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Hypervalent species of silicon: structure and reactivity

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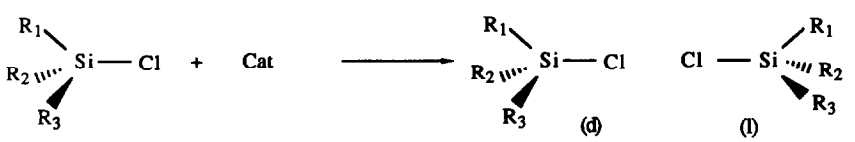
Introduction and preliminary results *(Studies carried out by Dr Henner-Leard, Dr Dabosi, Dr Martineau)*

Our interest in the mechanism of nucleophilic substitution at silicon [1] led us to seek some experimental evidence for the formation of pentacoordinated silicon species as intermediates in the course of nucleophilic substitution taking place with retention or with inversion at silicon [2,3]. The possibility for a silicon atom to extend its coordination number and to become penta- or hexacoordinated is one of the most important factors in the mechanisms of reactions at silicon.

The first case in which we were faced directly with these species involved the racemisation of chlorosilanes induced by solvents. It was Sommer [4] who observed that optically active chlorosilanes were not optically stable in some solvents (acetonitrile, nitromethane, nitrobenzene). In studying this phenomenon, it appeared to us that the driving force for the racemisation was not the polarity but the nucleophilicity of the solvent [5–10]. Furthermore, using very efficient agents like HMPA, DMF or DMSO, it was possible to induce racemisation using a small amount of these reagents and to perform kinetic studies. The kinetic law was second order in the racemising agent (Cat), and first order in chlorosilane. The reaction also involved a very high negative entropy of activation. The activating nucleophile (Cat) acts as a catalyst (Scheme 1). It does not appear in the final composition of the products.



Scheme 1. $V = k[R_3SiCl][Cat]_0^2$; $-70 < \Delta S^{\ddagger} < -50$ e.u. Process controlled by $\Delta S^{\ddagger}$. Cat = HMPA, DMSO, DMF, CH_3CN, RNO_2, etc.

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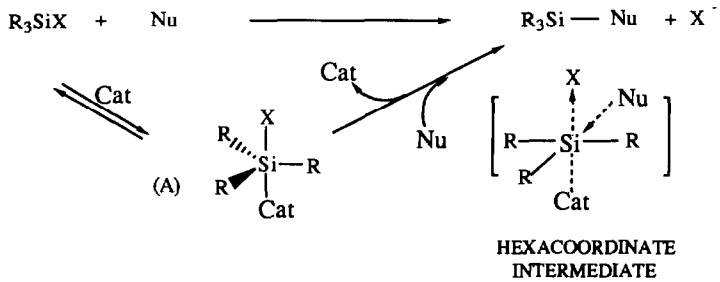
The large negative values for the activation entropy are consistent with a highly organized transition state. The mechanism we proposed [7] involves the formation of a hexacoordinated intermediate (or transition state) during the rate-determining step. This step involves attack by a second molecule of the catalyst on the pentacoordinate silicon formed in the preequilibrium.

The same mechanistic features were observed in the case of nucleophilic substitutions (hydrolysis and alcoholysis) occurring at silicon and assisted by nucleophilic catalysts. In this case also the kinetics are controlled by the activation entropy (sometimes, the reaction proceeds faster when the temperature is lowered) and the kinetic law is first order in chlorosilane, first order in alcohol and first order in activating nucleophile (Cat). A mechanism similar to the mechanism proposed in the case of the racemisation of chlorosilanes has been suggested [11] (Scheme 2).



Scheme 2. $V = k[R_3SiCl][Nu][Cat]_0$; $-40 < \Delta S^{\ddagger} < -60$ e.u. X = H, OR, NR_2, Cl. Cat = HMPA, F^-, RCO_2^-, Cl^-, etc.

This mechanism involves the formation of a pentacoordinated intermediate in a preequilibrium, followed, during the rate determining step, by nucleophilic attack of the nucleophilic reagent (Nu) on this pentacoordinated silicon. The proposed mechanistic pathway agrees with the kinetic law and the high negative entropy of activation. The mechanism has been established in the case of chlorosilanes. However, the number of cases which could be concerned by this mechanism is very large since many functional groups at silicon (Si–H, Si–OR, Si–NR_2, Si–Cl) can be activated either by neutral nucleophiles (HMPA, NMI, DMF) or by anionic ones (F^-, RCO_2^-, etc).

The stereochemistry of nucleophilic attack on pentacoordinate silicon has been studied only in the case of the Si–Cl bond [12] and found to be retention instead of the inversion of configuration usually observed for nucleophilic displacements on tetracoordinate chlorosilanes. In fact the precise geometry of nucleophilic attack is not known and may depend on many factors.

The mechanistic implications of these processes are the following:

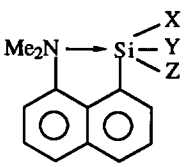
- The pentacoordinated species (A) formed between the nucleophilic catalyst and the substrate must be stable and easily formed.
- (A) must react faster with nucleophiles than the starting tetracoordinate silane since the catalytic procedure results in an acceleration of the rates. This point is very important since the silicon atom in (A) can be negatively charged in the case of coordination with anions like F^- or RCO_2^- for instance. It might thus be expected to be more crowded and less electrophilic than in the starting tetracoordinate silane.
- The rate-determining step involves nucleophilic attack on a pentacoordinated

silicon atom. This step implies the formation of a *hexacoordinate intermediate* (or transition state) in which the bond between the nucleophile and silicon is formed during the breaking of the bond between the silicon and the leaving group.

These considerations incited us to study in more detail the stability and properties of pentacoordinated silicon species, their reactivity towards nucleophiles and also the possible transformation from penta- to hexacoordination at silicon. The results obtained during this research will be discussed in the main part of this paper. We will also present some recent results concerning the reactivity of hexacoordinated silicon compounds.

Stability of pentacoordinated neutral complexes ***(Studies carried out by Dr Royo, Dr Brelière, Dr Carré, M. Poirier, A. Kpoton)***

Several pentacoordinated species of silicon have been reported [3,13–18] and many studies have been performed. The silatranes have been particularly studied [19–23]. For our part, we were interested by molecules having a possible intramolecular coordination which might permit a measure of the $\Delta G^{\ddagger}$ for the breaking of the intramolecular coordinative bond, allowing an access to the stability of some pentacoordinated intermediates. Compounds **1–3** have been studied [24] by extension of results obtained with Sn compounds [25–30].



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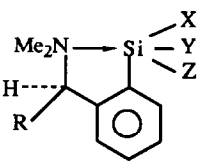
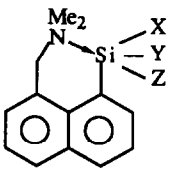


2 { a: R = H; b: R = Me }

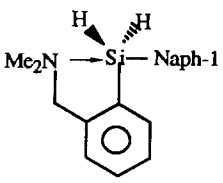


3

^{1}H Variable-temperature NMR studies [24,31] of the derivatives **1** and **2** where X = Me or Ph; Y = H; Z = OR, SR, OAc, F, Cl, Br, revealed intramolecular coordination at low temperatures by the presence of two signals from diastereotopic *N*-dimethyl groups. From the coalescence of these signals, free energies of activation for ring opening were found to lie in the range 8 to 15 kcal mol^{-1}. They measure the stability of the chelated form as a function of the nature of the groups attached to silicon. The following order was established: H < OR < F, SR < OAc, Cl, Br. In these systems therefore it may be concluded that the major factor determining the aptitude for pentacoordination is the ability of the Si–X bond to be stretched under the influence of the donor atom. This feature is very well illustrated by some X-ray structures reported [22,32] for chlorosilanes in which the silicon–chlorine bond is longer than the normal, tetracoordinate covalent bond by more than 15%. Interestingly the sequence above parallels the tendency to inversion in nucleophilic substitution of X at a chiral silicon center, and the susceptibility to racemization in nucleophilic solvents.

During our initial studies, no coordination was detected when hydrogen was the only functional group attached to silicon [24,31]. However the dihydrogenosilane **4** was shown by its ^{29}Si chemical shift to be chelated in solution [33] and subsequent X-ray crystallographic analysis of this compound [24] and of **5** and **6** [34] showed

significant N → Si coordinative interaction. These structures confirmed the generally trigonal bipyramidal geometry of the ligands about the silicon atom, and the coordination of the nitrogen atom from an apical site. Very interestingly, the hydrogen atoms were found to occupy equatorial sites, in preference even to the aryl groups, which explains the isochronous *N*-methyl groups in **4**. Equatorial placement of hydrogen was also found by Ebsworth and co-workers for crystalline **7** [37].



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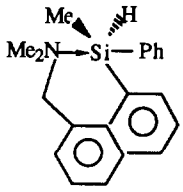

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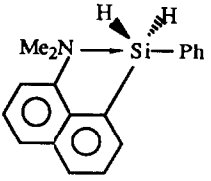

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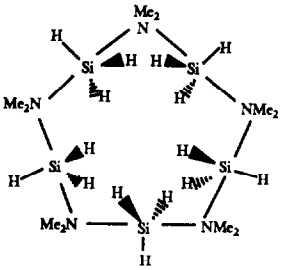

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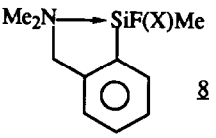
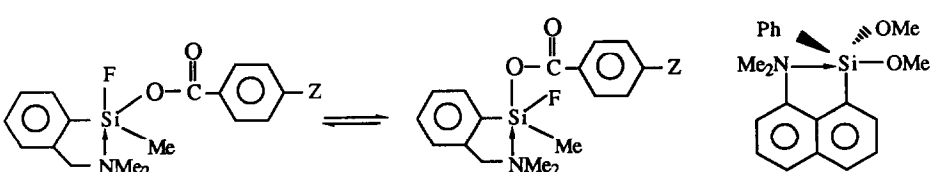


8

Consideration of the available information on the preferred disposition of substituents permits the tentative assignment of a relative apicophilicity series, analogous to that determined [38] for trigonal bipyramidal phosphorus. NMR data on bifunctional organosilanes, **8**, containing fluorine and a range of other groups establish the apicophilicity of X relative to fluorine according to the direction in which the fluorine resonance shifts as the temperature is lowered [39]: a downfield shift indicates preferential occupation by fluorine of an axial site; an upfield shift correspondingly indicates occupation of an equatorial site. These experiments showed that fluorine was more apicophilic than hydrogen, alkoxy or dialkylamino, but less apicophilic than chlorine. In cases where X = benzoyloxy (Scheme 3), a slow equilibrium was apparent at −95 °C in which both topomers **9** and **10** could be distinguished. Although that with F equatorial was always present in greater amount, the proportion was enhanced as electronwithdrawing substituents *Z* on the phenyl group increased the apicophilicity of the benzoyloxy moiety.



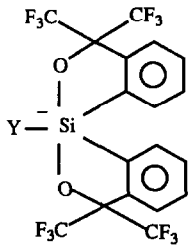
9 (Z = NO_2, H, OMe) 10 11

Scheme 3

In combination with the preferred conformation found [36] by ^1H NMR for compound **11**, and the data from the crystal structures discussed earlier, the apicophilicity of substituents in these intramolecularly coordinated compounds is: $H < Csp_2 < OR$, $NR_2 < F < Cl$, OCOR, Br.

Fluxionality of pentacoordinated organosilanes ***(Studies carried out by Dr Royo, Dr Brelière, M. Poirier, A. Kpoton, Dr Boyer)***

In the case of fluorosilicates, isomerization by a regular mechanism (pseudorotation) was studied early [40,41]. The validity of this mechanism was confirmed later [42–44] with a series of substituted fluorosilicates and by the isomerization of **14** by interaction with parasubstituted benzaldehydes [45–49].



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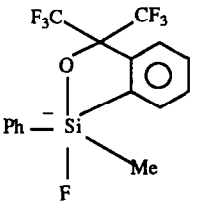

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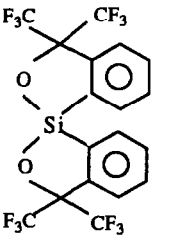

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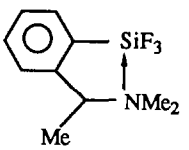
In order to distinguish between the regular mechanism (pseudorotation) and the possible irregular process (equilibrium between open and closed structures) we made an extensive study of compounds **15** and **16** in which the chirality of the benzylic carbon atom permits discrimination between the regular and irregular mechanisms since the two methyls at nitrogen are no longer diastereotopic when the nitrogen is not coordinated at silicon because of the nitrogen "umbrella" inversion.



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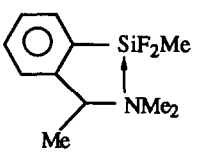


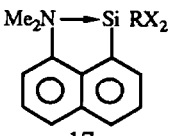
16

At low temperature the ^{19}F NMR spectrum of **15** shows the three absorptions expected for one axial and two diastereotopic equatorial fluorine atoms, and the ^1H NMR spectrum exhibits the absorptions of two diastereotopic *N*-methyl groups.

As the temperature is raised equivalence of the fluorine atoms results from a process with a free energy of activation of 13.1 kcal mol^{-1}, significantly lower than that responsible for equivalence of the *N*-methyl groups ($\Delta G^{\ddagger} = 15.8$ kcal mol^{-1}). Similarly for compound **16**, both the ^{19}F and ^1H NMR signals permit discrimination between the regular and irregular mechanisms and the evaluation of $\Delta G^{\ddagger}$ for each process. At low temperature, because of the two chiralities at both carbon and silicon, two diastereoisomers are visible. Each displays diastereotopy of the NMe_2 groups and each has one equatorial and one apical fluorine atom. The regular mechanism occurs with $\Delta G^{\ddagger} = 9.3$ kcal mol^{-1}, the same value being obtained from

Table 1

Free energies of activation for equivalence of $-NMe_2$ groups in homobifunctional and of ligands X in homotrifunctional derivatives (data from coalescence temperature) [35]



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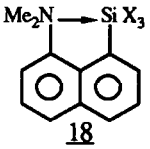

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Compound	$\Delta G^{\ddagger}$ (kcal mol^{-1})	Compound	$\Delta G^{\ddagger}$ (kcal mol^{-1})
$RX_2 = PhCl_2$	11	$X_3 = F_3$	12
$RX_2 = PhF_2$	12	$X_3 = H_3$	< 7
$RX_2 = Ph(OMe)_2$	9	$X_3 = (OMe)_3$	< 7
$RX_2 = MeCl_2$	9	$X_3 = (OEt)_3$	< 7

the coalescence of the NMe_2 and F signals. The irregular mechanism ensues when the NMe_2 is free to invert its configuration; $\Delta G^{\ddagger} = 11.8$ kcal mol^{-1}. The existence of a mechanism for permutting fluorine atoms between sites on silicon, without inversion occurring at the adjacent dimethylamino group, is thus established.

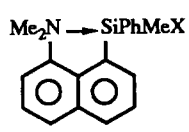
The results obtained are confirmed by compounds derived from the *N*-dimethylaminonaphthyl ligand which exhibit low values for activation corresponding to the equivalence to the methyl groups attached to nitrogen in the case of bi and trifunctional compounds (cf. Table 1).

These values correspond to the pseudorotation energy barrier. By contrast, with monofunctional compounds or with bifunctional compounds H, X, very high values are observed for $\Delta G^{\ddagger}$ corresponding to the irregular mechanism because of the great ability of the ligand to coordinate to silicon (Table 2).

The case of trihydrosilanes is a very interesting one: whatever the structure, (**21a, b, c, d**) we did not obtain a measure of $\Delta G^{\ddagger}$ since the Si–H signal appears always as a very sharp absorption even at very low temperature ($-110\,^{\circ}C$). These observations imply very easy pseudorotation for the SiH_3 group, in agreement with the

Table 2

Free energies of activation for equivalence of $-NMe_2$ groups in monofunctional and heterobifunctional derivatives (data from coalescence temperature) [35]



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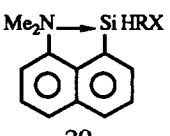

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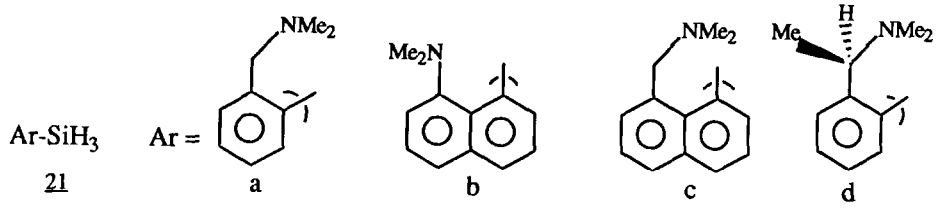
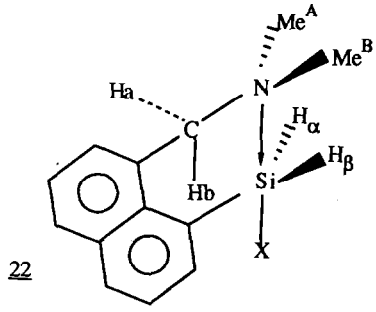
Compound	$\Delta G^{\ddagger}$ (kcal mol^{-1})	Compound	$\Delta G^{\ddagger}$ (kcal mol^{-1})
X = H	22	R, X = Me, Cl	22
X = Cl	20	R, X = Ph, Cl	> 22
X = F	23	R, X = Ph, Br	> 21
X = OMe	22		

aptitude of SiH to occupy the equatorial position [34]. Coordination of the nitrogen to silicon is again proved by the ^{29}Si NMR shift observed and by the $\Delta G^{\ddagger}$ measured by dynamic ^{1}H NMR spectroscopy in the case of **21d** ($\Delta G^{\ddagger} = 10$ kcal mol^{-1}) [50]. ^{29}Si NMR chemical shifts for compounds **21**: **21b**, $\delta = -68.3$ ppm; **21c**, $\delta = -81.19$ ppm; **21d**, $\delta = -75.96$ ppm.



Special mention must be made of all the compounds **22** containing the ligand [(*N*-dimethyl)aminomethyl]naphthyl for which a measure of $\Delta G^{\ddagger}$ may be obtained in three ways: benzylic protons H_aH_b, *N*-dimethyl group Me_AMe_B and the SiH_2 group which shows two diastereotopic H_α and H_β. The $\Delta G^{\ddagger}$ evaluated for the N → Si breaking are the same with the three probes ($\Delta G^{\ddagger} = 10.2$ for X = Ph) [36].



Reactivity of pentacoordinated organosilanes

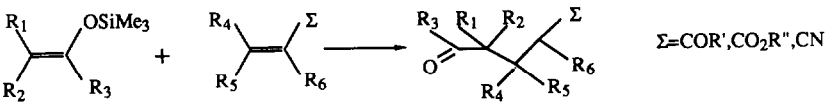
The chemical behaviour and the reactivity of pentacoordinate silicon compounds has been of great interest to us in recent years and we have approached this chemistry from three angles. The first is the exploitation of nucleophilic activation at silicon in order to develop new synthetic methods and catalytic processes for reduction, aldolisation and Michael type reactions. The second is exploration of the new chemistry to be anticipated as a result of the very unexpected reactivity of the pentacoordinated silicon compounds which we have isolated. The third involves investigation of the reactivity of isolated pentacoordinated silicon compounds in order to provide further evidence for the mechanism we proposed previously [7] for the nucleophilic activation of nucleophilic substitution at Si.

I. Synthetic methods

(1) Nucleophilic assistance in reactions of enoxysilanes (Studies carried out by Dr Reyé, Dr Perz, Dr Boyer, Dr Chuit)

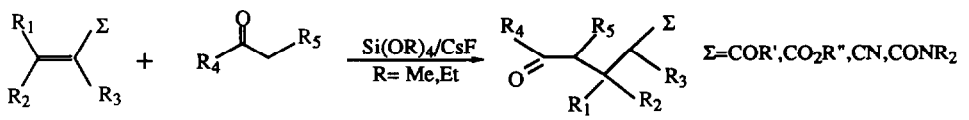
The activation of enoxysilanes by fluoride ions provides a general method for carbon–carbon bond formation. The most extensively studied reactions are the cross-aldolization and the Michael reactions (see Scheme 4). These reactions can be

activated by CsF in heterogeneous conditions [51,52], and by R_4NF in homogeneous conditions [53] or by $Me_3SiF_2^-TAS^+$ which permits the preparation of free enolates [54].



Scheme 4

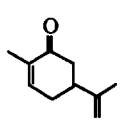
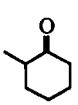
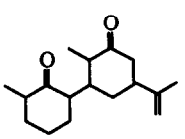
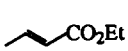
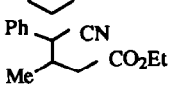
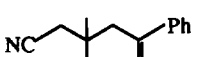
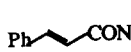
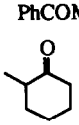
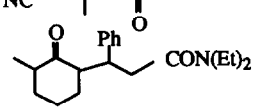
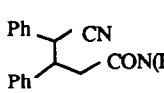
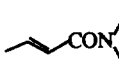
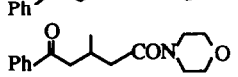
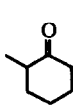
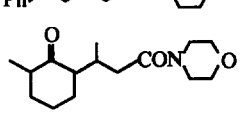
In these studies we reported a one-pot procedure for Michael addition without preparation of the enoxysilane. This procedure permits Michael-type additions to α,β-unsaturated ketones, esters, nitriles [52,55,56] and amides [57,58] (Scheme 5).

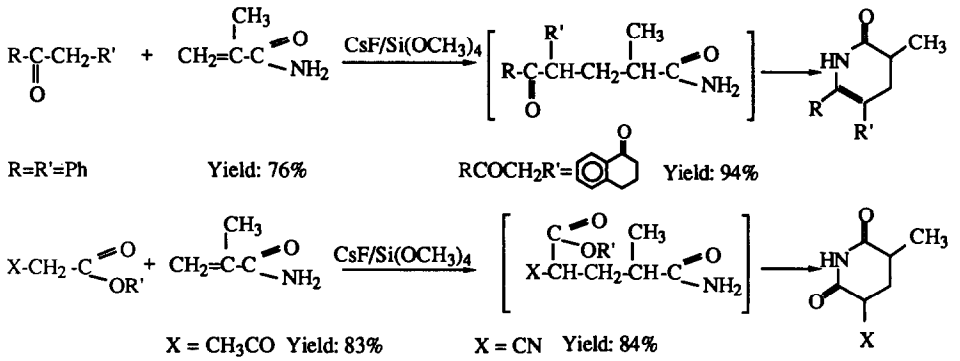


Scheme 5

Table 3

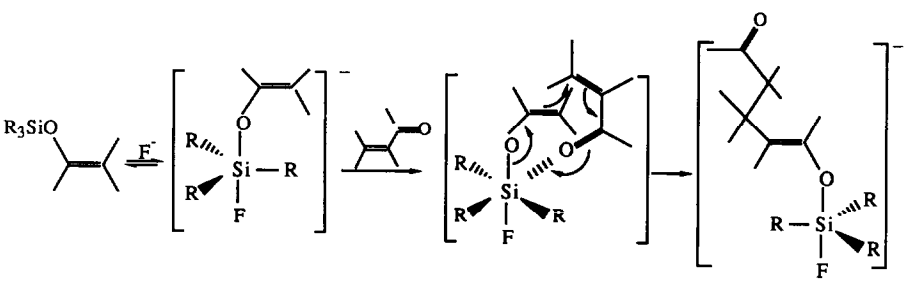
Michael additions in the presence of $CsF/Si(OCH_3)_4$

Electrophile	Michael donor	Reaction Conditions t(h)	T°C	Isolated product	Yield (%)
		4	25		70
	$PhCH_2CN$	1	25		85
	PhCOMe	3	80		55
		5	80		86
	$PhCH_2CN$	1	65		92
	PhCOMe	7	80		76
		5	70		75



Scheme 6

In the case of primary amides an in situ cyclisation was observed leading directly in very good yield to cyclic amides [57] (Scheme 6). This reaction implies the in situ formation of the enoxysilane which is activated by the catalyst (F^-) with formation of pentacoordinated silicon in a pre-equilibrium, followed by concerted attack of the Michael acceptor in the rate-determining step, giving a hexacoordinate intermediate [52] (Scheme 7).



Scheme 7

The same mechanism involving a hexacoordinate silicon intermediate in the rate-determining step has been demonstrated during studies concerning group transfer polymerisation (59).

(2) Nucleophilic assistance for silicon–hydrogen bond reactions: carbonyl reduction (Studies carried out by Dr Reye, Dr Perz, Dr Boyer)

Fluoride ion is a particularly effective catalyst [56,60,61] and has been widely used since the report [62] of CsF catalysed addition of hydrosilanes to carbonyl compounds. This activation provides a very selective reduction of carbonyl groups of aldehydes, ketones and esters using various hydrosilanes as reducing agents [52,56,61,63] (Table 4).

The aldehydes react faster than ketones which are themselves reduced more easily than esters. The silylation of alcohols was also observed [64] (Table 5).

Table 4

Reduction of carbonyl compounds

Carbonyl compound	Reducing system [a]	Reaction conditions		Alcohol isolated	Yield (%)
		t (h)	T (°C)		
$C_6H_{13}CHO$	A	1.75	10	$C_6H_{13}CH_2OH$	85
$CH_2{=}CH(CH_2)_2COCH_3$	A	5	60	$CH_2{=}CH(CH_2)_2CHOHCH_3$	85
$PhCO_2C_2H_5$	B	6.5	80	$PhCH_2OH$	80
PhCOCHBrMe	C	0.5	25	PhCHOHCHBrMe	70
$MeCOCH_2CONHPh$	C	10	25	$MeCHOHCH_2CONHPh$	90
$CH_2{=}CH(CH_2)_2COMe$	C	0	25	$CH_2{=}CH(CH_2)_2CHOHMe$	90
$MeCOCH_2CONHPh$	C	10	25	$MeCHOHCH_2CONHPh$	90

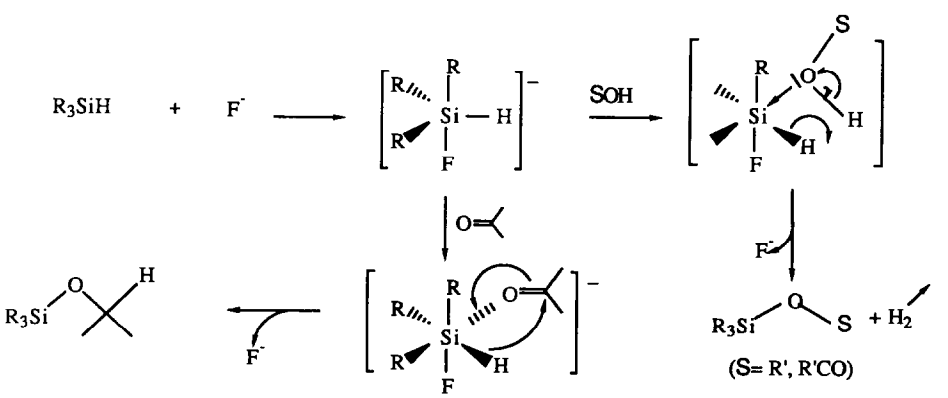
[a] A = $HSiMe(OEt)_2/KF$; B = $Me_3SiO(HSiMeO)_nSiMe_3/KF$; C = $(EtO)_3SiH/CsF$.

Table 5

Silylation of alcohols

ROH	$R_1R_2SiH_2$	Salt	Conditions		$R_1R_2SiH(OR)$ (%)	$R_1R_2Si(OR)_2$ (%)
			t	T (°C)		
m-Cresol	$R_1 = R_2 = Ph$	KF	4 min	25	0	100
Menthol	$R_1 = R_2 = Ph$	KF	30 min	180	0	100
Menthol	$R_1 = Ph$, $R_2 = Me$	KF	1 h	180	15	85
m-Cresol	$R_1 = Ph$, $R_2 = \alpha Np$	KF	5 min	100	0	100
Heptanol	$R_1 = Ph$, $R_2 = \alpha Np$	KF	15 min	180	10	90
Menthol	$R_1 = Ph$, $R_2 = \alpha Np$	KF	30 min	180	10	90
Menthol	$R_1 = Ph$, $R_2 = \alpha Np$	CsF	1 h	180	0	100
Menthol	$R_1 = Ph$, $R_2 = \alpha Np$	CsF	1 h	80	30	70
Menthol	$R_1 = Ph$, $R_2 = \alpha Np$	CsF	1 h	25	100	0

Other nucleophilic catalysts have been found effective for similar reactions, especially the alkoxide ion [65–68]. The mechanism we have proposed involves the coordination of F^- at silicon, followed by the concerted attack of the carbonyl group at silicon with formation of alkoxysilanes after the transfer of hydride to the



Scheme 8

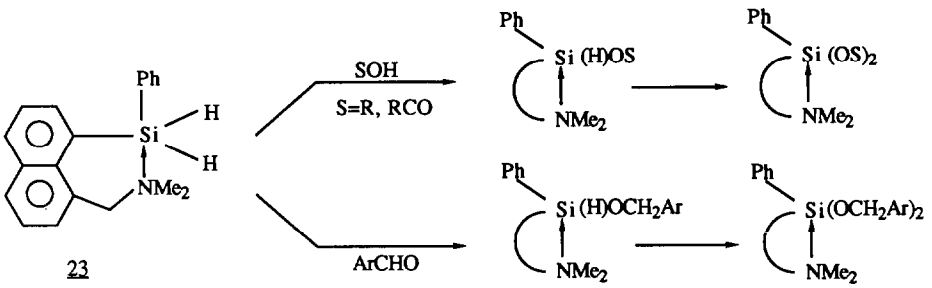
electrophilic carbon (Scheme 8). This mechanism is supported by kinetic studies [70] and by high reactivity of the pentacoordinate hydrosilanes [71].

II. Unexpected reactivity of pentacoordinated silicon compounds

(1) Neutral pentacoordinated silicon hydrides as reducing agents (Studies carried out by Dr Lanneau)

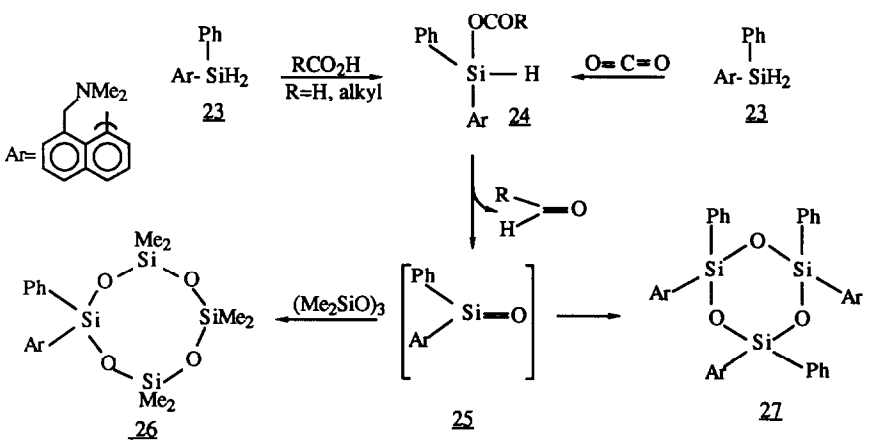
An early report by Eaborn [72] suggested hydrosilatranes as possible reducing agents for benzaldehydes, in contrast to tetracoordinated hydrosilanes, which do not exhibit any reactivity towards alcohols, acids or carbonyl groups.

The intramolecularly coordinated dihydrosilanes previously prepared [71] exhibit high reactivity towards alcohols, acids and carbonyl groups without any activation (Scheme 9). Under the same conditions tetracoordinate dihydrosilanes do not react at all.



Scheme 9

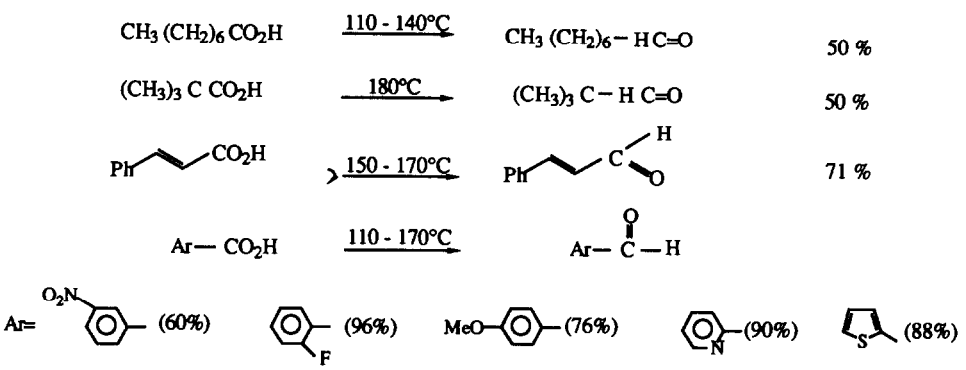
Confirmation of the high reactivity of pentacoordinate silicon compounds towards carbonyl groups was obtained in the reaction of **23** with carbon dioxide, from which the silyl ester of formic acid (**24**) can be isolated and characterized. The same compound was obtained from the reaction of **23** with formic acid. The thermal decomposition of this ester gave $H_2C{=}O$ and trisiloxane. When the reaction was



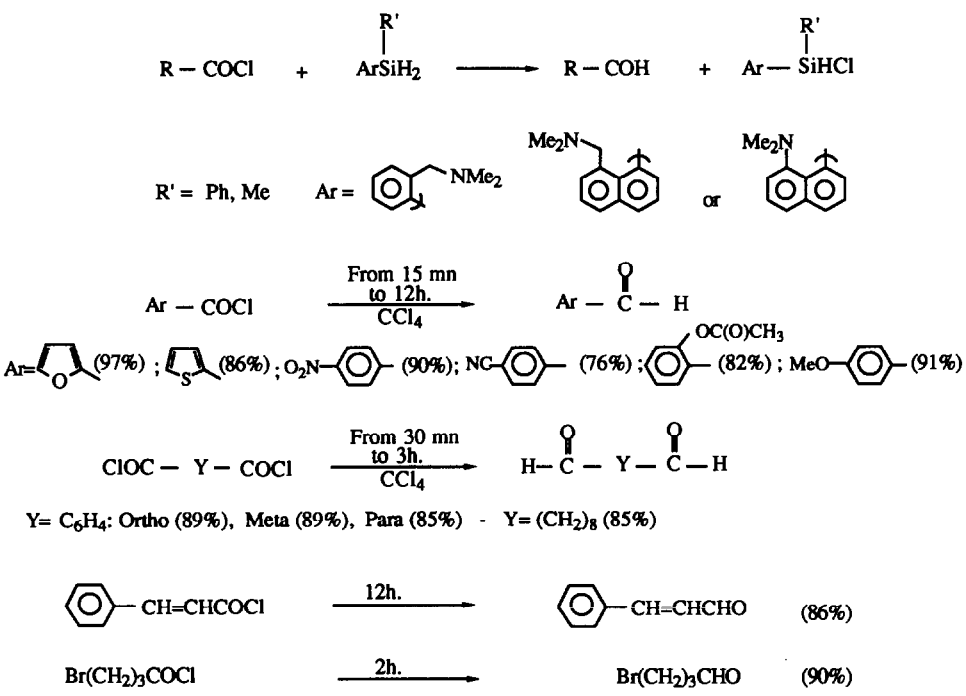
Scheme 10

performed in presence of hexamethyltrisiloxane, the adduct **26** corresponding to insertion of the silanone into the Si–O bond was observed. The mechanism proposed is described in Scheme 10. The transient formation of silanone from hypervalent silicon compound **24** is proven by formation of **26** and **27** [73].

An other application is the thermal reduction of silyl esters of carboxylic acids to aldehydes. The silyl esters are easily prepared by direct reaction of acids with pentacoordinated hydrosilanes. Thermal decomposition of the monocarboxylate esters provides a new route [74] for the reduction of carboxylic acids to aldehydes (Scheme 11).

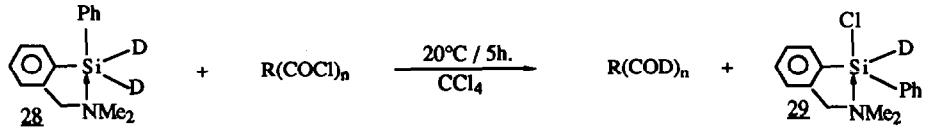


Scheme 11



Scheme 12

This reaction may proceed via the transient formation of a chelated silanone (**25**), since the trisiloxane (**27**) is isolated as the silicon-containing product. 1-NaphPh(H)SiOCOPh is not significantly converted to benzaldehyde on thermolysis, even at temperatures considerably higher than those (100–160 ° C) which are effective with the chelate system. The same pentacoordinate dihydrosilanes have been found to be very reactive towards acyl chlorides under mild conditions, leading to a very general Rosenmund-type reaction [75] (Scheme 12). This method appears to be a good one for the preparation of deuterated aldehydes (Scheme 13).



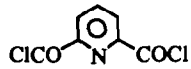
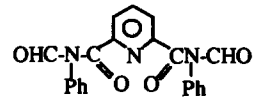
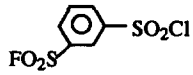
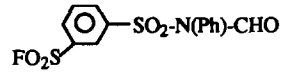
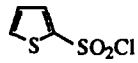
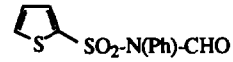
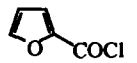
Scheme 13

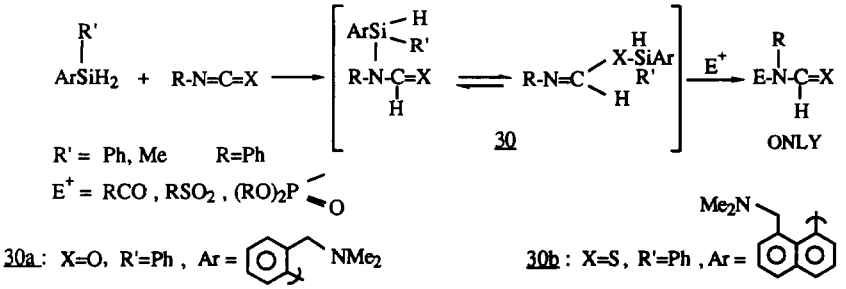
(2) Reactivity towards isocyanates and isothiocyanates (allenoids) (Studies carried out by Dr Lanneau)

The same compounds react also very efficiently with isocyanates and isothiocyanates (allenoids) at room temperature with reaction times from 5 minutes to one hour according to the substrate. A similar reaction was reported [76] to occur at 100 ° C with Pt catalyst in the case of tetracoordinate R_3SiH. The one-pot synthesis of complex organic molecules can be performed by this way (Scheme 14). Some examples of compounds prepared [77] are listed in Table 6.

Table 6

Compounds prepared by the reaction of silanes **30a, b** with acid chlorides

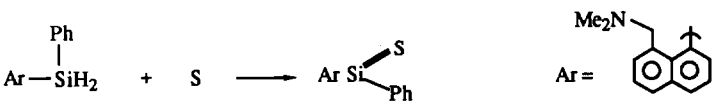
Silane	Acid Chloride	Product	Yield %
30 a	PhO-CS-Cl	Ph-O-CS-N(Ph)-CHO	69
30 a			80
30 a			79
30 a			74
30 b			70
30 b	ClCO-$(CH_2)_8$-COCl	HCS-N-CO-$(CH_2)_8$-CO-N-CHS	72



Scheme 14

(3) Synthesis of stabilized silathiones (Studies carried out by Dr Lanneau and Dr Carré)

The high reactivity of pentacoordinate hydrosilanes has been used for the preparation of low-valent silicon species stabilized by intramolecular coordination. By reaction with molecular sulfur, CS_2 or H_2S, a silathione has been obtained (Scheme 15) and isolated, providing good support for the transient formation of silanone **25** (Scheme 10).



Scheme 15

The structure of the silathione determined by X-ray diffraction has been reported [78]; it has a zwitterionic-type structure with a very short Si–N bond (1.96 Å), and with the length of the Si–S bond 2.01 Å.

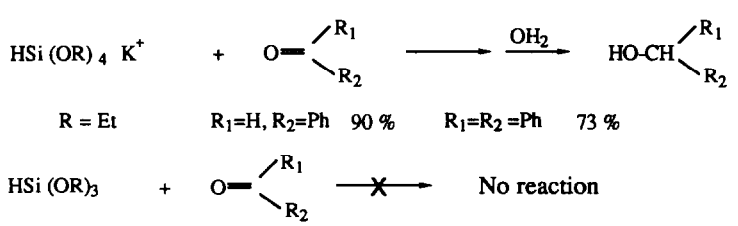
III. Reactivity of pentacoordinate silicon towards nucleophiles

(1) Reactivity of anionic hydridosilicates (Studies carried out by Dr Guerin, Dr Henner)

Anionic hydridosilicates have been prepared by coordination of KOR to $HSi(OR)_3$ without addition of 18-crown-6 [42,101].

$$HSi(OR)_3 + RO^-K^+ \xrightarrow{THF} HSi(OR)_4^-\ K^+ \qquad (R = Me, Et, i\text{-}Pr, n\text{-}Bu \text{ and } Ph)$$

Interestingly, LiOR leads only to the substitution of the Si–H bond, certainly because of the stability of LiH [80]. NMR data are shown in Table 7.



Scheme 16

Table 7

^{29}Si NMR data [a] for $HSi(OR)_3$ and $HSi(OR)_4^-K^+$

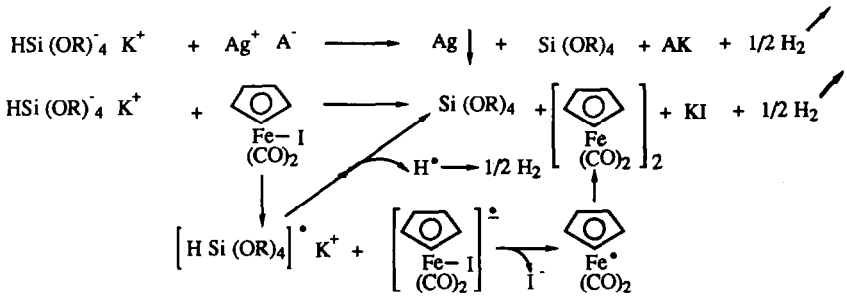
Silane	δ (ppm)	^1J(Si–H) (Hz)	Silane	δ (ppm)	^1J(Si–H) (Hz)
$HSi(OMe)_3$	−62.6	290	$HSi(OnBu)_3$	−59.2	286
$HSi(OMe)_4^-K^+$	−82.5	223	$HSi(OnBu)_4^-K^+$	−86.1	219
$HSi(OEt)_3$	−59.6	285	$HSi(OPh)_3$	−71.3	320
$HSi(OEt)_4^-K^+$	−86.2	218	$HSi(OPh)_4^-K^+$	−112.6	296
$HSi(OiPr)_3$	−63.4	285			
$HSi(OiPr)_4^-K^+$	−90.5	215			

[a] THF as solvent with a capillary containing C_6D_6 to lock the instrument.

These reagents are able to react with carbonyl groups without activation. The reaction occurs very quickly at room temperature [89]. $HSi(OR)_3$ does not react at all under the same conditions (Scheme 16). These observations provide good support for the mechanism proposed for the reduction of carbonyl groups by hydrosilanes activated by F^- and RO^- [52,61,63,79] (Cf. Scheme 8).

These hydridosilicates appear to be very versatile reagents:

• They react as reducing agents by single electron transfer (Scheme 17). ESR signals corresponding to the triphenyl methyl radical [82] and to the 2,6-di-t-butyl benzoquinoyl radical anion [81] have been observed when $HSi(OEt)_4K$ is treated by Ph_3CBr and 2,6-di-t-butylbenzoquinone, respectively.



Scheme 17

• They can be very quickly hydrolysed with loss of H_2 leading to silica powders or gels (cf. Table 8). These results strongly support the formation of pentacoordinate intermediates in the course of the formation of silica by sol-gel process catalysed by bases [83].

• They also react as electrophilic centers with Grignard and organolithium reagents:

$$3\ RMgX + HSi(OR)_4^-K^+ \rightarrow HSiR_3 \qquad (R = Ph,\ PhCH_2)$$

Furthermore, dihydridosilicates may be prepared by the reaction of KH with $HSi(OR)_3$ [89]:

$$HSi(OR)_3 + HK \rightarrow H_2Si(OR)_3^-K^+ \quad (R = Et,\ n\text{-}Bu,\ i\text{-}Pr)$$

NMR data for $H_2Si(OR)_3^-K^+$ are shown in Table 9.

Table 8

Results of hydrolysis of hydridosilicates

$HSi(OR)_4^-$	[C] (mol/l)	Temperature	t_{gel}	Product
OMe	0.25	room temp.	*	white powder
	0.10	room temp.	*	white powder
		0 °C	*	white powder
	0.05	room temp.	*	white powder
		0 °C	*	white powder
OEt	0.50	room temp.	*	white powder
	0.25	room temp.	~ 5 min	gel
	0.10	room temp.	~ 13 min	gel
OPh	0.10	room temp.	*	gel
	0.05	room temp.	~ 3 min	gel
OiPr	0.10	room temp.	~ 30 h	monolithic gel

*: Reaction occurs instantly. IR spectroscopy shows no SiH bond in any of the products.

Table 9

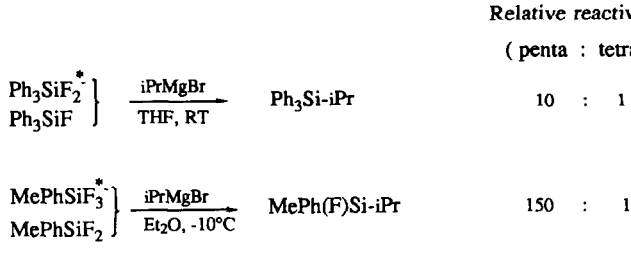
^{29}Si NMR data [a] for $H_2Si(OR)_3^- K^+$

Silane	δ (ppm) (multiplicity)	^1J(Si–H) (Hz)	Silane	δ (ppm) (multiplicity)	^1J(Si–H) (Hz)
$H_2Si(OEt)_3^- K^+$ [b]	−81.85 (t)	217	$H_2Si(OiPr)_3^- K^+$	−87.1 (t)	213
$H_2Si(OnBu)_3^- K^+$ [b]	−80.8 (t)	215	$H_2Si(OiPr)_3^- K^+$ [c]	−87.3 (dd)	224
					193

[a] THF as solvent with a capillary containing C_6D_6 to lock the instrument. [b] Not isolated. [c] C_6D_6 as solvent.

(2) Reactivity of pentacoordinate organofluorosilicates and alkoxysilicates (Studies carried out by Dr Guerin, Dr Henner, Dr Wong Chi Man)

The pentacoordinate organofluorosilicates $Ph_3SiF_2^-$ and $MePhSiF_3^-$, as their ether-complexed 18-crown-6 potassium salts, have proved to be very reactive towards strong nucleophiles (RLi, RMgX, RO^-, metal hydrides) [97]. In fact the pentacoordinate ions react more rapidly than the corresponding neutral tetravalent compounds (lacking an F^- ion). Semi-quantitative comparisons of the relative reactivity are shown in Scheme 18. Similar results were obtained with pentacoordinated alkoxysilicates which also react faster than the tetracoordinated parent [97].

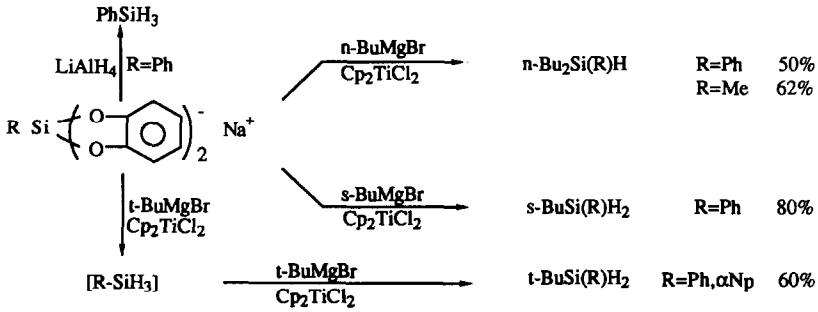


* as K^+/18-crown-6 salts

Scheme 18

(3) Reactivity of organobis(benzene-1,2-diolato)silicates (Studies carried out by Dr Cerveau, Dr Chuit, Dr Reyé)

The complexes $Na^+[RSi(o\text{-}OC_6H_4O)_2]^-$ (R = Me, Ph, 1-naphthyl) were also found [84] to be very reactive towards nucleophilic reagents such as organometallic reagents and hydrides. An excess of hydride leads to trihydrogenosilanes. Reaction with three moles of organolithium reagent or allyl and alkynyl magnesium bromide leads to the tetrasubstituted product. However, hydrosilanes can be obtained in the reactions of alkyl Grignard reagents (2 equivalents) followed by in situ reduction. A one-pot procedure has been reported using alkylmagnesium bromide activated by Cp_2TiCl_2 [85]. Primary Grignard reagents lead to monohydrosilanes while secondary and tertiary Grignard reagents lead to dihydrosilanes (Scheme 19).



Scheme 19

This activation of Grignard reagents containing an hydrogen atom on the β carbon [86–88] has been found to be very efficient in reduction of Si–O bonds [86]. It provides a direct route to trisubstituted organosilanes $R_1R_1R_2SiH$. This is also a particularly useful method in the case of t-BuMgBr providing direct access to Ph-t-$BuSiH_2$.

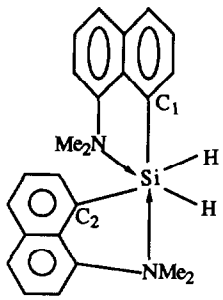
Hexacoordination at silicon (Studies carried out by Dr Brelière, Dr Carré, Dr Royo)

In all the hexacoordinated silicon complexes described previously, the silicon atom was surrounded by electronegative substituents. We succeeded in the preparation of hexacoordinate compounds having two silicon–carbon bonds.

Molecular and crystal structures have recently been determined for compounds **31**, **32** and **33** [90]. The hydrogen and/or fluorine atoms are *cis* to each other, and the position of the ligands appears to be determined by the *cis* position of the two coordinative NMe_2 groups. Furthermore the coordination at silicon takes place *trans* to a Si–F bond and *cis* to Si–H.

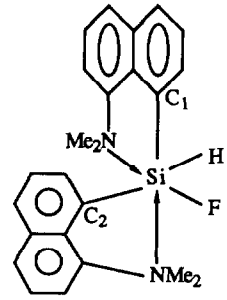
One of the most interesting features of structures **31** to **33** is that the tetrahedral configuration is largely preserved at silicon. The best picture for this geometry is that of a bicapped tetrahedron resulting from twofold nucleophilic coordination. The C(1)–Si–C(2) angle of 135.5° for **33**, for instance, is very far from the 180° of a regular octahedron and larger than tetrahedral angle (109°). Following the ideas of Dunitz [91], compounds corresponding to a tetrahedral silicon atom undergoing two nucleophilic attacks can be considered as good models for hexacoordinate intermediates (or transition states). They thus lend credence to the possible formation of these species in the course of reactions such as nucleophilic displacement at silicon with nucleophilic activation.

(Idealized drawings)



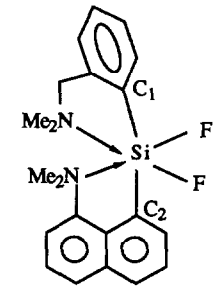
31

Si - H 1. 44, 1. 54 Å
Si - N 2. 61, 2, 80 Å
C_2SiC_1 108°2
C_2SiH 130.4°



32

Si - H 1. 55 Å
Si - F 1. 63 Å
Si - N 2. 65, 2. 68 Å
C_2SiC_1 109°7
C_2SiH 127.3°



33

Si - F 1. 60, 1. 62 Å
Si - N 2. 60, 2. 80 Å
Si - C 1. 84, 1. 87 Å
C_2SiC_1 135.5°

Dissymmetric compounds of general structure **32** have been utilised in studies of their fluxional behaviour.

At the low temperature limit the ^1H NMR spectra show two diastereotopic naphthyl groups and two distinct diastereotopic pairs of methyl groups bound to nitrogen. As the temperature is raised, the two sets of naphthyl signals coalesce, and the four methyl signals are reduced to two. Each of the latter signals corresponds to two methyl groups: one on each nitrogen atom as proved by double irradiation experiments (cf. Fig. 1). Free energy of activation data are given in Table 10.

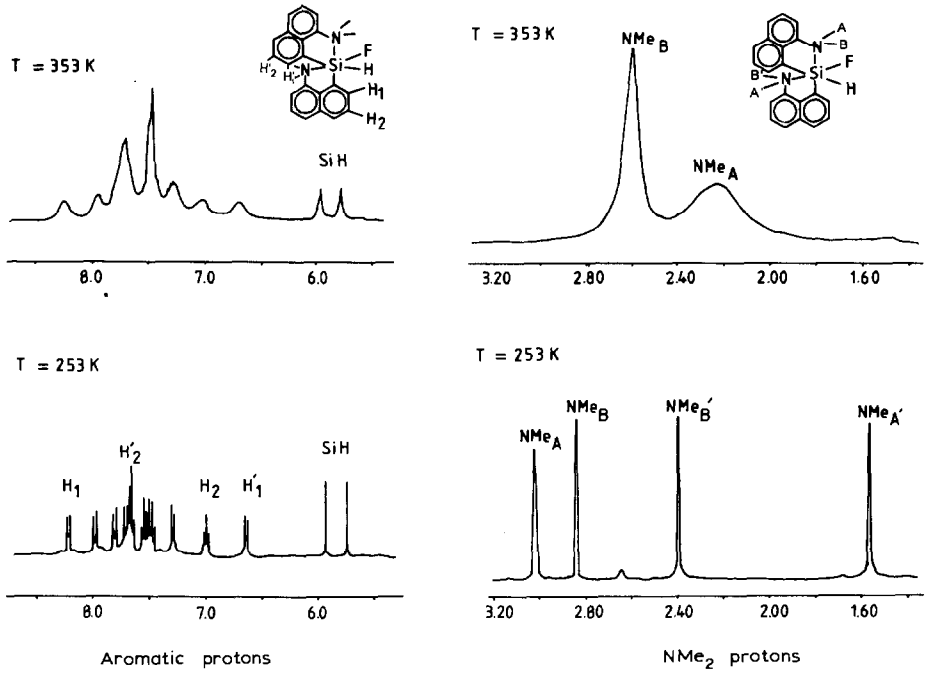
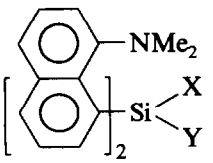


Fig. 1. Variable-temperature ^1H-NMR spectra of **34**.

Table 10

Free energy of activation for isomerization of hexacoordinate compounds from line-shape data [92]



X	Y	$\Delta G^{\ddagger}$ (kcal) (at 300 K)
H	F	14.7
H	OMe	15.2
H	Me	9.3
Me	Ph	12.7

Reactivity of hexacoordinate silicon compounds (Studies carried out by Dr Reyé, Dr Chuit, Dr Cerveau)

The tris(benzene-1,2-diolato)silicon complex **35** was found to react very rapidly with Grignard or organolithium reagents [93]. The extent of substitution depends on the organometallic reagent as follows:

(1) When RM is an alkyl (except MeMgBr) or benzyl Grignard reagent, three silicon–carbon bonds are formed whatever the ratio **35**/RM. (MeMgBr leads only to the formation of Me_4Si in good yield.)
(2) When RM is an alkyllithium reagent, a mixture of tri- and tetra-organosilanes is obtained.
(3) When RM is an allyl, vinyl, phenyl or alkynyl Grignard reagent, R_4Si is formed directly whatever the ratio **35**/RM.

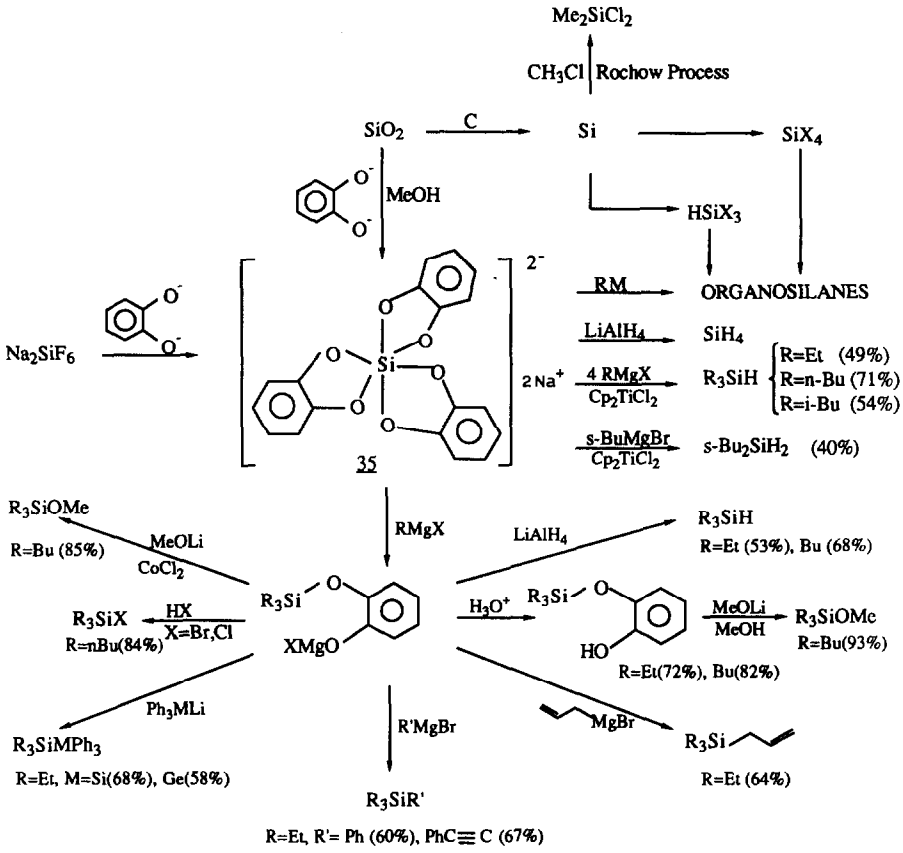
The intermediates $R_3SiOC_6H_4OMgX$ obtained in the reaction of an alkyl Grignard reagent can be isolated by hydrolysis, leading to catechoxysilanes. However, they can be treated directly with different reagents leading to various organosilicon compounds (cf. Scheme 20). Complex **35** can also be treated with a reducing agent such as $LiAlH_4$ to give SiH_4 in quantitative yield.

These reactions correspond to an alternative route for the preparation of organosilanes. The normal route implies the reduction of SiO_2 to elemental silicon which is transformed into SiX_4 or $HSiX_3$. These two compounds are the general precursors, leading to organosilanes either by hydrosilylation or by organometallic coupling reactions. In our case, the trisbenzenediolato complex **35** can be directly prepared from silica and also from Na_2SiF_6 which is a very common by-product from the fertilizer industry.

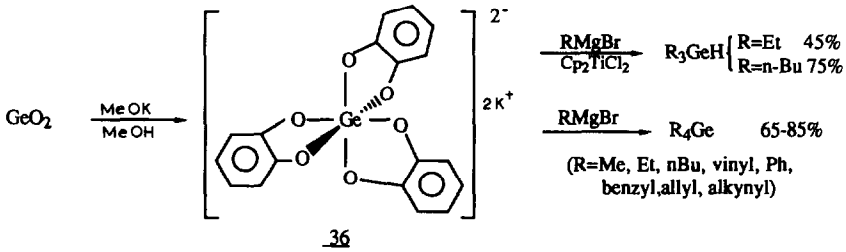
These reactions are useful for the preparation of functional compounds [93]. The reaction of β-hydrogenated Grignard reagents activated by Cp_2TiCl_2 (Cp = cyclopentadienyl) [94] on **35** produces the trisubstituted hydrosilanes (Scheme 20). This is an excellent way to obtain hydrosilanes from silica in two steps [85].

The germanium compounds exhibit the same properties. Hexacoordinate catechol complexes of germanium can be prepared directly from GeO_2. Their reactivity with Grignard reagents is a good way to prepare organogermanes [95] (Scheme 21).

Interestingly, the reactivity of hexacoordinate germanium compounds is higher than the reactivity of $GeBr_4$. For instance from **36** $GePh_4$ is obtained by reaction of C_6H_5MgBr at 20 °C after 25 min. In contrast, the preparation of $GePh_4$ from $GeBr_4$ needs 6 hours in boiling toluene [96].



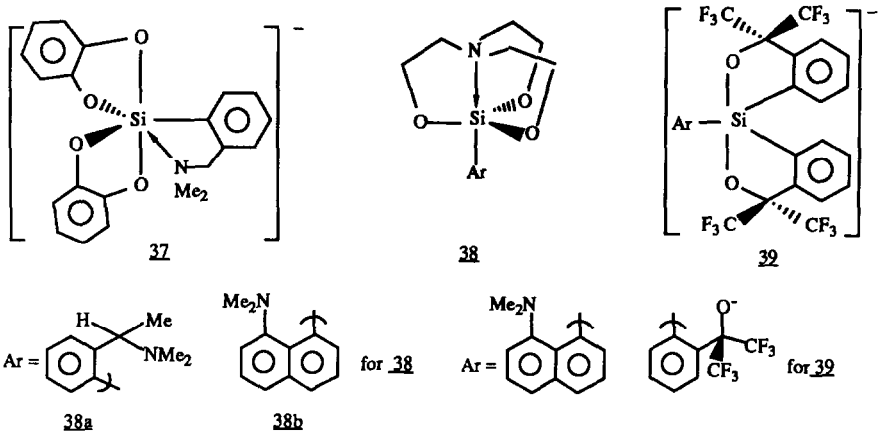
Scheme 20



Scheme 21

From penta- to hexacoordination (Studies carried out by Dr Carré, Dr Cerveau, Dr Chuit, Dr Reyé)

Pentacoordinate silicon compounds exhibit electrophilic properties since they react efficiently with nucleophiles faster than the corresponding tetracoordinate ones. These reactions between pentacoordinate silicon and nucleophiles imply the formation of hexacoordinate intermediates or transition states. In order to determine if the possibility for hexacoordination is a general property of pentacoordinate species, we have compared the behaviour of three different pentacoordinate silicon compounds with respect to possible intramolecular coordination at silicon.



Following the ideas of Dunitz [91] the intramolecular coordination of nitrogen at silicon observed by X-ray studies should correspond to the ability of this atom to undergo a nucleophilic attack.

The X-ray structure of **37** shows that this anion is hexacoordinated with a geometry very close to the octahedral structure [98]. The length of silicon–nitrogen bond is very short (2.15 Å), much shorter than the coordinative bond observed in other neutral hexacoordinated silicon compounds (2.5 to 2.8 Å) (**31–33**). This feature illustrates the high electrophilicity of the silicon atom in the pentacoordinated biscatecholate silicon compounds. This electrophilicity is in agreement with the experimental results showing the high reactivity of phenylcatecholates towards nucleophiles [84]; cf. Scheme 19 [99].

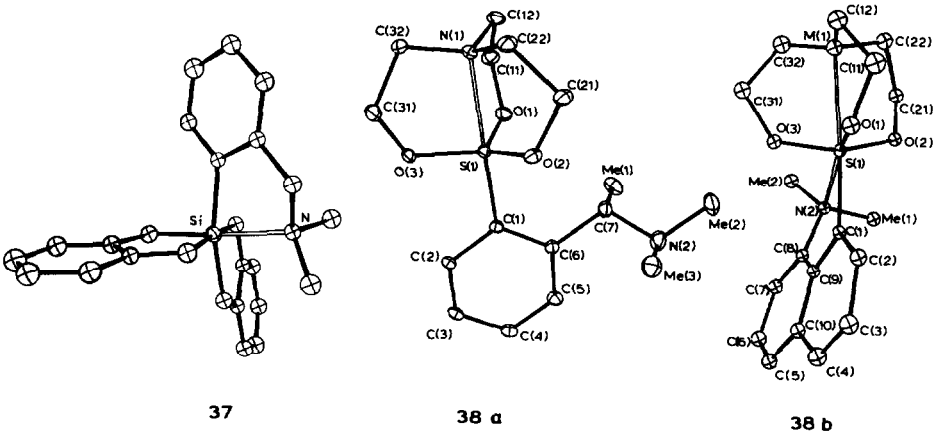
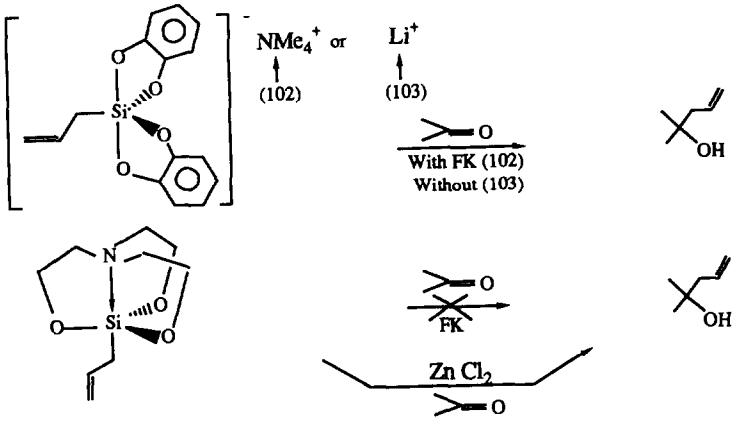


Fig. 2. Molecular structures of compounds **37**, **38a** and **38b**. Some important bond lengths and angles: **37**: Si–N = 2.157 Å; **38b**: Si–N = 2.95 Å, C_1–Si ∧ C_8–N_2 = 26.9°, C_2, C_1, C_9 ∧ C_9, C_8, C_7 = 13.3°, C_3–C_2 ∧ C_6–C_7 = 9.6°.

By contrast the silatrane presents a lower ability to accept intramolecular coordination [100]: in the case of compound **38a** in which benzyl ligand possesses a degree of freedom allowing non coordination, we do not observe any coordination at silicon. However, in the case of the naphthylamino ligand, the geometry of which imposes coordination at silicon because of the complete lack of freedom (**38b**), intramolecular coordination is observed but with very severe deformation of the naphthyl group and a very long silicon–nitrogen bond (2.95 Å); see Fig. 2. This bond is longer than the same bond observed in the case of previously reported silicon–nitrogen coordinative bond (2.5–2.7 Å) and the difference from the bis-catecholate system (2.15 Å) is very illustrative of the difference of electrophilicity of the two silicon atoms.

This difference between silatranes and silylcatecholates is illustrated by a marked difference in reactivity towards nucleophiles [23]. The reactivity of silatranes is lower than that reported for silylcatecholates and the main reaction involves a breaking of the silicon–oxygen bond.

The comparative reactivity of allylsiliconates and allylsilatranes is very illustrative [102]; allylsiliconates react with carbonyl groups without catalyst (103) or with nucleophilic activation, leading to homoallylic alcohols. At the opposite extreme, allylsilatrane does not react at all under the same conditions, cleavage of the silicon allyl bond being observed only in the presence of a Lewis acid catalyst (cf. Scheme 22).



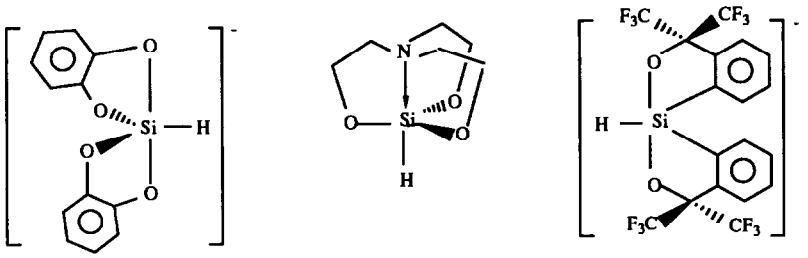
Scheme 22

This low reactivity of silatranes towards nucleophilic reactions is very well illustrated by the chemical behaviour of chlorosilatrane [104]. This compound does not react with any nucleophile. Furthermore organometallic reagents attack first the Si–O and not the Si–Cl bond: it is not possible to substitute the Si–Cl bond without disrupting the silatrane structure [23].

The low reactivity of the Si–Cl bond in chlorosilatrane can be understood from its structure: both Si–N and Si–Cl bonds are shorter than is usually observed in pentacoordinate compounds. The Si–Cl bond (2.12 Å) is only 4% longer than the Si–Cl bond in tetracoordinate compounds (2.04 Å) and the Si–N bond (2.02 Å) is one of shortest coordinative bond observed in silatranes (2.0–2.4 Å). This fact is completely unexpected in relation to the usual situation observed when the coordinative Si–N bond is in the apical position opposite to a silicon–chlorine bond: the

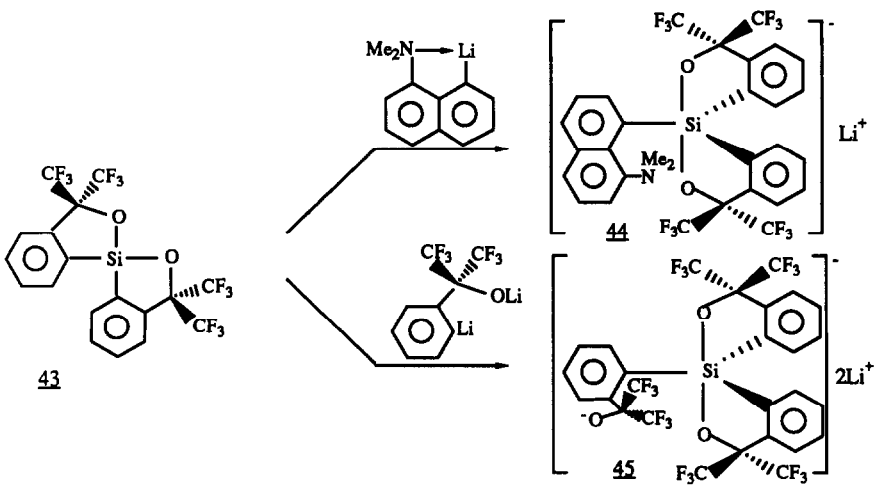
shorter the silicon–nitrogen bond, the longer is the silicon–chlorine bond in the opposite apical position, and vice versa [22]. The difference in behaviour arises from the particular structure of silatranes. We propose that the stereoelectronic overlap between the lone pairs at oxygens and the coordinative silicon nitrogen bond might explain the particular structure of chlorosilatrane and so its very particular reactivity which is not typical of the reactivity of pentacoordinate chlorosilanes.

In order to illustrate how the reactivity of pentacoordinate silicon can be highly dependent on the structure, it is interesting to compare the reactivity of the three pentacoordinate hydrosilanes, shown below. The hydrosilatrane **41** has been shown to react with aldehydes [72]. However, as expected from the weak electrophilicity of silicon atom in silatranes, it reacts slowly (72 hours in boiling xylene with *p*-hydroxybenzaldehyde). On the other hand the bis(benzene-1,2-diolato)hydridosilicate **40** prepared in situ reacts efficiently with aldehydes and ketones [105] like the acyclic hydridosilicates, in agreement with the high electrophilicity of the silicon atom. The anionicity of the compounds seems not to be a very significant factor for the reactivity since, in contrast to the high reactivity of **40**, it was recently reported that the hydridosilicates **42** do not react with carbonyl groups in the absence of electrophilic activation of the >C=O group [106].



40 41 42

In order to understand better the reactivity of **42**, we have prepared related compounds in which the silicon atom could undergo further intramolecular coordination (Scheme 23).



43 44 45

Scheme 23

Interestingly, and in agreement with the lack of reactivity of the corresponding hydride, we do not observe any coordination at silicon, as determined by NMR studies. In compound **44** the NMe_2 group of the naphthylamino ligand does not exhibit any diastereotopy. Furthermore the ^{29}Si chemical shift is in the range for pentacoordinate silicon compounds. The case of **45** is also illustrative: its geometry corresponds to that of a pentacoordinated silicon which contains an external ligand without any further coordination, since the ^{19}F NMR spectrum exhibits two A_3B_3 type signals for the four CF_3 groups of the spiro structure and only one ^{19}F signal for the two CF_3 groups [107].

Conclusion

In conclusion, both penta- and hexacoordinate hypervalent silicon species offer great interest from both the structural and reactivity point of view. The isolation of these compounds and their very particular chemical behaviour open new possibilities in silicon chemistry and confirm the validity of the mechanistic propositions based on extension of coordination at silicon.

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