si–F bonds [3]. The greater case of elongation of Si–Cl than of Si–F bonds may be seen in compounds **5** [14] and **6** [15], for which X-ray structural data show Si–F = 1.65 Å and Si–Cl = 2.31 Å, compared with the relevant "standard" bond lengths [16] of 1.52 Å and 2.02 Å, respectively.

The situation with respect to hydrogen is also interesting in that this element shows a marked preference for equatorial sites, while enhancing significantly the acceptor properties of the silicon atom. Its low position in the apicophilicity series also contrasts with the high apicophilicity assigned to it in phosphoranes by Trippett [2(b)], mainly on the basis of dynamic NMR studies of a series of compounds containing highly-strained four-membered C–C–C–P ring systems. The barriers to the interconversion of diastereomers which were obtained in these studies however measure the activation energies required to attain the high energy intermediates, rather than the relative stabilities of the ground states, and the "kinetic apicophilicity" deduced from these experiments is here clearly at variance with the low value obtained for the "thermodynamic apicophilicity" [17]. The lower value is, however, supported by the data on the acyclic trifluoromethylphosphoranes [2a] and by the parametrisation by Holmes [18] for the calculation of conformational energies.

The apicophilicity series correlates well with the stereochemistry of nucleophilic substitution reactions at silicon, in that the most apicophilic groups (Cl, OCOR) are invariably substituted with inversion (in acyclic compounds) whereas the least apicophilic functional group (H) is almost always displaced with retention in direct substitutions. The displacement of the more apicophilic groups with inversion clearly results from the intermediate geometry $\mathbf{I}^1$, with the nucleophile and leaving group in axial sites, as expected. Retention similarly requires axial entry of the nucleophile, with the less apicophilic leaving group now initially occupying an equatorial site, $\mathbf{I}^2$. Furthermore, in bifunctional derivatives the more apicophilic

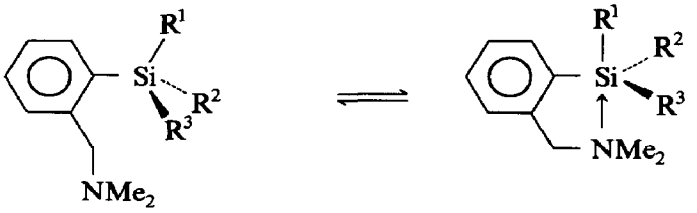


group is generally displaced with inversion; e.g. Cl in 1-NpFcSiFCl [19] and in 1-NpPhSi(OMen)Cl [20]. "Soft" nucleophiles also replace the more apicophilic fluorine atom with inversion of configuration in 1-NpFcSi(OEt)F and 1-NpPhSi(OMen)F [21]. Amongst these less apicophilic substituents however, the nature of the reagent assumed greater importance. Thus in 1-NpFcSiHF [19] and 1-NpPhSi(OMen)H [22], although the more electronegative group is always substituted, both inversion and retention are observed, the latter more particularly with "hard" reagents. Fluoro(alkoxy)-derivatives also react with "hard" nucleophiles with partial or complete displacement of the alkoxy group rather than the fluorine atom, and with retention of configuration [23]. This behaviour implies that in such cases the preferred structure for the intermediate has both groups in equatorial sites, $\mathbf{I}^3$ and $\mathbf{I}^4$.

Aptitude of silicon for pentacoordination

In chiral compounds containing the (dimethylaminomethyl)phenyl group, a single resonance for the *N*-methyl groups is expected in the ^{1}H NMR spectrum unless inversion at the nitrogen atom is significantly hindered, for the barrier to inversion of free amines is normally less than 6 kcal mol^{-1} [24]. The observation of diastereotopic methyl groups in the spectra of many of the silanes studied is therefore an indication that coordination of the NMe_2 group to the silicon has occurred, and that the chelate is chiral. This may be the case for derivatives of ligand $\mathbf{L}^1$ when the tetravalent silicon itself constitutes a chiral centre, or when the increased coordination at the silicon atom is responsible for the generation of chirality (Scheme 7).

An independent probe [25] of coordination is provided in the case of compounds of ligand $\mathbf{L}^2$ by the presence of a stable chiral centre at the benzylic carbon atom, which can also reveal the diastereotopy of the methyl groups attached to the coordinated nitrogen atom. Table 4 lists the coalescence temperatures, and the derived free energies of activation, for the NMR equivalence of the NMe_2 groups in a range of monofunctional silicon compounds containing ligands $\mathbf{L}^1$ and $\mathbf{L}^2$. Table 5 gives similar data for monohydrogenosilanes containing one other functional group. These activation energies reflect the extent to which the inversion of the nitrogen atom is impeded, and may reasonably be taken as a measure of the relative stability of the intramolecular coordination. The order Cl, OAc > F ≫ OMe, H is essentially that of the apicophilicity series.



NMe_2 not diastereotopic,
even if $R^1 \neq R^2 \neq R^3$

NMe_2 diastereotopic
if $R^1 \neq R^2 \neq R^3$
or if $R^2 \neq R^3$; $R^1 = R^2 (R^3)$

Scheme 7

A possible alternative explanation of the coalescence of the methyl resonances, namely that the configuration of the silicon atom is inverted by a regular permutational isomerisation while pentacoordination is maintained, is excluded unambiguously for compounds $\mathbf{A_{14}}$, $\mathbf{A_{23}}$, and $\mathbf{A_{29}}$ by the observation that the diastereotopy of the benzylic protons ($-C_6H_4CH_2N<$) is maintained at all temperatures above and below coalescence, as it is for $\mathbf{A_1}$ for which no splitting of the resonance of the NMe_2 is observed. In other cases e.g. $\mathbf{A_2}$, the diastereotopy of the methylene protons appears only at the lower temperatures; in yet others, e.g. $\mathbf{A_{30}}$, it does not appear at all, but this seems to be due to a chance coincidence of the chemical shifts at the higher temperatures, and the coalescence of the NMe_2 group resonances, when observed in these cases, can also be attributed to inversion at the nitrogen atom.

In the case of the monofunctional silicon hydrides $\mathbf{A_{28}}$ and $\mathbf{B_{16}}$ any coordination of the NMe_2 group is presumably too weak in the accessible temperature range to give rise to observable diastereotopy. Dihydrogenosilanes, including $\mathbf{A_{20}}$, are however known [1,26] from ^{29}Si NMR spectroscopy to be chelated in solution. The strong preference of hydrogen for equatorial sites results in the complex having in solution the symmetrical structure found for the solid state, thus precluding the appearance of diastereotopy of the NMe_2 groups as a consequence of chelation. Table 6 shows, however, that in the case of the related compounds *o*-$C_6H_4CH(Me)NMe_2SiH_2R$ [R = 1-Np ($\mathbf{B_5}$), Ph ($\mathbf{B_7}$), or Me ($\mathbf{B_{12}}$)], in which the benzylic carbon atom is itself chiral, the NMe_2 group does become diastereotopic as a consequence of this chirality and as the inversion of the nitrogen atom is slowed at low temperatures. Comparison of the data for monofunctional compounds, such as $\mathbf{A_{31}}$ with $\mathbf{B_{18}}$ and $\mathbf{B_{15}}$, shows that the free energies of activation for equivalence of the NMe_2 groups are comparable for a given functional group, whether or not the ligand contains the chiral centre, and it may therefore be assumed that two hydrogen substituents are necessary for reasonably strong chelation to occur.

It is noteworthy that the presence of a third hydrogen atom, which must necessarily occupy an axial position, does not seem to affect the relative stability of the chelate formed, $\mathbf{B_2}$, whereas the chlorodihydrogenosilane $\mathbf{B_3}$ is significantly more stable. In this case the chlorine atom can occupy its "natural" axial site. The trifluorosilane also seems to be significantly more stable than the monofunctional fluorosilanes. In general, however, the data for the polyfunctional compounds do not lead to any clear conclusion as to the additivity of the effects of the different functional groups on the acceptor character of the silicon atom. In part this is because the stereochemical significance of permutational isomerisation at silicon is much more important for the polyfunctional compounds than for the monofunctional derivatives. In the former therefore the free energies of activation obtained often relate to the isomerisation rather than to the coordination as such. The results of our investigations of this problem will be presented in a forthcoming publication.

However, in agreement with the results obtained for complexation of silicon compounds by non-chelating donors, it is clear that the compounds in the present series in which the remaining groups are alkyl, aryl, or even alkoxy, or a combination of these, show little tendency towards intramolecular coordination. The ^1H NMR spectra for compounds $\mathbf{B_1}$, $\mathbf{B_{11}}$, $\mathbf{B_{14}}$, and $\mathbf{B_{17}}$, as well as for $\mathbf{B_{16}}$, do not reveal the potential diastereotopy of the NMe_2 groups, implying that $\Delta G^{\ddagger}_{(TC)} < 7$ kcal mol^{-1}, which is consistent with the conclusions from earlier ^1H and ^{29}Si NMR data.

In the case of compound $\mathbf{B_4}$, $Me_2NCH(CH_3)C_6H_4Si(OMe)_3$, coalescence temperature could be determined only by means of the ^1H NMR spectrum at 360 MHz. Under these conditions $\Delta G^{\ddagger}_{(TC)}$ is calculated to be 7.6 kcal mol^{-1}, a value which is in accord with the earlier data, given that $\Delta G^{\ddagger}$ is a function of temperature and that the coalescence temperature will increase with the operating frequency of the spectrometer.

Conclusion

These studies demonstrate that, except in the case of hydrogen, the stability of a pentacoordinated chelate of silicon is related primarily to the nature of the most apicophilic ligand, which necessarily takes up the position *trans* to the donor atom. The apicophilicity in turn is a function of the polarisability of the silicon-substituent bond. Hydrogen however preferentially occupies equatorial sites, (i.e. it is "apicophobic"). The stereochemistry of nucleophilic substitution reactions at silicon can be understood in terms of the apicophilicity series.

Experimental

All reactions were carried out under dry nitrogen.

Fluorine-19 NMR spectra were determined at 84.67 MHz and proton NMR spectra at 90 MHz on a Varian EM-390 spectrometer. Proton NMR spectra were determined at 60 MHz with a Varian EM-360 spectrometer, at 100 MHz with a Varian HA-100 spectrometer, and at 360 MHz with a Bruker WM 360 WD spectrometer. Silicon-29 NMR spectra were determined at 39.76 MHz with a Bruker 200 SY spectrometer.

Mass spectra were obtained with a JEOL JMS D-100 instrument.

Organolithium reagents were prepared by published methods [1,27]; the syntheses of compounds $\mathbf{A_{10}}$, $\mathbf{A_{11}}$, $\mathbf{A_{20}}$, and $\mathbf{B_5}$, have been described previously. Where necessary, solvents and reagents were distilled or recrystallised before use; other commercial reagents (Aldrich, Janssen, Merck, or Fluka) were used as received.

Melting points and boiling points are uncorrected. Elemental analyses were performed by the Centre de Microanalyse du C.N.R.S.

2-(Dimethylaminomethyl)phenyl-t-butoxy(methyl)silane (A_1). 2-(Dimethylaminomethyl)phenyl-lithium (**A**) (0.275 mol, in ether) was added slowly to a solution of methyldi-t-butoxysilane (52.4 g, 0.275 mol) in ether at 0 °C. The mixture was stirred for 20 h then hydrolysed rapidly, and the ether layer separated and dried (Na_2SO_4). After removal of the ether, distillation in vacuo gave $\mathbf{A_1}$, (37.7 g, 0.15 mol, 55%). B.p. 142 °C at 18 mmHg. Found: C, 66.9; H, 10.0; N, 5.58. $C_{14}H_{25}NOSi$ calcd.: C, 66.93; H, 9.96; N, 5.53%.

2-(Dimethylaminomethyl)phenylfluoro(methyl)silane (A_2). A sample of $\mathbf{A_1}$ (4.0 g, 16 mmol), prepared as above, was treated with $BF_3 \cdot Et_2O$ (0.67 cm^3, 5.4 mmol), and the mixture rapidly distilled in vacuo. $\mathbf{A_2}$, b.p. 68 °C at 0.03 mmHg, was obtained in 78% yield, identified by its ^{19}F and ^1H NMR spectra, but contaminated by $\mathbf{A_{11}}$, ($Me_2NCH_2C_6H_4SiMeF_2$), 19%, based on $\mathbf{A_1}$. Found: M^+, 197. $C_{10}H_{16}FNSi$ calcd.: M, 197.

2-(Dimethylaminomethyl)phenyl-t-butoxyfluoro(methyl)silane (A_3). To a sample of $\mathbf{A_2}$ (1 g) was added 2-methylpropan-2-ol (0.375 g, 5 mmol), freshly distilled from

sodium. The mixture was stirred overnight to give A_3, identified by its ^{19}F and ^1H NMR spectra, mixed with A_{11}, as a 60/40 mixture. Found: M^+, 269. $C_{14}H_{24}FNOSi$ calcd.: M, 269.

2-(Dimethylaminomethyl)phenylchlorofluoro(methyl)silane (A_4). To a sample of A_2 (0.2 g), dissolved in CCl_4, was added *N*-chlorosuccinimide (0.13 g, 1 mmol). After 30 min at 0 °C the lower layer was withdrawn by means of a syringe and the solution filtered. The ^{19}F spectrum of the filtrate showed the presence of A_4 and A_{11} as a 40/60 mixture.

2-(Dimethylaminomethyl)phenylbenzoyloxyfluoro(methyl)silane (A_5). To a sample of A_2 (1.0 g) was added benzoic acid (0.618 g, 5.07 mmol). After 20 h at ambient temperature, ^{19}F and ^1H NMR spectroscopy showed the presence of A_5, (44%), A_{11}, (48%), and bis(2-dimethylaminomethyl)phenylfluoro(methyl)disiloxane, (8%).

*2-(Dimethylaminomethyl)phenylfluoro(*p*-methoxybenzoyloxy)methylsilane (A_6).* To a sample of A_2 (0.2 g) was added *p*-methoxybenzoic acid (0.15 g, 1 mmol). The mixture was left overnight at room temperature. ^{19}F and ^1H NMR spectroscopy showed the presence of A_6, (15%), A_{11}, (60%), and the disiloxane, (30%).

*2-(Dimethylaminomethyl)phenylfluoro(methyl)*p*-nitrobenzoyloxysilane (A_7).* To a sample of A_2 (0.2 g) was added *p*-nitrobenzoic acid (0.17 g, 1 mmol). The mixture was stirred at 0 °C for 3 h, then at ambient temperature overnight. ^{19}F and ^1H NMR spectroscopy showed the presence of A_7, (30%), A_{11}, (50%) and the disiloxane, (20%).

2-(Dimethylaminomethyl)phenyl(diethylamino)fluoro(methyl)silane (A_8). To a sample of A_2 (0.2 g) was added diethylamine (0.08 g, 1.11 mmol) that had been freshly distilled from KOH. The mixture was kept at 0 °C for 1 h, and then at ambient temperature for 24 h. The ^{19}F spectrum showed the presence of A_8, (30%), A_{11}, (37%), and the disiloxane, (33%).

2-(Dimethylaminomethyl)phenylfluoro(methyl)thiobutoxysilane (A_9). To a sample of A_2 (0.15 g) was added butanethiol (0.25 g, 2.8 mmol). The mixture was left for 24 h at ambient temperature. The ^{19}F NMR spectrum showed the presence of A_9, (24%), A_{11}, (45%), and the disiloxane, (31%).

2-(Dimethylaminomethyl)phenylmethylsilane (A_{12}). $LiAlH_4$ (3.2 g, 84 mmol) was added to A_{10} (21.2 g, 80 mmol) in ether and the mixture stirred for 10 h. After hydrolysis with ice-water and extraction with ether, the extract was dried over Na_2SO_4 and the ether removed. Distillation at reduced pressure gave A_{12} (11.5 g, 64 mmol, 80%). B.p. 98 °C at 18 mmHg. Found: C, 67.2; H, 9.48; N, 7.7. $C_{10}H_{17}NSi$ calcd.: C, 67.04; H, 9.50; N, 7.82%.

2-(Dimethylaminomethyl)phenylbromo(methyl)silane (A_{13}). Bromine (0.31 cm^3, 6 mmol) dissolved in CCl_4 (10 cm^3) was added dropwise over 30 min to a mixture of A_{12} (1.09 g, 6 mmol) and triethylamine (0.85 cm^3, 6 mmol) in CCl_4 (10 cm^3). The precipitate was removed by filtration and the solvent evaporated in vacuo. A_{13} (1.29 g, 5 mmol, 83%) remained. Found: C, 46.6; H, 6.18; N, 5.38. $C_{10}H_{16}BrNSi$ calcd.: C, 46.51; H, 6.20; N, 5.43%.

2-(Dimethylaminomethyl)phenylchloro(methyl)silane (A_{14}). *N*-Chlorosuccinimide (0.373 g, 2.8 mmol) was added to A_{12} (0.5 g, 2.8 mmol) dissolved in CCl_4 (5 cm^3). After stirring for 2 h, the lower layer was withdrawn by means of a syringe. Removal of the solvent in vacuo left A_{14} (0.43 g, 2.0 mmol, 72%). Found: M^+, 213. $C_{10}H_{16}ClNSi$ calcd.: M, 213.

2-(Dimethylaminomethyl)phenyldichloro(methyl)silane (A_{15}). *N*-Chlorosuccinimide (2.26 g, 17 mmol) was added to A_{12} (1.516 g, 8.5 mmol) dissolved in CCl_4 (10cm^3). After 14 h stirring the lower layer was withdrawn and the solvent removed in vacuo. A_{15} (1.73 g, 7.0 mmol, 82%) remained. Found: C, 48.4; H, 6.10; N, 5.81. $C_{10}H_{15}Cl_2NSi$ calcd.: C, 48.58; H, 6.07; N, 5.67%.

2-(Dimethylaminomethyl)phenylmethylthioethylsilane (A_{16}). Ethanethiol, (1.85 cm^3, 25 mmol) was added to a mixture of A_{14} (5.3 g, 24.8 mmol) and triethylamine (3.4 cm^3, 25 mmol) dissolved in CCl_4 (15 cm^3). After 15 min the precipitated amine hydrochloride was filtered off and the solvent removed in vacuo. A_{16} (3.2 g, 13.4 mmol, 54%) was recovered. Found: C, 61.0; H, 8.50; N, 5.95. $C_{12}H_{21}NSSi$ calcd.: C, 60.25; H, 8.79; N, 5.86%.

2-(Dimethylaminomethyl)phenylacetoxy(methyl)silane (A_{17}). Acetic acid (0.30 cm^3, 5.3 mmol) was added to A_{12} (0.944 g, 5.3 mmol) dissolved in CCl_4 (6 cm^3). After 1 h the solvent was removed in vacuo to leave A_{17} (1.09 g, 4.6 mmol, 87%). Found: C, 61.1; H, 7.8; N, 5.6. $C_{12}H_{19}NO_2Si$ calcd.: C, 60.76; H, 8.02; N, 5.91%.

2-(Dimethylaminomethyl)phenyldiacetoxy(methyl)silane (A_{18}). Acetic acid (0.63 cm^3, 11 mmol) was added to A_{12} (0.993 g, 5.5 mmol) dissolved in CCl_4 (8 cm^3). After 4 h the solvent was removed in vacuo to yield A_{18} (1.36 g, 4.6 mmol, 84%). Found: C, 57.1; H, 7.16; N, 4.66. $C_{14}H_{21}NO_4Si$ calcd.: C, 56.95; H, 7.12; N, 4.75%.

2-(Dimethylaminomethyl)phenylchloro-1-naphthylsilane (A_{21}). *N*-Chlorosuccinimide (1.33 g, 10 mmol) was added slowly to 2-(dimethylaminomethyl)phenyl-1-naphthylsilane (A_{20}), (2.91 g, 10 mmol) in CCl_4. After stirring for 30 min, the clear lower layer was withdrawn by means of a syringe. Removal of the solvent left A_{21} (3.0 g, 9.2 mmol, 92%). Found: C, 71.5; H, 6.10; N, 4.6. $C_{19}H_{20}ClNSi$ calcd.: C, 70.05; H, 6.14; N, 4.30%.

2-(Dimethylaminomethyl)phenyldichloro-1-naphthylsilane (A_{22}). A_{20} (2.91 g, 10 mmol) in CCl_4 (15 cm^3) was treated with *N*-chlorosuccinimide (2.66 g, 20 mmol) and stirred for 3 h. A_{22} (3.1 g, 8.6 mmol, 86%), was isolated as above. Found: C, 63.2; H, 5.12; N, 3.69. $C_{19}H_{19}Cl_2NSi$ calcd.: C, 63.16; H, 5.26; N, 3.88%.

2-(Dimethylaminomethyl)phenylacetoxy-1-naphthylsilane (A_{23}). Acetic acid (0.12 g, 2 mmol) was added to A_{20} (0.582 g, 2 mmol) dissolved in CCl_4. After 1 h removal of the solvent gave A_{23} (0.62 g, 1.7 mmol, 89%). Found: C, 72.8; H, 6.08, N, 3.9. $C_{21}H_{23}NO_2Si$ calcd.: C, 72.2; H, 6.59; N, 4.01%.

2-(Dimethylaminomethyl)phenyldiacetoxy-1-naphthylsilane (A_{24}). Acetic acid (0.24 g, 4 mmol) was added to A_{20} (0.582 g, 2 mmol) dissolved in CCl_4. The mixture was warmed to 50 °C for 6 h, and the solvent then removed in vacuo. A_{24} (0.69 g, 1.7 mmol, 85%) was recovered. Found: M^+, 407. $C_{23}H_{25}NO_4Si$ calcd.: M, 407.

2-(Dimethylaminomethyl)phenyldimethoxy-1-naphthylsilane (A_{25}). A solution of A_{20} (10 g, 34.4 mmol) in anhydrous methanol (15 cm^3) was allowed to stand for 48 h. After removal of the excess of methanol, A_{25} (11.2 g, 31.9 mmol, 93%) was recovered by distillation in vacuo. B.p. 160 °C at 0.4 mmHg. Found: C, 71.3; H, 7.29; N, 3.90. $C_{21}H_{25}NO_2Si$ calcd.: C, 71.79; H, 7.12; N, 3.99%.

2-(Dimethylaminomethyl)phenyldifluoro-1-naphthylsilane (A_{26}). $BF_3 \cdot Et_2O$ (1.5 cm^3, 12.2 mmol) was added to A_{25} (3.2 g, 9.1 mmol) dissolved in hexane (5 cm^3). After 8 min distillation in vacuo gave A_{26} (2.3 g, 7 mmol, 77%). B.p. 160 °C at 1 mmHg. Found: C, 69.0; H, 6.13; F, 11.3; N, 4.1. $C_{19}H_{19}F_2NSi$ calcd.: C, 69.72; H, 5.81; F, 11.62; N, 4.28%.

2-(Dimethylaminomethyl)phenylmethoxy(methyl)-1-naphthylsilane (A_{27}). Methylmagnesium bromide (34 mmol, in ether) was added slowly to A_{25} (11.98 g, 34 mmol) dissolved in ether (20 cm^3). The mixture was stirred for 4 h then hydrolysed and extracted with ether, and the extract was dried over Na_2SO_4. After removal of the solvent, distillation in vacuo yielded A_{27} (7.0 g, 20.9 mmol, 61%). B.p. 170 °C at 0.1 mmHg. Found: C, 75.2; H, 7.36; N, 4.17. $C_{21}H_{25}NOSi$ calcd.: C, 75.20; H, 7.52; N, 4.21%.

2-(Dimethylaminomethyl)phenylmethyl-1-naphthylsilane (A_{28}). A_{27} (5.0 g, 14.9 mmol) was stirred with $LiAlH_4$ (0.57 g, 15.0 mmol) in ether for 2 h, the mixture hydrolysed, extracted with ether, and the extract dried over Na_2SO_4. After removal of the solvent, distillation in vacuo yielded A_{28} (4.0 g, 13.1 mmol, 88%). B.p. 165 °C at 0.25 mmHg. Found: C, 78.7; H, 7.57; N, 3.86; Si, 9.41. $C_{20}H_{23}NSi$ calcd.: C, 78.68; H, 7.54; N, 4.59; Si, 9.18%.

2-(Dimethylaminomethyl)phenylchloro(methyl)-1-naphthylsilane (A_{29}). *N*-Chlorosuccinimide (0.241 g, 1.8 mmol) was added to A_{28} (0.551 g, 1.8 mmol) dissolved in CCl_4 (5 cm^3). After 6 h, the lower layer was withdrawn by means of a syringe and the solvent removed in vacuo to give A_{29} (0.35 g, 1.0 mmol, 57%). Found: C, 71.0; H, 6.32; N, 3.9. $C_{20}H_{22}ClNSi$ calcd.: C, 70.69; H, 6.48; N, 4.12%.

2-(Dimethylaminomethyl)phenylacetoxy(methyl)-1-naphthylsilane (A_{30}). Acetic acid (0.14 cm^3, 2.3 mmol) was added to A_{28} (0.69 g, 2.3 mmol) in $CHCl_3$ (4 cm^3). After 48 h at 40–50 °C, the solvent was removed in vacuo to leave A_{30} (0.47 g, 1.3 mmol, 56%). Found: M^+, 363. $C_{22}H_{25}NO_2Si$ calcd.: *M*, 363.

2-(Dimethylaminomethyl)phenylfluoro(methyl)-1-naphthylsilane (A_{31}). $BF_3 \cdot Et_2O$ (0.95 g, 6.7 mmol) was added to A_{27} (3.16 g, 9.4 mmol) dissolved in hexane (5 cm^3). After 5 min, the mixture was distilled in vacuo to yield A_{31} (1.9 g, 5.9 mmol, 63%). B.p. 170 °C at 0.5 mmHg. Found: C, 74.1; H, 6.70; F, 5.95; N, 4.11. $C_{20}H_{22}FNSi$ calcd.: C, 74.30; H, 6.81; F, 5.88; N, 4.33%.

2-[1-(Dimethylamino)ethyl]phenyltriethoxysilane (B_1). A solution of 2-[1-(dimethylamino)ethyl]phenyl-lithium (**B**), prepared from 1-(dimethylamino)ethylbenzene (12 g, 0.088 mol) by exchange with n-butyl-lithium, was added slowly to a solution of tetraethoxysilane (21.76 g, 0.104 mol) in ether (200 cm^3). The mixture was stirred at ambient temperature for 72 h and the precipitated salts were then filtered off. The filtrate was evaporated under reduced pressure and the residue extracted with pentane. The extract was filtered and the solvent removed. The crude product was distilled in vacuo to yield B_1 (14 g, 0.045 mol, 56%) as a colourless liquid. B.p. 116 °C at 0.2 mmHg. Found: C, 62.2; H, 9.42; N, 4.41; Si, 8.8. $C_{16}H_{29}NO_3Si$ calcd.: C, 61.69; H, 9.38; N, 4.49; Si, 9.01%.

2-[1-(Dimethylamino)ethyl]phenylsilane (B_2). A solution of B_1 (4.5 g, 14.4 mmol) in ether (20 cm^3) was added slowly to a suspension of $LiAlH_4$ (0.54 g, 14.4 mmol) in ether (80 cm^3). The mixture was stirred at room temperature for 12 h, hydrolysed rapidly in ice-water, and extracted with ether. The extract was washed (H_2O), dried (Na_2SO_4), the ether removed, and B_2 (1.8 g, 10 mmol, 70%) recovered as a colourless liquid by distillation at reduced pressure. B.p. 120 °C at 16 mmHg. Found: C, 67.1; H, 9.58; N, 7.69; M^+, 179. $C_{10}H_{17}NSi$ calcd.: C, 66.97; H, 9.55; N, 7.81%; *M*, 179.

2-[1-(Dimethylamino)ethyl]phenylchlorosilane (B_3). *N*-Chlorosuccinimide (0.094 g, 0.7 mmol) was added in small portions to a solution of B_2 (0.115 g, 0.64 mmol) in CCl_4 (5 cm^3). The mixture was cooled in ice and stirred for 1 h. The ^1H NMR

spectrum of the lower layer then confirmed the absence of $\mathbf{B_2}$ and the presence of $\mathbf{B_3}$.

2-[1-(Dimethylamino)ethyl]phenyltrimethoxysilane ($\mathbf{B_4}$). Anhydrous methanol (20 g, 0.625 mol) was added to $\mathbf{B_2}$ (1.3 g, 7.25 mmol). The mixture was stirred for 24 h, by which time all the starting material had reacted (NMR). The excess of methanol was removed in vacuo, and the residue distilled to yield $\mathbf{B_4}$ (0.8 g, 3.0 mmol, 41%) as a colourless liquid. B.p. 150 °C at 25 mmHg. Found: C, 58.6; H, 8.29; N, 5.58 $C_{13}H_{23}NO_3Si$ calcd.: C, 57.95; H, 8.60; N, 5.20%.

2-[1-(Dimethylamino)ethyl]phenylchloro-1-naphthylsilane ($\mathbf{B_6}$). *N*-Chlorosuccinimide (0.134 g, 1 mmol) was added in small portions to a solution of $\mathbf{B_5}$ (0.270 g, 0.9 mmol) in CCl_4 (15 cm^3), cooled in ice. After 1 h stirring the clear lower layer was withdrawn. The ^1H NMR spectrum of this solution confirmed the formation of $\mathbf{B_6}$ as a 60/40 mixture of diastereomers and the absence of $\mathbf{B_5}$.

2-[1-(Dimethylamino)ethyl]phenyl(phenyl)silane ($\mathbf{B_7}$). A solution of **B** prepared from 1-(dimethylamino)ethylbenzene (15.9 g, 0.107 mol) was added slowly to a solution of phenylsilane (13.8 g, 0.128 mol) in ether (150 cm^3). The mixture was stirred at room temperature for 60 h then hydrolysed with ice-water. The ether layer was separated and dried, the ether removed, and the residue distilled in vacuo to yield $\mathbf{B_7}$ as a colourless liquid (18.0 g, 0.07 mol, 66%). B.p. 195 °C at 0.6 mmHg. Found: C, 74.95; H, 8.17; N, 5.19. $C_{16}H_{21}NSi$ calcd.: C, 75.23; H, 8.28; N, 5.48%.

2-[1-(Dimethylamino)ethyl]phenyl(chloro)phenylsilane ($\mathbf{B_8}$). *N*-Chlorosuccinimide (0.292 g, 2.2 mmol) was added in small portions to $\mathbf{B_7}$ (0.51 g, 2 mmol) in CCl_4 (15 cm^3), cooled in ice. After 1 h stirring the clear lower layer was withdrawn. The ^1H NMR spectrum of this solution confirmed the presence of $\mathbf{B_8}$ and the absence of $\mathbf{B_7}$.

2-[1-(Dimethylamino)ethyl]phenyl(dichloro)phenylsilane ($\mathbf{B_9}$). *N*-Chlorosuccinimide (0.46 g, 3.4 mmol) was added in small portions to a solution of $\mathbf{B_7}$ (0.42 g, 1.6 mmol) in CCl_4 (20 cm^3). The mixture was stirred for 2 h at room temperature and the lower layer then withdrawn. The ^1H NMR spectrum of this solution confirmed the absence of starting material, and permitted the identification of $\mathbf{B_9}$.

2-[1-(Dimethylamino)ethyl]phenyl(dimethoxy)silane ($\mathbf{B_{10}}$). Anhydrous methanol (20 cm^3) was added slowly to $\mathbf{B_7}$ (2.7 g, 10.6 mmol). After 12 h stirring at room temperature, NMR analysis showed that all the starting material had been consumed. The excess of methanol was removed and the product recovered by distillation at reduced pressure as a colourless oil (2.0 g, 6.34 mmol, 60%). B.p. 185 °C at 16 mmHg. Found: C, 68.74; H, 7.91; N, 4.35. $C_{18}H_{25}NO_2Si$ calcd.: C, 68.52; H, 7.98; N, 4.43%.

2-[1-(Dimethylamino)ethyl]phenylmethyl(diethoxy)silane ($\mathbf{B_{11}}$). A solution of **B** prepared as above from the amine (0.14 mol) was added slowly to a solution of methyltriethoxysilane (32.4 g, 0.182 mol) in ether (200 cm^3). The mixture was stirred for 24 h at room temperature and a further 24 h under reflux, then filtered, and the ethereal solution concentrated in vacuo. Fractional distillation of the residue gave $\mathbf{B_{11}}$ as a colourless oil (16 g, 0.057 mol, 40%). B.p. 120 °C at 0.1 mmHg. Found: C, 63.75; H, 9.57; N, 4.73. $C_{15}H_{27}NO_2Si$ calcd.: C, 64.00; H, 9.66; N, 4.97%.

2-[1-(Dimethylamino)ethyl]phenylmethylsilane ($\mathbf{B_{12}}$). A solution of $\mathbf{B_{11}}$ (14.05 g, 50 mmol) in ether (50 cm^3) was added slowly to a suspension of $LiAlH_4$ (2.5 g, 50 mmol) in ether (100 cm^3). The mixture was stirred at room temperature for 24 h then hydrolysed with ice-water, and the ethereal extract dried and distilled in vacuo. $\mathbf{B_{12}}$ (9 g, 46.5 mmol, 93%) b.p. 125 °C at 20 mmHg, was recovered as a colourless

liquid. Found: C, 67.6; H, 9.9; N, 7.3. $C_{11}H_{19}NSi$ calcd.: C, 68.32; H, 9.9; N, 7.24%. δ Si(CD_2Cl_2) −47.5.

*2-[1-(Dimethylamino)ethyl]phenyldifluoro(methyl)silane (**B_{13}**).* A solution of $BF_3 \cdot OEt_2$ (0.9 cm^3, 7.2 mmol) in ether (5 cm^3) was added slowly to a solution of **B_{11}** (2.0 g, 7.1 mmol) in ether (10 cm^3). After 15 min stirring the mixture was distilled at reduced pressure to yield **B_{13}** (1.0 g, 4.4 mmol, 61%). B.p. 130°C at 18 mmHg. Found: C, 58.23; H, 7.56; N, 6.14; M^+, 229. for $C_{11}H_{17}F_2NSi$ calcd.: C, 57.60; H, 7.47; N, 6.10%; *M*, 229.

*2-[1-(Dimethylamino)ethyl]phenylmethoxy(dimethyl)silane (**B_{14}**).* A solution of **B** prepared from the amine (0.11 mol) was added dropwise to a solution of dimethoxydimethylsilane (16 g, 0.133 mol) in ether (150 cm^3). After 2 d stirring at room temperature the mixture was filtered and the filtrate concentrated in vacuo. The residue was extracted with pentane, the extract filtered, and the pentane removed pentane. Fractional distillation at reduced pressure gave **B_{14}** as a colourless oil (17 g, 0.072 mol, 65%). B.p. 142°C at 20 mmHg. Found: C, 65.75; H, 9.92; N, 5.67. $C_{13}H_{23}NOSi$ calcd.: C, 65.76; H, 9.76; N, 5.89%. δ Si(CD_2Cl_2) −7.6.

*2-[1-(Dimethylamino)ethyl]phenylfluoro(dimethyl)silane (**B_{15}**).* A solution of $BF_3 \cdot OEt_2$ (0.8 cm^3, 6.3 mmol) in ether (5 cm^3) was added slowly to a solution of **B_{14}** (3.0 g, 12.6 mmol) in ether (10 cm^3). After 15 min stirring fractional distillation of the mixture at reduced pressure yielded **B_{15}** as a colourless liquid (1.5 g, 6.7 mmol, 53%). B.p. 125°C at 18 mmHg. Found: C, 63.31; H, 9.11; N, 5.88. $C_{12}H_{20}FNSi$ calcd.: C, 63.95; H, 8.94; N, 6.21%. δ Si(CD_2Cl_2) −3.3.

*2-[1-(Dimethylamino)ethyl]phenyldimethylsilane (**B_{16}**).* A solution of **B_{14}** (8.23 g, 34.7 mmol) in ether (50 cm^3) was added dropwise to a suspension of $LiAlH_4$ (1.5 g, 39.4 mmol) in ether (100 cm^3). The mixture was stirred for 12 h at room temperature, then hydrolysed with ice-water and the ether layer separated. This extract was washed twice (H_2O), dried (Na_2SO_4), the ether removed, and the residue fractionally distilled. **B_{16}** (4.67 g, 22 mmol, 64%) was recovered as a colourless liquid. B.p. 124°C at 18 mmHg. Found: C, 68.52; H, 10.26; N, 6.78. $C_{12}H_{21}NSi$ calcd.: C, 69.49; H, 10.20; N, 6.75%. δ Si(CD_2Cl_2) −23.27.

*2-[1-(Dimethylamino)ethyl]phenylethoxy(methyl)phenylsilane (**B_{17}**).* A solution of **B**, prepared as above from 0.1 mol of amine, was added dropwise to a solution of diethoxy(methyl)phenylsilane in ether (100 cm^3). The reaction mixture was stirred at room temperature for 72 h and the precipitated salts then filtered off. The filtrate was concentrated, the residue extracted with pentane, and the extract filtered. After removal of the pentane, fractional distillation of the residue in vacuo gave **B_{17}** (10 g, 0.032 mol, 32%). B.p. 153°C at 0.5 mmHg. Found: C, 72.82; H, 8.81; N, 4.33. $C_{19}H_{27}NOSi$ calcd.: C, 72.79; H, 8.68; N, 4.46%.

*2-[1-(Dimethylamino)ethyl]phenylfluoro(methyl)phenylsilane (**B_{18}**).* A solution of $BF_3 \cdot OEt_2$ (0.5 cm^3, 4 mmol) in ether (5 cm^3) was added slowly to a solution of **B_{17}** (2.3 g, 7.3 mmol) in ether (10 cm^3). After 20 min stirring at room temperature, fractional distillation in vacuo yielded **B_{18}** (1 g, 3.5 mmol, 47%) as a colourless oil, identified by its NMR spectrum. B.p. 125°C at 0.1 mmHg.

*2-[1-(Dimethylamino)ethyl]phenyltrimethylsilane (**B_{19}**).* A solution of **B** prepared from the amine (0.11 mol) was added slowly to a solution of chlorotrimethylsilane (10.87 g, 0.10 mol) in ether (150 cm^3). The mixture was stirred for 24 h at room temperature, then hydrolysed in ether/ice-water and the ether layer separated. The organic extract was washed with water, dried (Na_2SO_4) and the ether removed.

Fractional distillation at reduced pressure gave $\mathbf{B_{19}}$ (15 g, 68 mmol, 68%) as a colourless oil. B.p. 135 °C at 20 mmHg. Found: C, 70.33; H, 10.53; N, 6.08. $C_{13}H_{23}NSi$ calcd.: C, 70.51; H, 10.46; N, 6.32%.

8-(Dimethylamino)-1-naphthyldi(methoxy)phenylsilane (C_1). A suspension of 8-(dimethylamino)-1-naphthyl-lithium (0.06 mol) in ether was added dropwise to phenyltrimethoxysilane (11.8 g, 0.06 mol). The mixture was stirred at 0 °C for 8 h. The ether was then removed in vacuo, the residue extracted with pentane, and the extract filtered. Evaporation of the solvent and recrystallisation from hexane gave $\mathbf{C_1}$ (12.0 g, 0.036 mol, 60%). M.p. 82 °C. NMR (δ H (CD_2Cl_2, 30 °C), 2.02(6H, s, $N(CH_3)_2$), 3.46(6H, s, $Si(OCH_3)_2$), 7.15–7.98(10H, ar), 8.46(1H, d, ar); (−100 °C), 1.50 and 2.42(2s, $N(CH_3)_2$), 3.38 and 3.60(2s, $Si(OCH_3)_2$.

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