The Structure and Reactivity of Hypervalent Organosilicon Compounds

Thesis

How to cite:

O'Neill, Henry Raymond (2001). The Structure and Reactivity of Hypervalent Organosilicon Compounds. The Open University.

UNRESTRICTED

The Structure and Reactivity of Hypervalent Organosilicon Compounds

by

Henry Raymond O'Neill

Thesis Presented for the Degree of
Bachelor of Philosophy
Open University

2001

DATE OF SUBMISSION: 30 SEPTEMBER 1999
DATE OF AWARD: 31 OCTOBER 2001

Acknowledgements

I would like to thank Professor Bassindale and Dr Taylor for their assistance and my wife for her tolerance

HYPERVALENT SILICON COMPOUNDS

The purpose of this thesis is to review the structure and reactivity of hypervalent silicon and to consider the underlying explanation for the observed enhanced reactivity of such compounds towards nucleophiles.

CONTENTS

CHAPTER 1: STRUCTURE OF ORGANOSILICON COMPOUNDS

1.1 - INTRODUCTION

The study of hypervalent silicon compounds dates back to the work of Davy (1812)[1] and Gay-Lussac and co-workers (1814)[2]. Some of the most recent studies of organosilicon compounds have been on their biochemistry. For example, the Ghosh group (1996)[3] have studied the immunochromic effect when antibodies interact with tetravalent silicon to form hypervalent compounds. Tacke and co-workers (1998)[3a] have studied various theoretical aspects of zwitterionic penta coordinate silicon using a Si/O_2N_2C framework. In addition, major work on the industrial application of organosilicon compounds continues apace. For example, the Corriu group (1998)[4] have utilized organosilicon compounds as a way of synthesizing porous silica with uniform pore diameter. Interest in hypervalent compounds has been extended to the synthesis and structural determination of hypervalent compounds of other elements such as arsenic (Akiba group 2000)[4a]. However, over the last decade a major effort has gone into the study and synthesis of hypervalent silicon compounds as they provide a model for the nucleophilic substitution of intermediates of silicon. Interest in hypervalent compounds of carbon has also grown since the detection of CLi_6 by Kudo (1992)[5]

1.2 - ^{29}Si N.M.R.

Several techniques have been applied to the elucidation of the structures of organosilicon compounds. A particularly powerful technique is ^{29}Si N.M.R. This area has recently been reviewed by Williams (1989)[6]. However, a few salient features are worth mentioning at this point. ^{29}Si has a chemical shift range that is similar to carbon and hence significantly larger than that of hydrogen. This means that ^{29}Si can be a very sensitive technique for subtle changes in structure. In addition, Magic Angle Rotation (Spinning) has provided additional information for solid state structural determination. ^{29}Si has a spin of ½ but has a low abundance (4.7%). In addition, it has a long T_1 and a negative gyromagnetic ratio that results in a negative Nuclear Overhauser Effect. These factors combine to reduce the sensitivity of this nucleus. However, this does not detract from the large amount of information this technique can provide. The spectrum is often recorded in the presence of $Cr(acac)_3$ that will reduce T_1 to a few seconds. Other methods have been developed for recording spectra such as selective population transfer (Linde and co-workers, 1975)[7] and J cross polarization (Murphy, 1979)[8]. Both these techniques give rise to a signal enhancement of about a factor of five. Other pulse techniques such INEPT and DEPT have also been used to study the chemical environment of ^{29}Si (Morris group (1979)[9]. The reported range is 825ppm which includes Cp^{*}_2Si whose resonance occurs at -577ppm (Jutzi and co-workers, 1986)[10].

With respect to hypervalent species there is a pronounced shift in the ^{29}Si chemical shifts to the lower frequencies when the co-ordination number increases to beyond four. Several studies have shown that intramolecular co-ordination gives rise to shielding effects. Some examples are shown below in table 1:

TABLE 1 - SELECTED ^{29}Si RESONANCES

COMPOUND	CHEMICAL SHIFT (ppm)	REFERENCE
$(Me_2C_3H_2O_2)_2SiMeCl$	-192.4	Cella group, 1980[11a]
$(MeN_2C_3H_3)_2SiMe_2H$	-81	Bassindale group, 1984[11b]

^{29}Si assignments have proved a useful technique and several trends have been discerned including:

1) Compounds with a co-ordination number six are more highly shielded than co-ordination number five.

2) Substituents on aromatic rings can have a profound effect on the ^{29}Si chemical shifts. Co-ordination number 5 have a normal chemical shift range of about -50 to –150 ppm and co-ordination number 6 is in the range -130 to –200 ppm.

1.3 - GENERAL STRUCTURAL CONSIDERATIONS

A major review containing a significant number of references and crystallographic data has been prepared by Corriu group (1993)[11] and Lukevics group (1989)[12]. They both contain a large amount of information about the structure of penta and hexa coordinated compounds of silicon. They have divided the review into parts dealing with neutral, anionic and cationic complexes. In addition the synthesis and structure of hypervalent compounds up to 1986 have been reviewed by Voronkov (1986)[13]. This large review is supported by a large number of references.

In the review Voronkov (1986)[13] analyzed the atomic and structural differences between carbon and silicon. The main differences include the following:

1) The covalent radius is approximately 1.5 times that of carbon.

2) The outer electrons of silicon are shielded from the nucleus by eight additional electrons.

3) Silicon has a lower electronegativity.

4) Silicon has available low lying and vacant d orbitals.

5) Silicon is more easily polarized than carbon due to the greater spatial expansion of the outer atomic orbitals.

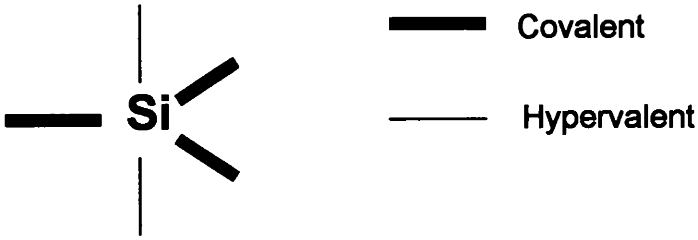
6) The ionisation energy of silicon is lower than carbon.

Many of the above properties are also shared with germanium.

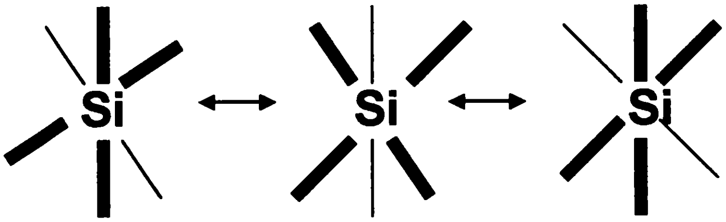
As mentioned above, silicon has five vacant d orbitals that in principle can lead to penta and hexa co-ordination. The trigonal bipyramidal (TBP) structure can in principle involve the $3d_z^2$ atomic orbitals in a sp^3d hybrid and the square pyramidal (SP) structure involves the $d_{x^2-y^2}$ orbital. The result is two sets of non-equivalent bonds of different lengths. In the octahedral case, the atomic orbitals d_z and d_{x-y} may be considered to be involved in the sp^3d^2 hybrids. The remaining orbital could be available for π bonding with the appropriate ligands.

However, the involvement of the 3d orbitals has been argued against. It has been suggested by Kutzelnigg (1984)[14], that the increase in valency of silicon has very little to do with the availability of vacant d orbitals, partly due to their very diffuse nature, but more to do with the large size of the Si atom and hence, reduced steric hindrance. It is further argued that the correct approach would be to consider the formation of electron rich multicentred bonds. In addition Rundle (1963)[15], whose paper was originally applied to noble gas compounds proposed electron rich three centred bonds. This work was extended by Musher (1969)[16], based on groups 15 - 18 in which he developed the idea of two types of hypervalent bond. In one type, only the p orbitals are involved, whereas in the second type s and p orbitals are involved. Musher suggested that when silicon expands it co-ordination shell, the ligands are added along the axis of one of the of p orbitals thereby forming a three centred four electron covalent bond.

In SiF_5^-, the formation of the axial fragments of the complex involves the silicon $3p_z$ orbital. The bonding molecular orbital is formed by the in phase overlap between the central $3p_z$ orbital and the p orbitals of the fluorine. Of the four electrons, two occupy the bonding molecular orbital while the remaining two occupy an approximately non-bonding molecular orbital. The bond orders of these bonds are of a much lower order than the two-centred two-electron covalent bond. Experimental data suggests that the axial bonds in TBP are longer and more polar than the equatorial bonds:



In the anions of the type SiF_6^{2-}, the bond lengths are equivalent and this may be explained by the actual structure being a resonance hybrid:



The mixing of bonding and non-bonding atomic orbitals, which result in a shift of electron density from the central silicon atom to the ligands, as they have become known, thus forms hypervalent molecular orbitals. Several workers have suggested that the following conditions have to be met in order for hypervalent bonds to form:

1) The ligands must be more electronegative than the silicon.

2) The most electronegative ligands participate in such bonding

3) The Si-X bond lengths are greater than in the tetrahedral case.

4) The hypervalent bonding results in a reduced electron density at the silicon.

Reed and co-workers (1986)[17] have investigated the contribution of d orbitals to hypervalent bonding in SF_6. They found that, although not essential, the participation of these orbitals would lower the energy of the system.

A useful set of relationships has been identified by Gutman (1975, 1976 and 1978)[18] , which are known as the donor acceptor approach. He has produced a series of rules that are not based on any bonding theory but are useful in rationalizing crystallographic data. The rules may be stated as follows:

1) The stronger and the shorter the bonds between a donor and an acceptor, the greater will be the lengthening of adjacent bonds.

2) A sigma bond is lengthened when, because of the interaction, an electron shift occurs from a nucleus carrying a positive fractional charge. However, bond shortening occurs when there is an electron shift in the opposite direction. As the co-ordination number increases, the bond length increases.

The early literature indicates that for 5 co-ordinate compounds there are two favoured geometric arrangements, that of trigonal bipyramidal (TBP) (D_{3h}) and square pyramid

(SP) which has a C_{4v} symmetry. The TBP is usually observed in acyclic penta co-ordinate compounds while the SP is usually found in transition metal derivatives. Calculations indicate that the TBP structure is about 8% more stable than the SP structure. However, the presence of two unsaturated five membered rings in spirocyclic derivatives is likely to produce a SP structure.

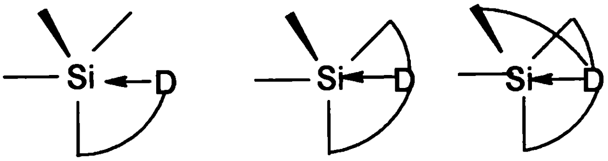
For TBP compounds that are not homoleptic, various achiral isomers are possible for compounds of the form $SiX_{5-n}D_n$. The most electronegative substituent will always be located in the axial position

In compounds that are hexa co-ordinate such as SiX_4D_2, there are two possible isomers. In one case, the D groups are *trans* to each other and hence the complex is D_{4h} while in the other they are cis to each other and therefore C_{2v}. In general, it has been shown that D will occupy a *cis* position if the steric requirements are less than X. Adley and co-workers (1972)[19] has shown this assertion to be correct when applied to of $SiX_4(bipy)_2$ and $SiX_4(Py)_2$, where py = pyridine and bipy = bipyridine. In the case of bipy, it will occupy a *cis* position.

Voronkov also points out that the bond angles of silicon are far easier to distort than carbon. This means that CH_4 is much more difficult to convert from Td to D_{4h} symmetry (Collins group, 1980)[20]. Erker and Rottger (1997) [20a], have recently reviewed planar tetra co-ordinated carbon.

Spirocyclic compounds containing five co-ordinate silicon often form stable compounds with bases. The geometry of the ligand can have a large effect on the co-ordination stability of organosilicon compounds, although up until 1986 only qualitative analysis of ligand effects were available. However, many of the effects could be explained in terms of the 'chelate effect'. The existence of the effect is said to depend on a balance of entropy and enthalpy. In the former case this arises from a smaller configurational entropy at the cyclic ligand but decreases with increasing size of the saturated ring (Fransto da Silva 1983)[21]. The enthalpy effect arises from the fact that the ring is already under strain and consequently does not have to be forced into a new conformation. However, Bell (1977)[22] has questioned the existence of the chelate effect, and has suggested that its existence is simply due of the method by which stability constants are calculated.

The Lehn group (1975)[23] have examined macrocyclic and cryptate silicon complexes. These results indicate that the stability of other complexes should increase in the following order:



One of the most stable compounds studied has been the silatranes of the type $XSi(OCH_2CH_2)_3N$. The basal nitrogen is linked to the oxygen atom via three CH_2CH_2 groups and the resulting structure is TBP. This is a direct result of having an intrabridgehead arrangement of the ligands.

Another important factor that has a bearing on the structure of organosilcon compounds is the medium. The co-ordination number of many compounds changes with the state of solvation. The strength of the donor-acceptor bond increases on going from gas to solution to the solid phase and with increasing pressure and decreasing temperature.

Sheldrick (1989)[24] has produced a major review on structural organosilicon chemistry. He has noted several features that can result in the stabilization of the SP geometry:

1) Four electronegative substituents such as oxygen may occupy the basal position of the SP. If TBP geometry were adopted, two of the oxygen atoms would have to occupy a possibly unfavourable equatorial position.

2) Two unsaturated five membered rings containing similar electronegative groups directly bonded to the central silicon must be present. Stabilisation is achieved by Π bonding that is greater in magnitude than can be achieved by ring puckering. Therefore, a reduction in strain energy may be achieved by assuming SP geometry.

3) Apical ligands should be of low electronegativity. A large bulky ligand in this position is also favoured.

Many compounds are displaced along the Berry pseudorotation pathway between TBP and SP. The extent of the displacement may be determined by using the dihedral angle method which was put forward by Holmes (1977)[25]. In addition, the displacement of the silicon atom from the trigonal plane has been studied by Voronkov (1978)[26]. He has suggested the following relationship for the compounds that contain a dative Si-N bond:

$$\Delta Si = -1.41 + 0.62d(Si\text{-}N)\ \ (\text{Å})$$

In addition, the Schomburg group (1985)[27] have proposed an expression for the average angle (a) between the axial and equatorial substituents:

$$\mathrm{Cos}\alpha = 1.249/d(Si\text{-}N)-0.6915$$

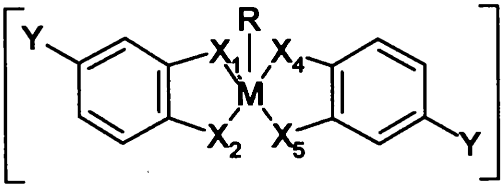
$$\mathrm{Cos}\alpha = 1.281/d(Si\text{-}O)-0.788$$

These attempts provide a mathematical description of the change on going from a tetrahedral to TBP geometry.

Another review on hypervalent compounds has been produced by the Corriu group 1989)[28]. This deals with the synthesis, structure and dynamic stereochemistry. Of particular importance is the topology of penta and hexa coordinated compounds. Again, this review contains a large number of references. An older review of penta co-ordinate compounds of phosphorus and silicon was published by Holmes (1984)[29].

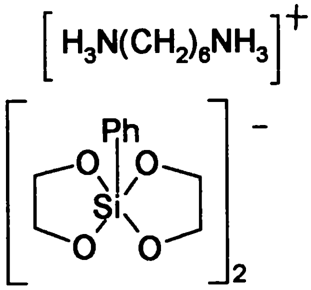
1.4 - HYPERVALENT SILICON COMPOUNDS CONTAINING ONLY SINGLE Si-L BONDS

Holmes and coworkers (1984)[30] have carried out an extensive study of pseudorotation of 5 coordinated compounds. The compounds prepared were cyclic anionic species that are isoelectronic with 5-co-ordinate group 15 compounds for elements such as phosphorus. They have the general form shown below:

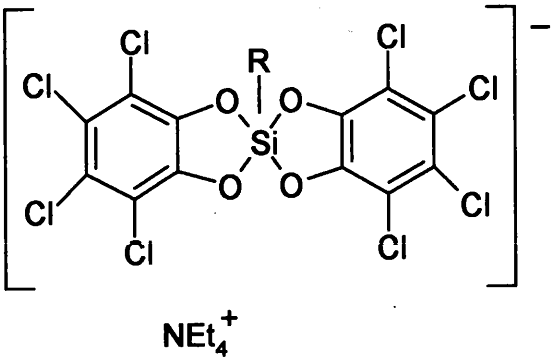


1

M	R	X	Y
Si	F	O	H
Ge	Cl	O	H
Sn	Cl	S	CH_3



2

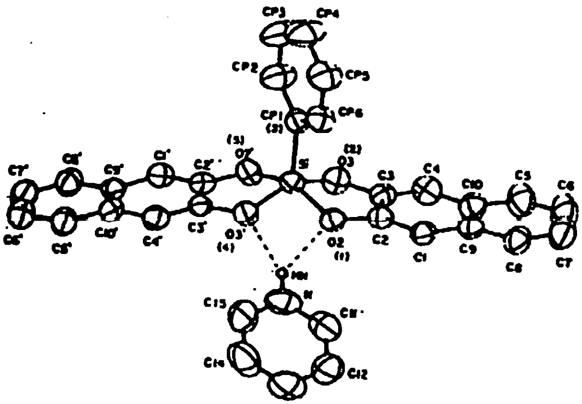


The structure of compound (1) (M=Si) is 72% displaced from the ideal trigonal planar structure towards the square planar configuration. The results indicate that anionic compounds can form a continuous series of structures from TBP to SP along a Berry pseudorotation pathway. The ideal TBP structure is achieved by using two five membered unsaturated rings and one group attached to the silicon. Compound (1) fulfills this requirement.

The structure of (2) was found to be 72,1% displaced towards SP whereas (3) was 89.8% displaced towards SP. The Si-O bond lengths vary, depending on the structure, from 1.78A axial to 1.68A equatorial for TBP and 1.73A in the base of SP. The results again suggest a Berry pseudorotation pathway and indicate that there is no stereochemical rigidity in such compounds. The structures also indicate that different amounts of hydrogen bonding occur to the cation.

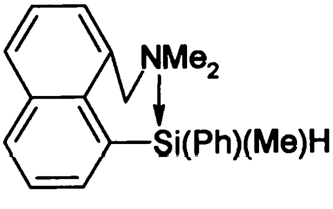
The ability to achieve SP is due in part to the use of large unsaturated ring systems. This may partly be explained by the greater electron delocalisation that reduces electron pair repulsion for bonds directed towards the central Si atom. Such an effect would result in a reduction in energy for the less stable SP with respect to the TBP. The structure of (3) is less easily explained because the Ph group is significantly less displaced towards SP and the bond distances involved indicate a steric effect.

Holmes (1984)[31] prepared a series of 5 co-ordinate compounds including pyridinium bis (2,3 naphthalendiolate) phenyl silicates and the X-ray structures were determined:

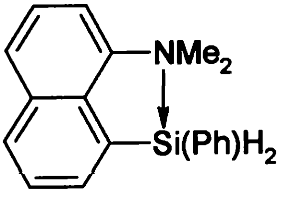


Analysis of the bond lengths of this and related compounds indicate a continuous range of ring Si-O bond lengths that vary from 1.78Å (axial) and 1.68Å (equatorial) for TBP to 1.73Å (basal) for SP. The results suggest a high degree of structural non-rigidity. There are also indications of the presence of hydrogen bonding between the hydrogen associated with the nitrogen of the pyridinium ion and the oxygen of the anion.

The Corriu group (1986)[32] have studied two hypervalent silanes by X-ray diffraction and ^{29}Si N.M.R. A diagram of the compounds are shown below together with the Si-N bond lengths and the ^{29}Si N.M.R. chemical shifts:



^{29}Si NMR = - 25.84ppm



^{29}Si NMR= - 35.62ppm

Si<-N distance 2.66Å

Si<-N distance 2.59Å

In both cases, it was shown that the H atoms take up an equatorial position in a trigonal bipyramidal structure. The ^{29}Si N.M.R. chemical shifts were found in the range associated with pentavalent compounds,

A more recent study was carried out by Corriu (1989)[33] on intramolecularly coordinated compounds. The crystal structure of 2-(dimethylaminomethyl)phenyl-1-naphthylsilane was obtained. In this structure the silicon shows an essentially TBP structure with the axial positions being occupied by the naphthyl and nitrogen donor groups. The two hydrogen atoms occupy the equatorial positions (see page 18). Five membered rings often select this conformation, where the axial equatorial bond angle is 90^0 in order to minimize ring strain. This has been reviewed by Mislow (1970)[34]. The five membered chelating rings are essentially planar but in a six membered ring such as in [8-(dimethylaminomethyl)-1-naphthyl]methyl(phenyl)silanes, show significant folding along the Si-CH_2 axis occurs and the position of the Si-N bond is about 1.2Å above the plane of the other members of the ring. Additional studies were carried out on other compounds including:

2-(Dimethylaminomethyl)phenyl-1-naphthylsilane (4),
2-(Dimethylaminomethyl)phenyl(fluoro)methylsilane (5),
[8-(Dimethylamino)-1-naphthyl)trifluorosilane (6),
[8-(Dimethylamino)-1-naphthyl]phenylsilane (7),
[8-(Dimethylaminomethyl)-1-naphthyl]phenylsilane (8)
[8-(Dimethylaminomethyl)-1-naphthyl]methyl(phenyl)silane (9).

Some of the physical and spectroscopic data is shown in Table 2.

TABLE 2 - SPECTROSCOPIC DATA ON SELECTED COMPOUNDS

Compound	Mp/Bp(°c)	^{19}F	^{29}Si	M/E	Yield(%)
(4)	59(MP)	-	-	291	80
(5)	162(BP)*	-111	-52.53	215	80
(6)	62(MP)	-148	-102.2	-	85
(7)	84(MP)-	-	-	41	
(8)	53(MP)	-	-	60	
(9)$^{+}$	81(MP)	-	-	-	29

*Recorded at 18mmHg +Crystal structures determined.

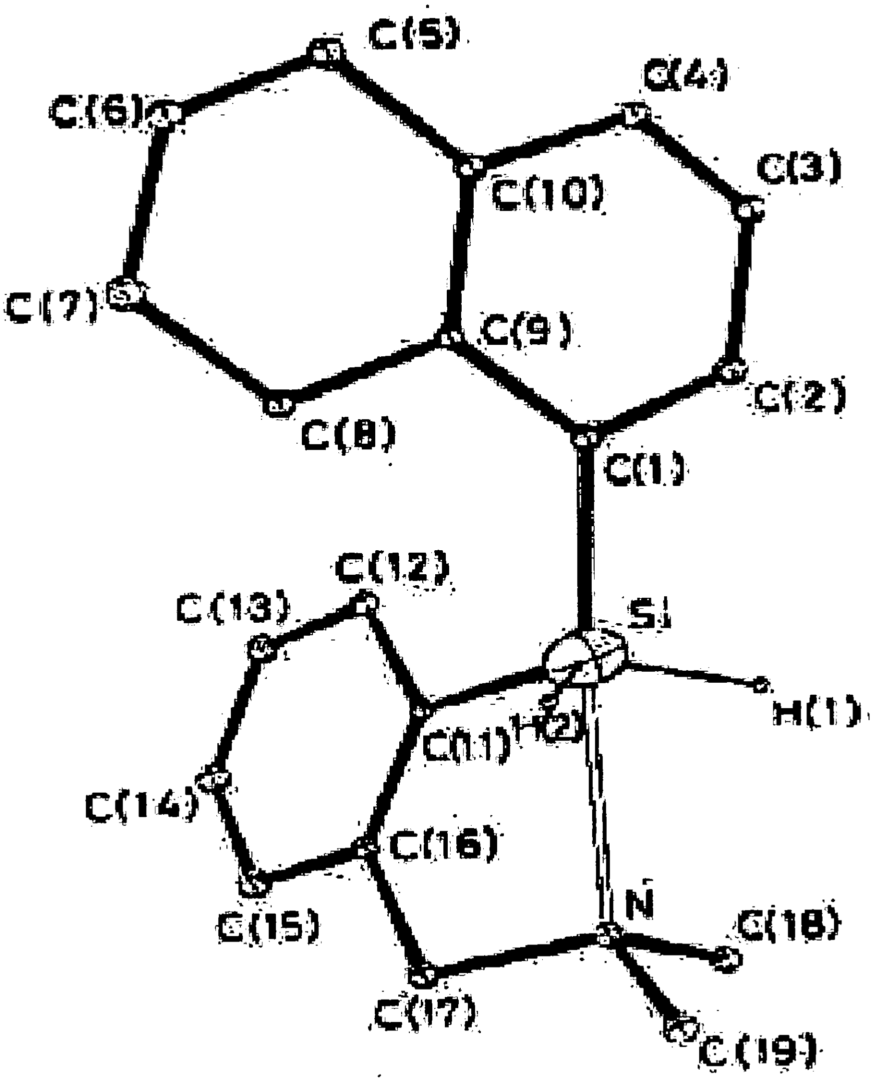
Additional studies in terms of both crystal structures and some ^{29}Si N.M.R. work has been carried out on other compounds, some data on which is shown in Table 3:

TABLE 3 - SELECTED BOND DISTANCES AND ^{29}Si RESONANCES

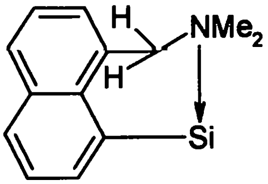
Compound*	N->M (A)	M-X (A)	^{29}Si	Reference
10	2.01	1.6	-94.6	Stevenson group (1985)[35]
11	1.92	2.35	-	Onan group (1978)[36]
12	2.03	2.27	-	Klebe group (1985)[37]

* Diagram of the compounds are shown on page 19

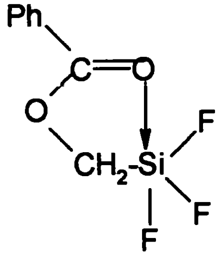
In all cases, a nitrogen donor occupied the axial position with the halogen (X) *trans* to the donor. The donor-silicon interaction is long but still suggests a significant interaction. The M-X distances are longer than in the tetracoordinated species. Additionally the work of Britton (1981)[38] on a very large number of tin compounds and the work of the Klebe group (1985)[37] on organosilicon compounds showed that the TBP structure is preferred.



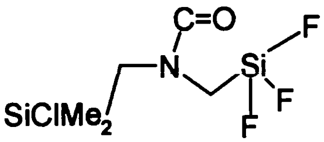
Corriu (1989)[33]



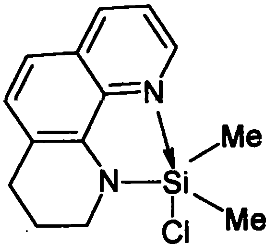
Corriu 1989



10



11



12

In the Corriu (1989)[33] paper he provides information on a comparison of N.M.R. data between the pentacoordinated species and the tetracoordinated species. It should be noted that those compounds which had three -OR groups or three alkyl groups attached to the silicon did not show any significant ^{29}Si chemical shift variation relative to the tetracoordinated species. This suggests that co-ordination to form five co-ordinate species did not occur. Voronkov and co-workers(1983)[39] have also made a study of these compounds using ^{19}F N.M.R.. They found that satellites due to ^{19}F and ^{29}Si coupling were present which indicates of slow fluorine exchange.

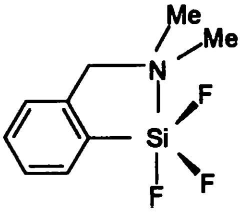
Using low temperature ^{19}F N.M.R., Corriu and co-workers (1989)[40] were able to show that in a number of compounds of the type shown below in Table 4, temperature lowering resulted in a highfield doublet and a low field triplet being observed. This indicates the presence of two equatorial and one axial fluorine.

TABLE 4 - ^{19}F N.M.R. RESONANCES

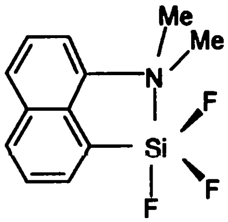
Compound	**^{19}F(ppm)**	**Temperature (^{0}C)**
$LSiF_3$	-142.5	30
$L'SiF_3$	-138	80
$L''SiF_3$	-140.7	30

Where:

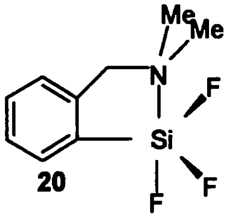
$LSiF_3$ =



$L'SiF_3$ =

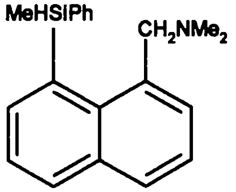


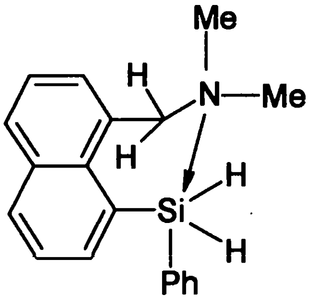
$L''SiF_3$ =



20

Additional information may be obtained by considering the ^{1}H N.M.R. The ^{1}H N.M.R. allows the detection of diastereotropic NMe_2 methyl groups that indicate the presence of intramolecular Si-N co-ordination. For example, in the two compounds below the methyl groups of the NMe_2 are equivalent and a sharp singlet is observed at room temperature. However, when the temperature is lowered a doublet is obtained indicating Si-N co-ordination.





The Holmes group (1989)[41] has further extended the study of hypervalent compounds by studying compounds of the type $RSiF_4^-$ using ^{29}Si, ^{19}F and X-ray diffraction. The compounds were prepared as 18-crown-6 salts of the type $[RSiF_4][K$-18-crown-6$]$ where R = :2,4,6,tri-tert-butylphenyl(TBP)(13), mesityl(14), *n*-propyl(15), ethanediylbis(tetrafluorosilicate)(16), tert-butyl(17), cyclohexyl(18), Benzyl(19), *p*-chlorophenyl(20), *p*-tolyl(21), *m*-tolyl(22), *o*-tolyl(23).

The synthesis involved the reaction between KF and the appropriate $RSiF_3$ in the presence of 18-crown-6 ether.

Some of the physical and spectroscopic data associated with these compounds is shown in Table 5:

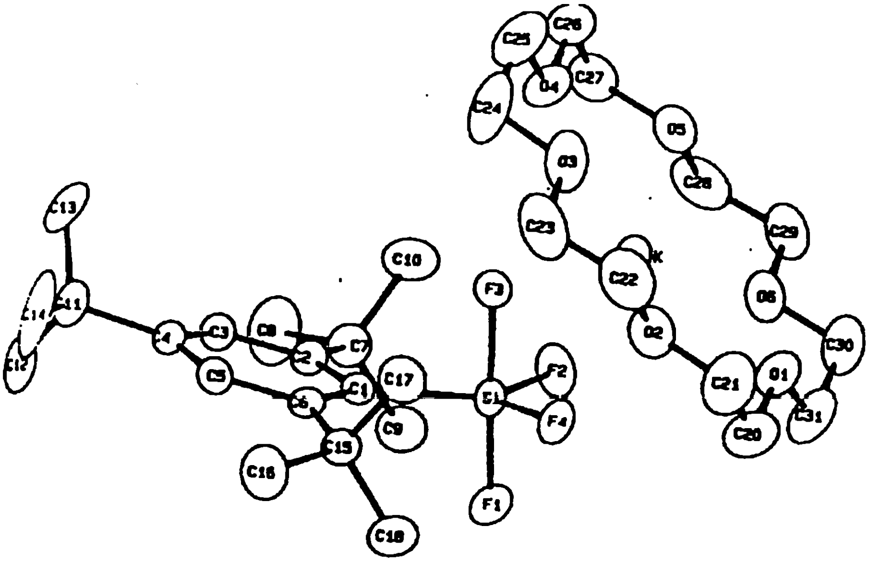
TABLE 5 - PHYSICAL PROPERTIES OF SELECTED COMPOUNDS

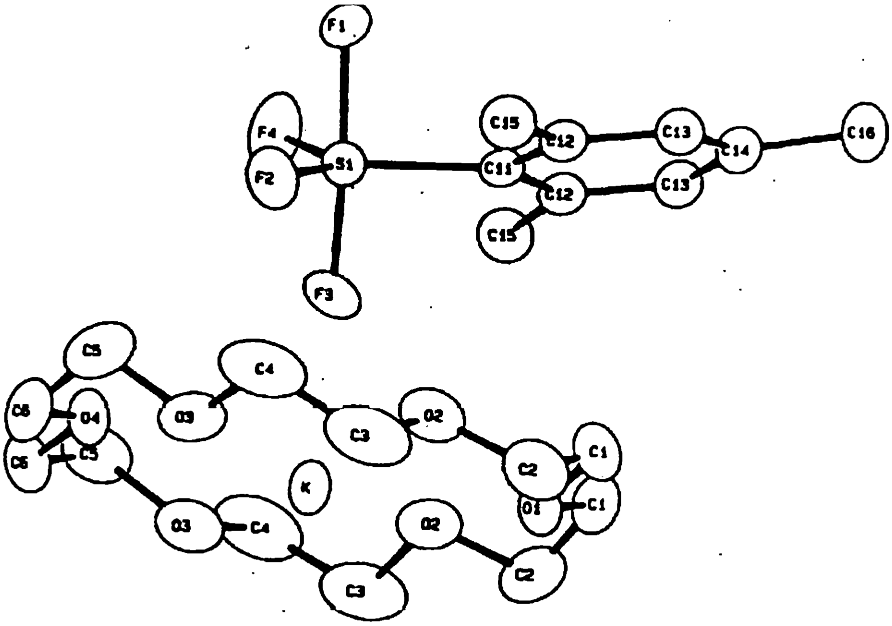
Compound	MP/BP(^{0}C)	^{29}Si	^{19}F	% Yield
13	184-186(MP)	-61.00	-124.00	80
14	37-40(BP)	-69.19	-130.60	67
15	78-81(MP)	-	-	-
16	196-196(MP)	-61.11	-139.70	48
17	89-93(MP)	-62.10	-149.80	83
18	92-94(MP)	-62.60	-144.20	79
19	139-143(MP)	-64.13	-138.90	70
20	189-192(MP)	-73.12	-140.80	-

21	160-165(MP)	-74.00	-38.90	94
22	141-145(MP)	-72.59	-140.20	87
23	120-122(MP)	-71.14	-138.90	88

In line with the observation made by Damrauer (1986)[42] these compounds are relatively resistant to hydrolysis. The area of reactivity is considered in detail in sections 1.8 to 1.13. The single crystal X-ray diffraction pattern was obtained for [TBPSiF$_4$][K-18-crown-6](13) and [MesSiF$_4$][K-18-crown-6](14). A representation of the structure is shown on page 24. The main features are that for both (13) and (14), the structures are essentially TBP and the aryl groups occupy the equatorial positions. In (13), the single crystal diffraction pattern shows the K$^+$ is close to the axial and equatorial fluorines and that the axial bond lengths are long relative to the equatorial Si-F. In addition, the F$_{eq}$-Si-F$_{eq}$ bond angle is only 107^0 which is due to extensive steric crowding. In compound (14), there is not the same interaction between the K$^+$ and the fluorines and the bond angle for F$_{eq}$-Si-F$_{eq}$ is 116^0 which is indicative of the reduced steric crowding. The silicon atom is essentially coplanar with the phenyl group in (14) but is displaced significantly in (13). Again, this is considered a measure of the steric crowding around the silicon.

The N.M.R. data in Table 4 indicates a limited range of chemical shifts for both ^{19}F and ^{29}Si N.M.R.. However, the chemical shifts reported are approximately 51 ppm upfield of the tetracoordinated analogues for ^{29}Si and 24 ppm downfield for ^{19}F. The aryl-substituted compounds are 10ppm upfield of the alkyl-substituted compounds. Oldfield (1985)[43] has reported a similar trend for various ligands attached to silicon.





Corriu (1991)[44] has synthesized a series of penta coordinated diamino silanes. These were obtained in high yield and characterized by full analytical procedures including ^{29}Si N.M.R. and mass spectroscopy. The method of synthesis was as follows:

$$R^1R^2SiX_2 + 2\ R^3R^4NLi \longrightarrow R^1R^2Si(NR^3R^4)_2 + 2\ LiX$$

Some physical and spectroscopic data for the various compounds of the form $R^1R^2Si(NR^3R^4)_2$ are presented in Table 6:

TABLE 6 - SPECTROSCOPIC AND PHYSICAL DATA OF SELECTED COMPOUNDS

	Compound $R^1R^2Si(NR^3R^4)_2$				
R Group	**24**	**25**	**26**	**27**	**28**
R^1	Ph	Me	Ph	Me	Me
R^2	A	B	B	B	Ph
R^3	Me	Me	Me	Me	Me
R^4	$(CH_2)_2$	$(CH_2)_2$	$(CH_2)_2$	Me	$(CH_2)_2$
^{29}Si	-13.48	-3.5	-16.01	-9.10	-2.06
Molecular ion m/e	375	263	326	265	206
BP/MP	-	95(BP)*	0<(MP)	84-87(BP)*	65(BP)*
Yield(%)	86	72	83	-	-

* BP recorded at a reduced pressure of 0.02mmHg.

The above compounds were subject to reactions with CS_2 and CO_2 and in the case of 25, PhNCO. Some of the results are shown in Table 7:

TABLE 7 - SELECTED PHYSICAL AND SPECTROSCOPIC

Compound	**24**	**25**	**26**	**27**	**28**
Reagent	CS_2(excess)	CS_2	CS_2	CS_2	CS_2
Product	A+B	C+D	E+F	G+H	I+T
m/e	-	772	-	-	-
^{29}Si	+22.3	+41(broad)	+34.18	+42	+4.1
MP/BP(°C)	-	250-252(MP)	-	-	-
% yield	-	16/17	-	-	77%

Where:

A = [8-dimethylaminomethyl]-1-naphthylphenyl silathione

B = N'N'dimethyl-2-thioimiidazolidine

C = [2-(dimethylaminomethyl)phenyl]methyl silane

D = Dimethylethylene trithiocarbamate

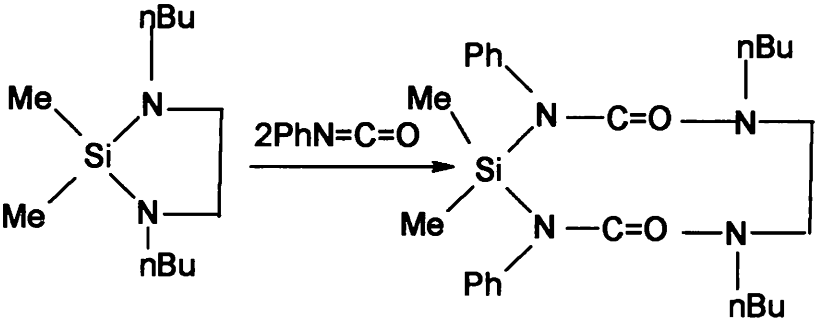
E = (2-dimethylaminomethyl)phenylsilathione

F = N-N'dimethyl-2-thioimidazolidine

G = Methylaminomethylphenylmethylsilane

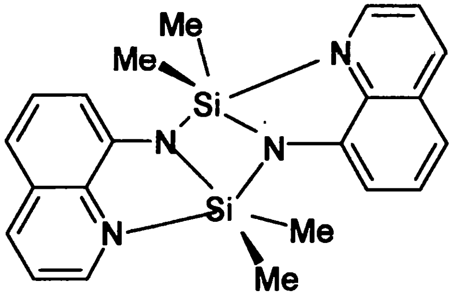
H = Tetramethylthiourea

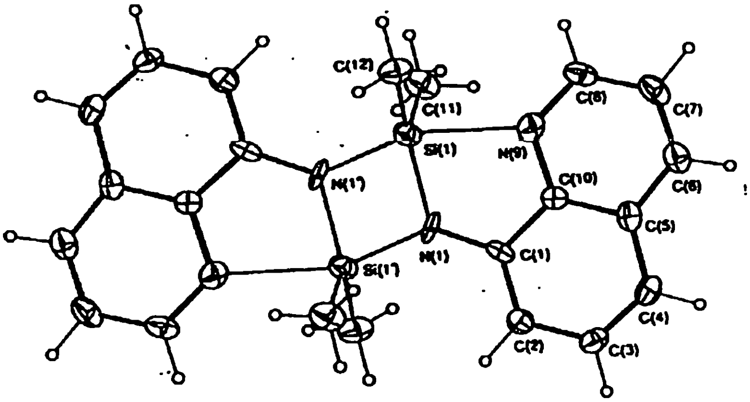
This work was an attempt to extend the research carried out by the Corriu group (1989)[45] and the Veith group (1990 and 1991)[46/47] to cover the full range of Si-N bonds. Lappert (1967)[48] has reviewed the facile aminosilation of heterocumulenes of the type:



The use of intra-molecular stabilisation by aminoaryl ligands has allowed the isolation of several Si=S compounds. The insertion of CO_2 into compound (24) to (27) was found to operate under mild conditions. The pentacoordinated diaminosilanes produced bi-insertion compounds that decomposed on warming.

Englehardt and co-workers (1991)[49] reported the preparation of a neutral pentacoordinate species:





The aim of their work was to prepare compounds of the form ML_2 where L=N(8-Quimolyl)($SiMe_3$) and M=Zn, Cd and Mg. The reaction may be represented by the following equation:

$$2LiL + MCl_2 \longrightarrow ML_2 + 2LiCl$$

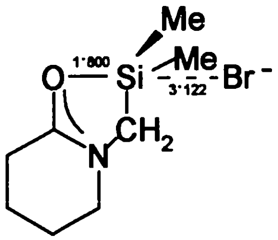
However, when this reaction was carried out using M=Cd the reaction product CdL_2 could not be isolated. On heating between 80-240°C $CdMe_2$ and orange crystals of the dimeric $[Me_2Si(\mu\text{-}N\text{-}C_9H_6N)(\mu\text{-}N\text{-}C_9H_6N)SiMe_2]$ were produced. The latter compound was prepared in low yield (15%) but had a melting point of 163°C. The crystal structure of this compound was obtained and the structure is shown above. The compound was characterized by ^1H and ^{13}C N.M.R. and mass spectrometry (M^+= 385). The reason for the formation of this compound in the case of the $CdCl_2$ reaction may be due to the "softer" character of the Cd, which allowed successful competition for the nitrogen by the silicon.

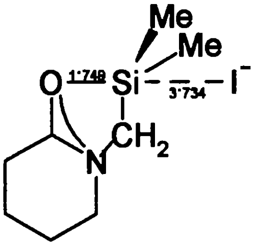
There has been renewed interest in the silatranes due to their physiochemical and biological properties. The latter has been reviewed by Tacke (1989)[50]. The Lukevics group (1991)[51] have synthesized a series of compounds in high yield (54-78%) using the following route:

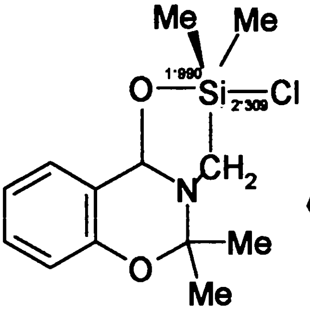
$$R_3SiCl + ClCH_2Si(OCH_2CH_2)_3N \xrightarrow[\text{Mg/THF/60}^{\circ}\text{C}]{} R_3SiCH_2Si(OCH_2CH_2)_3N$$

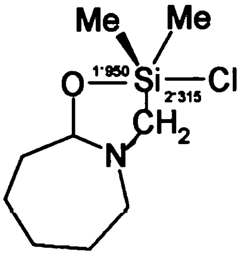
where R = Me, Me_2Ph, $CHMe_2$ or CHMePh. The compounds were characterized by N.M.R. and mass spectroscopy.

Macharashvili and co-workers (1988)[52] have synthesized a series of lactams in which the silicon atom is in a five membered heterocycle which is closed by a hypervalent Si-O bond. A diagram of some of the members of this class of compound is shown on page 31.



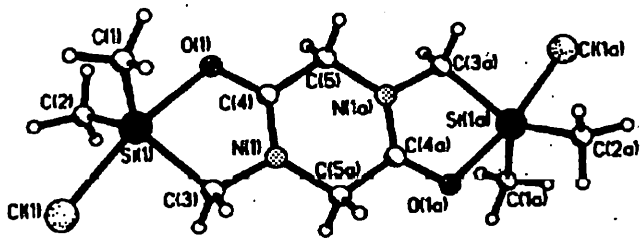


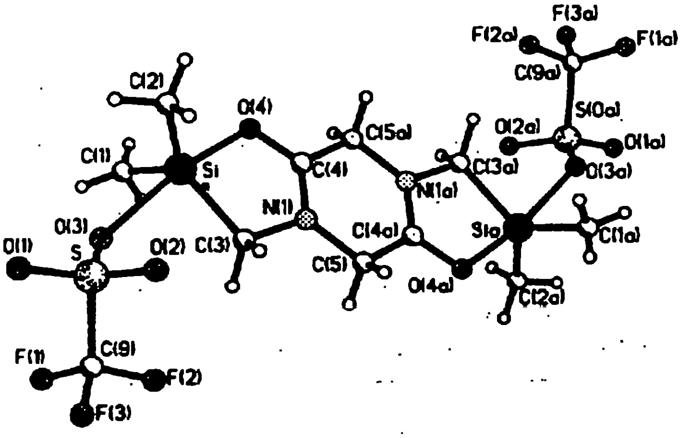




The electroconductivity of this series of compounds was studied in CH_2Cl_2 and it was found that as X changed in the series from I->F, the conductivity was reduced by a factor of about 100. This indicates that the bonds changed from mainly ionic to covalent. The infrared spectra showed a weakening of the Si-O interaction and a strengthening of the C-N and the C-O bonds respectively. From the X-ray diffraction data, the Si-O bond length was shown to be 1.749Å in the iodide and 2.395Å in the fluoride. The Si-X distance varied from 3.734Å in the iodide to 1.652Å in the fluoride.

Further work has been carried out on lactams by the Mozzhukhin group (1992)[53]. The paper presented the results of X-ray diffraction studies of dinuclear derivatives N-[dimethyltrifluoromethanesulphonyloxygermyl(silyl)methyl] and N-[dimethyltrifluoromethanesulphonyloxygermyl(silyl)methyl]-piperazine-2,5-diones and the mononuclear N-chlorodimethylgermylmethyl) and N-(dimethyltrifluoromethanesulphonyloxygermylmethyl)lactam were investigated by X-ray diffraction. Representations of the compounds are shown below:



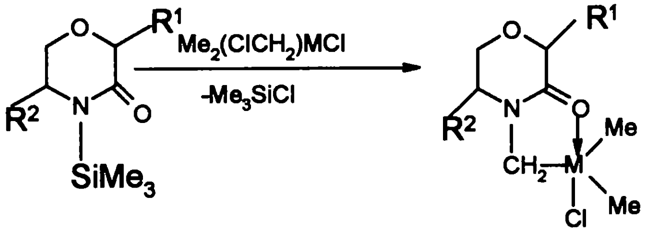


It was found that in the dinuclear species that the dative Si-O distance was greater than in the mononuclear species by about 0.09-0.13Å, but that the Si-Cl distance was shorter by about 0.04Å. However, this is much larger in the triflate derivative, being 0.5Å in the silicon derivative. In addition these workers analyzed the NC(4)O group in piperazine derivatives and found that the angle was 123°. Since the structure actually revealed a smaller angle, this could be due to the ring closure. A comparison of the dinuclear geometries suggests a weaker Si...O interaction but that the Si-Cl bond may well be stronger. The weakness of the former may be due to a reduction in electron transfer and to the rigidity of the central six-membered ring. One other point is worth noting. This is that the Si-O interaction is shorter in the triflate than in the chloro derivatives. This could be due to the triflate group being a better leaving group with the negative charge being significantly delocalized over the whole of the group.

Gavrilova and co-workers (1991)[54] have studied the infrared spectra of compounds containing –C=O interactions of a series of compounds of the form 4-X-$C_6H_4COOCH_2SiF_3$(X=H,Cl, OCH_3 or CH_3). In the infrared spectra, the bands near 350cm^{-1} were assigned to the Si<-O interaction. They found a significant change in the Si<-O stretch with substituent X.

It was also noted that changes in the νSi-O and νSiF_{ax} frequency was observed with increasing Si<-O strength. These changes may be due to a change in equilibrium geometry or purely electrostatic effects (change in force fields). Force field calculations indicate that the former predominates.

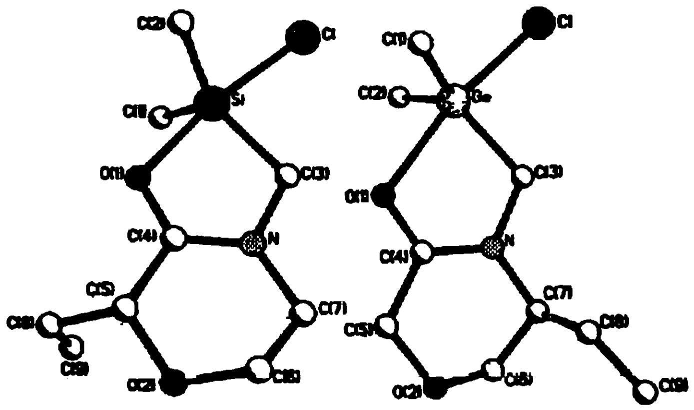
Orlova (1992)[55] has reacted N-trimethylsilyl derivatives of 3-morpholones with $Me_2(ClCH_2)MCl$, (where M = Si and Ge) in accordance with the scheme outlined below:



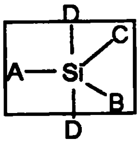
Where a) R^1 = H, R^2 = Et
b) R^1 = Et, R^2 = H
M = Si, Ge

The presence of the M....O interactions were suggested by the bathochromic shift of the ν_{CO} stretch compared with the uncoordinated form. Comparisons between various structures has shown that the replacement of a carbon atom in the six membered lactam ring causes an increase in the Si...O distance by about 0.067Å, whilst the Si-Cl distance is shortened by about 0.025Å.

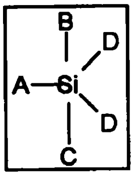
A representation of the crystal structure is shown below:



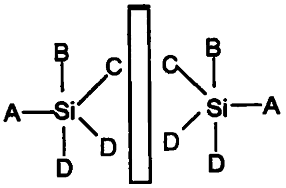
The Klebe group (1985)[56] have made a study of five co-ordinate silicon compounds with four different substituents. Under these conditions, two achiral isomers are possible and these are shown below (A&B):



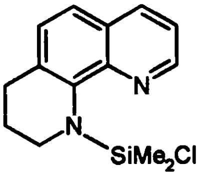
A

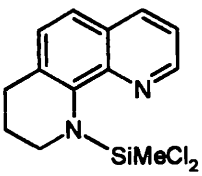


B

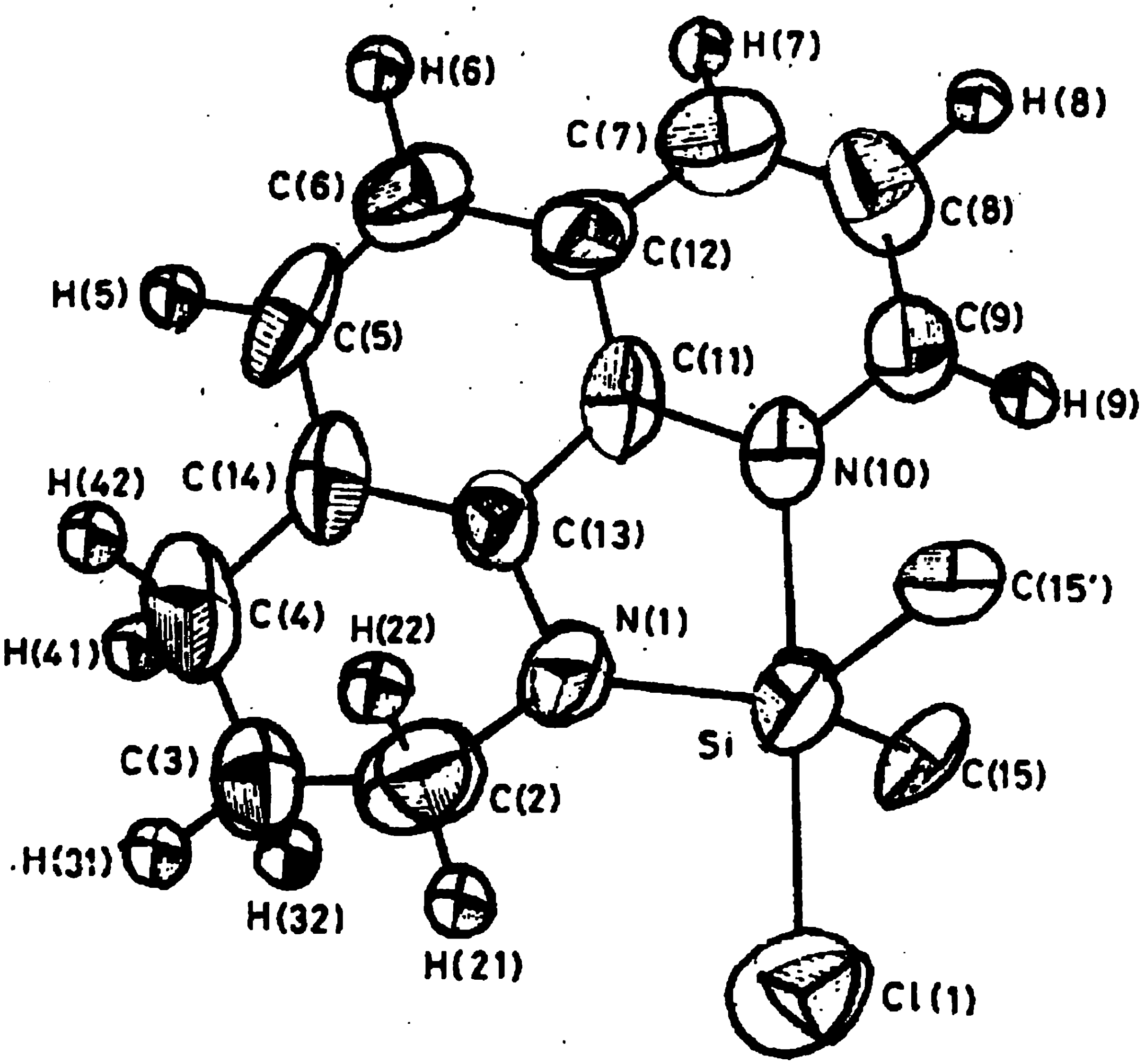


C





The crystal structures of the two chemically similar groups were obtained and a representation is shown on page 35.



(Klebe 1985)

The structures show a TBP structure in the solid state with the pyridine nitrogen occupying the apical position. and the saturated ring nitrogen occupying the axial position. In both structures the chlorine atoms are in the axial position opposite to the pyridine type nitrogen atoms. The compound 1-(chlorodimethylsilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline has a structure similar to (A) while 1-(dichloromethylsilyl)-1,2,3,4-

tetrahydro-1,10-phenantholine, the structure is similar to (C) with both enantiomers occupying the same crystal.

A synthetic route for the preparation of organosilanes has been put forward by Corriu (1988)[57]. What Corriu was able to do was to transform hexa co-ordinate species into silanes. Previously the Muller group(1984)[58] was able to obtain $MeEt_3Si$ from $Na_2[CH_3SiF_5]$ using strong nucleophiles such as EtLi.

Corriu reacted $[Si(O_2C_6H_4)_3]^{2-}$ with various nucleophiles, and in some case the yield was high but in others it was relatively low. Some results are shown in the Table 8:

TABLE 8 - REACTION PRODUCTS AND YIELDS

Reagent	Temperature(°C)	Product	Yield(%)
MeMgI	20	Me_4Si	73
EtMgBr	35	$Et_3Si(OC_6H_4OH)$	72
BuMgBr	20	Bu_3SiH	71

This procedure has provided a useful "one pot" synthesis for some silanes.

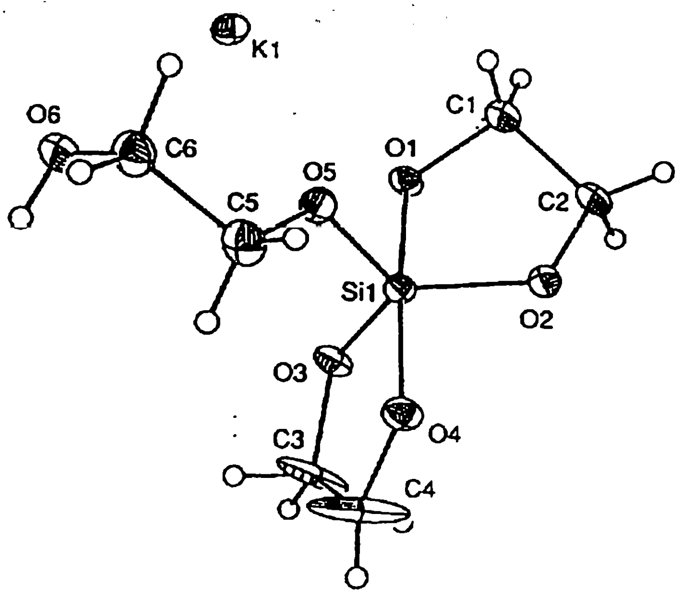
The Laine group (1991)[59] has used a novel approach to synthesize a series of penta co-ordinate compounds using the precursor SiO_2. This is of particular significance since SiO_2 is a common and cheap source of raw material. Previously Rosenheim and co-workers (1931)[60] and the Barnum group (1970)[61] have made tris(catecholato)silicate in an alkaline medium:

$$SiO_2 + 2KOH + 3\ 1,2\text{-}C_6H_4(OH)_2 \longrightarrow K_2[Si(1,2\text{-}C_6H_4(O)_2)_3] + 4H_2O$$

However, the reactivity is low and strong nucleophiles such as H^-, RMgBr or RLi are required for a reaction to occur. Laine has reacted SiO_2 with ethylene glycol in the presence of a base:

$$2SiO_2 + 2MOH + 5HOCH_2CH_2OH \longrightarrow M_2[(OCH_2CH_2O)_2Si\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}Si(OCH_2CH_2O)_2] + H_2O$$

The compounds are highly reactive which is possibly due to the presence of bridging $O\text{-}CH_2CH_2\text{-}O$ group. The ^{29}Si N.M.R. data, with a chemical shift of -103ppm was consistent with a pentacoordinated species. ^1H and ^{13}C N.M.R. were also reported. The reactivity of the dimer was shown to be high in that it reacted with MeOH to produce $K[Si(OCH_2CH_2O)_2OCH_2CH_2OH]$ plus glycol. A crystal structure of $KSi(OCH_2CH_2O)_2OCH_2CH_2OH$ was obtained and this is shown on page 38:



(Laine Group 1991)

The structure is TBP. The full kinetics of the reaction has yet to be fully elucidated.

A large amount of effort is now beginning to be put into a theoretical understanding, via ab-initio calculations, of both structure and reactivity. The compound $H_3N\text{-}SiF_4$ was first isolated by Ault (1981)[62]. On the basis of its infrared spectrum, Ault proposed a TBP arrangement for this compound. Calculations carried out by Marsden (1983)[63] confirmed the Ault findings and in addition agreed that the NH_3 group was located in the axial position. This brings up the question of electronegativity of the NH_3. It could be argued that the co-ordinated nitrogen carries a full positive charge formally and hence therefore more electronegative. This work has been extended by the Schaad group (1991)[64] who looked at other structures which may occur at a potential minima and hence calculate the spectra of two other possible structures and compare with the Ault's work. The results, which involved the calculation of spectra of isotopically substituted analogues (^2H and ^{15}N) confirmed Ault's proposal.

Tamao (1992)[65] have studied the steric and electronic effects of substituents in anionic penta coordinated diorganotrifluorosilicates. A series of compounds of the following form $R^1R^2SiF_3^-$ were studied. These included $(4\text{-}XC_6H_4)MeSiF_3^-$(31); $(MeC_6H_5)PhSiF_3^-$(32); $(2\text{-}MeC_6H_4)(4\text{-}MeC_6H_4)SiF_3^-$(33) and $(2,5\text{-}Me_2C_6H_3)(3,5\text{-}Me_2C_6H_3)SiF_3^-$(34). These were all prepared as 18-crown-6 potassium salts. The compounds synthesized may be represented by the following equation:

$$R^1R^2SiF_2 + KF \longrightarrow [R^1R^2SiF_3]^-K^+\text{18-crown-6}$$

It was also found that a 1:1 or less ratio of the parent silane to the KF produced an easily purified product. In addition the crystal structures of (31) were determined where $X=CF_3$, Me, OMe and NMe_2 (33) and (34). The structures indicate that in all the compounds the dihedral angle between the substituent phenyl groups and the equatorial plane depends on steric and electronic factors. However, the following additional points may be made:

1) In compound (31) and (34), the structure was TBP with the phenyl group in an equatorial position. The bond lengths and bond angles are not significantly different from $Ph_2SiF_3^-$. The Si-C bond lengths in $Si\text{-}C_6H_4CF_3$ appear longer than others in the series (1.918Å) and is similar to that found in $1\text{-}NpPh_2SiF_2^-$ (Holmes and co-workers (1987)[66].

2) The potassium cation interacts with the two fluorine atoms, one of which is in the axial position and the other in the equatorial position. The equatorial Si-F distance

was shown to be shorter than the axial Si-F distance.

3) There is a large dihedral angle between the aryl rings and the equatorial plane in some cases. The dihedral angle ranges from 81.6° in (4-$CF_3C_6H_4$)$PhSiF_3^-$ to 83.5^0 in (4-MeC_6H_4)$PhSiF_3^-$.This is larger than the 75^0 found in $Ph_2SiF_3^-$. In the case of (4-$NMe_2C_6H_4$)$PhSiF_3^-$, the Me_2N-C_6H_5 angle was found to be 87.6°.
4) A reason for this arises from electronic effects in that the CF_3 is electron-withdrawing while NMe_2 is electron donating giving rise to the aligned perpendicular arrangement of the ligands. However, it is not easy to define the electronic effects involved at this stage.

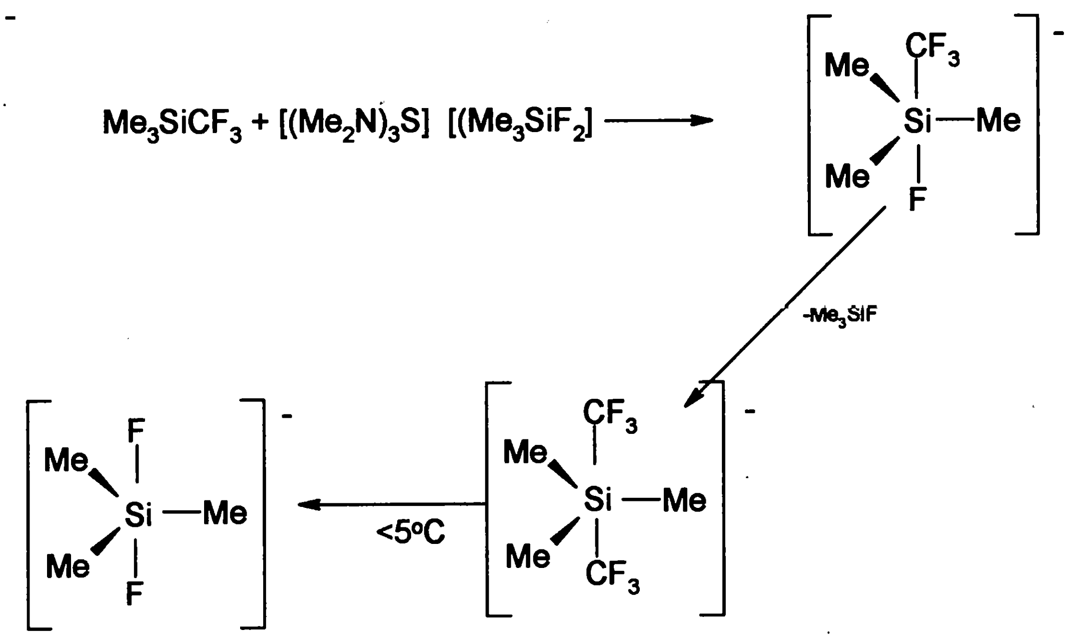
The NMe_2 group of (4-$NMe_2C_6H_4$)$PhSiF_3^-$ shows a high degree of planarity. This may be partly explained by the presence of the $PhSiF_3$ group that is electron accepting group. This is apparent when the ^{13}C N.M.R. data is considered.

The pentacoordinated species undergo Berry pseudorotation and hence at room temperature show only a singlet in the ^{19}F N.M.R. spectrum. However at -78°C, two peaks are observed and these are due to the presence of the axial and equatorial fluorine atoms. For the series of compounds, (4-XC_6H_4)$PhSiF_3^-$, the coalescence temperature was found to be -10 - -20°C. This higher coalescence temperature in the presence of electron withdrawing groups being consistent with the previous work on pseudorotation by Stevenson and co-workers (1985)[35] and Damrauer (1989)[67].

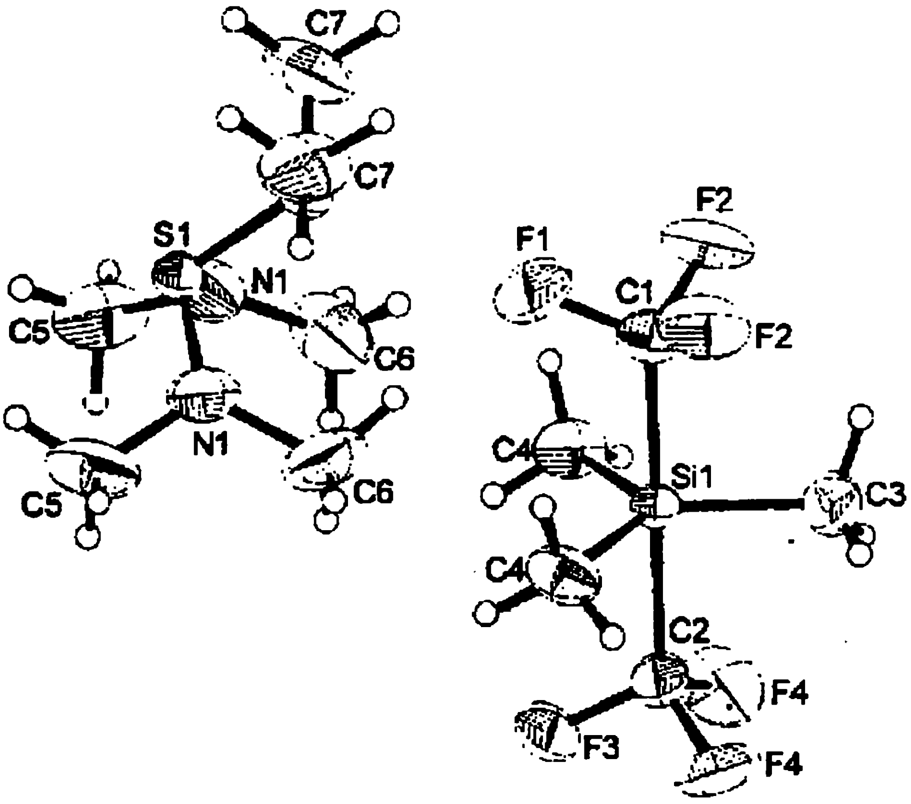
A good linear relationship was obtained between the energy barrier to rotation and the Hammett σ_p^+. From the Hammett constant, the relative electron densities on the silicon ipso carbons could be calculated. The ^{13}C data has provided useful information about the electronic situation of particular carbon atoms. The chemical shifts of the carbon para to the substituent in mono substituted benzenes are correlated to the electron density at the para position. The electronic effects exerted by the $SiPhF_2$ and the $SiPhF_3^-$ groups are opposite in that the former is a weak electron acceptor while the latter is an electron releasing group. The chemical shifts in the ^{13}C data are consequently shifted down field in $-SiPhF_2$ and upfield in $-SiPhF_3^-$. The $SiPhF_3^-$ operating via a π polarization effect.

A novel penta co-ordinate compound, 1-methyl-1,1-dihydrido-2,3,4,5,-tetraphenyl-1-silacyclopentadiene silicate ($[Ph_4C_4SiMeH_2]K$) has been reported by Boudjouk (1995)[68]. The synthesis involves a reaction between 1-methyl-2,3,4,5,-tetraphenyl-1-silacyclopentadiene and potassium hydride. This is a well-established route to silyl anions and silacyclopentadienide anions (Corriu, 1985)[69]. ^{1}H, ^{13}C and ^{29}Si N.M.R characterized the unexpected product. The ^{29}N.M.R. resonance was found to be 15.61ppm. The Si-H coupling constants were found to be similar to those of $[H_2Si(OR)_3]^-$ (Corriu and co-workers, 1991a+b)[70]. This suggests that the structure of the compound is trigonal bi-pyramidal with one of the hydrogen atoms and two of the carbons of the cyclobutadene group occupying the equatorial positions.

A significant development occurred when the Kolomeitsec (1999)[70a] group synthesized the first organosilicon compound containing five Si-C bonds. This involved the reaction between $[(Me_2N)_3S][Me_3SiF_2]$ and CF_3SiMe_3. The resulting product, $[(Me_2N)_3S][(CF_3)_2SiMe_3]$, was found to be thermally unstable above 5°C.



The ^{19}F NMR was recorded and showed a resonance at δ-64.04 ppm. The single crystal X-ray diffraction pattern was determined and a representation was shown on page 43:



The complex had a trigonal bipyramidal structure but the significant feature was the long apical Si-CF_3 (205.6 pm) and the considerably shorter Si-CH_3 bond length (188.2 pm).

1.5 - COMPOUNDS CONTAINING Si=X groups.

These compounds may be considered to have 10 electron M=Si group and hence they may be described as hypervalent although not hyper coordinate. They do display an interesting chemistry. The involvement of silanediyl-transition metal complexes in the chemical transformation of silicon compounds is an active area. This has recently been reviewed by Lickiss (1992)[71]. Several transition metal compounds containing Si=X groups (for example X = SiR_2L) have been prepared.

Various silylene complexes of transition metals have been prepared. For example when $Na_2Fe(CO)_4$ is reacted with $(BuO)_2SiCl_2$ in the presence of HMPT (hexamethylphosphotriamide), the compound $(CO)_4Fe{=}Si(OBu)_2(HMPT)$ is formed (Zybill group 1987 and 1988)[71a]. Zybill studied the variable temperature ^{13}C N.M.R. and found that the Fe=Si bond exhibited unhindered rotation down to -30°C where solubility problems prevented further study. A crystal structure of $(HMPT)(t\text{-}BuO)_2Si{=}Fe(CO)_4$ was obtained and the Si-Fe distance was determined to be 2.289Å and the Si-O (from HMPT) was found to be long at 1.730Å.

Straus and coworkers (1987)[72] have further extended this work by studying silylene complexes of ruthenium in the presence of acetonitrile, which was bound to the silicon atom. The synthesis was based on the work of the Tilley group (1984)[73] and involves the reaction between $HSiPh_2Cl$ and $Cp^*_2R_2RuCH_2SiMe_3$ in toluene at 100°C. The reaction utilized electrophilic abstraction to produce the cationic complex $[Cp^*(PMe_3)_2Ru{=}SiPh_2.NCCH_3]^+$. A crystal structure was obtained and the Ru-Si distance was found to be 2.328Å, which is short. The Si-N (from acetonitrile) distance was found to be significantly longer than the tetra coordinated species at 1.932Å. The ^1H N.M.R. indicates that acetonitrile exchange occurs on the N.M.R. time scale.

The Ogino group (1988)[74] has obtained a donor stabilized complex via the photolysis of $Cp^*(CO)_2FeSiMe_2SiMe(OMe)_2$. Tilley (1990)[75] has also reported the base free silylene compound $[Cp^*(PMe_3)_2Ru{=}Si(SR)_2][BPh_4]$ where R=tolyl and ethyl.

In addition, the Ogino group (1988)[74] has also studied an iron bisilylene consisting of two isomers of the type $Cp^*Fe(CO)_2(OMe)SiMe_2)(OMe)$.

The synthesis involved a reaction between $Na[Cp^*Fe(CO)_2]$ and $ClMe_2SiSiMe_2Cl$ followed by subsequent treatment with methanol. The yellow crystals obtained were subject to X-ray diffraction and the data showed very short Fe-Si distances of 2.207 and 2.222Å respectively. The Si-O (from MeOH) was shown to be long. The ^{29}Si N.M.R. indicates the presence of two isomers and sp^2 hybrid silicon atoms.

Additional work on osmium has been carried out by Woo (1991)[76]. They prepared a THF stabilized silylene complex of the type $(TPP)Os{=}SiMe_2.THF$, where TPP is meso-tetra-p-tolylporphyrin. The product was prepared by the following reaction:

$$\tfrac{1}{2}[Os(TPP)] + Me_2Si(CMe_2)_2 \longrightarrow (TPP)Os{=}SiMe_2.THF + Me_2C{=}CMe_2$$

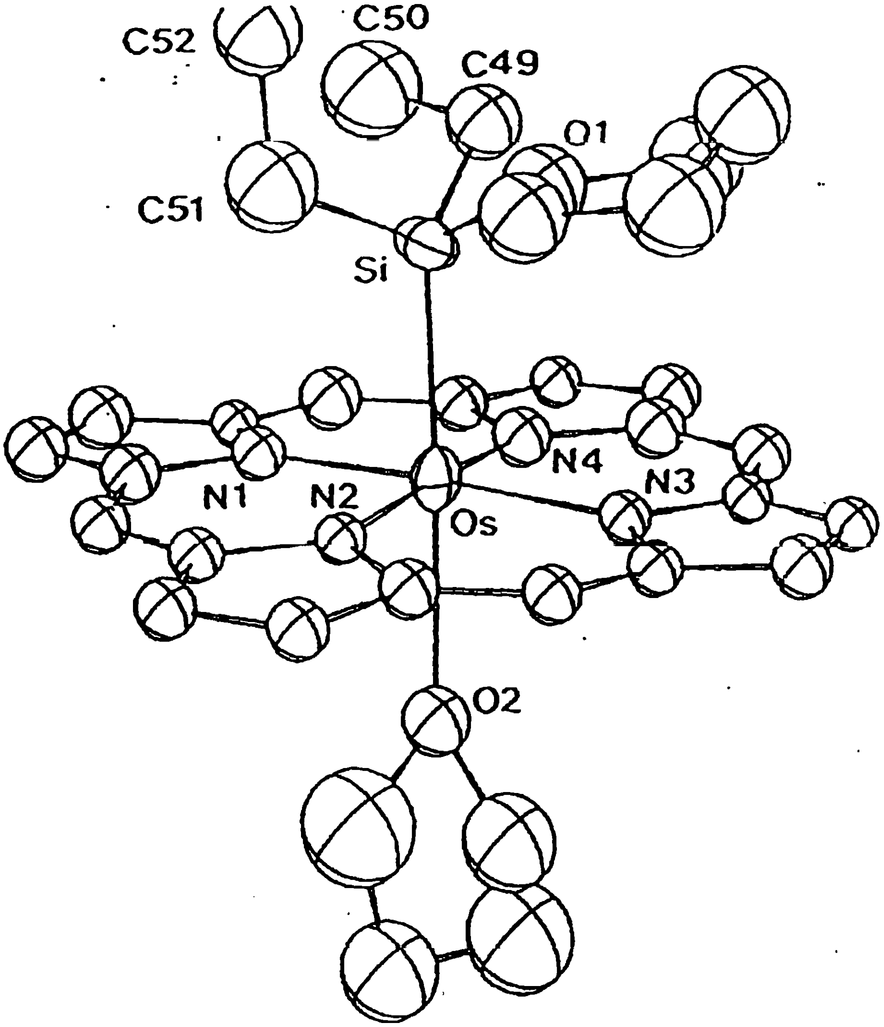
2-D NOESY N.M.R showed the fact that the THF was coordinated to the silicon atom. The Colman group (1985)[77] have prepared the above compound by an alternative route:

$$K_2[Os(TPP)] + Cl_2SiR_2 \longrightarrow (TPP)Os{=}SiR_2.THF + 2KCl$$

where R = Me, Et, and Pr. However, it was noted that when sterically hindered R groups, which would prevent donor solvent co-ordination, were used, no reaction was observed.

Simple displacement reactions at the silylene group can be carried out. For example the THF molecule can be easily substituted by pyridine. The crystal structure of

(TPP)Os=SiEt$_2$.2THF was obtained by Woo (1991)[76]. This is shown on page 46.



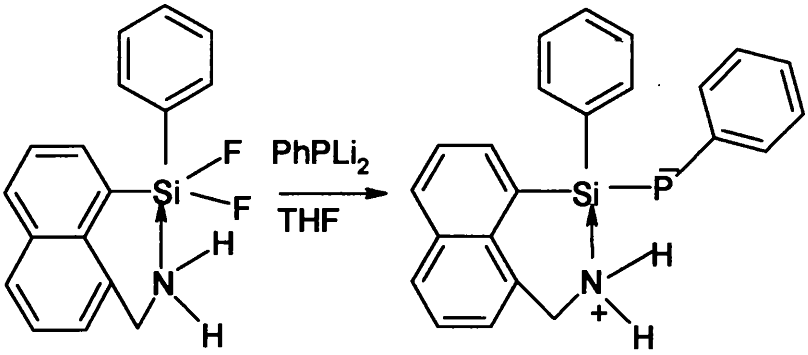
Molecular structure with 50% probability thermal ellipsiods and patrial atom numbering for (TTO)Os=SiEt$_2$.2THF (Woo 1991)

The Si-Os distance was found to be 2.325Å, which is very short. The Si-O distance (from THF) was found to be long (1.82Å).

Muller and co-workers (1992)[78] have studied the synthesis, structure and photochemistry of base stabilized silylenes of the type R$_2$(HMPA)Si=M(CO)$_n$ where M=Fe,Cr or W, n=4(Fe), n=5 (Cr and W). R=t-BuO, t-BuS, MeO, and Ada-O-.

These compounds were prepared by the reaction of R_2SiCl_2 with $M(CO)_n^{2-}$ in the presence of HMPT. This produced the appropriate silylene complex. Crystal structures of $Me_2(HMPA)Si{=}Cr(CO)_5$ and $Cl_2(HMPA)Si{=}Cr(CO)_5$ were obtained. The data obtained showed the M=Si distance to be very short with the Fe-Si distance of 2.280Å and the Cr-Si being 2.140Å. The Si-O distances were long being 1.683Å and 1.743Å respectively. The reported photochemistry was devoted to the substitution of the CO groups by the PMe_3 ligands.

Corriu co-workers (1991)[79] carried out an interesting piece of research into penta coordinated silicon containing a Si=X group. The groups studied included Si=N- and Si-P$^-$-Ph. The former N$^+$ is an obvious case of a zwitterion stabilized by an intramolecular co-ordination. The silaphosphene was obtained by the following reaction:

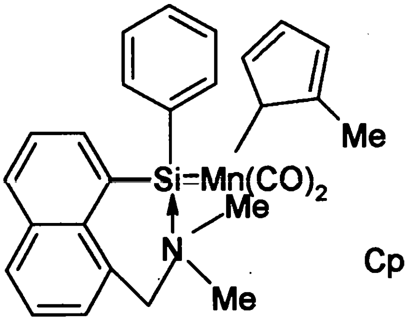


The ^{29}Si data shows a chemical shift of -9.6 ppm. In addition, some interesting hypervalent silicon-transition metal compounds were reported. The outline of the synthesis is shown overleaf. The ^{29}Si and ^{13}C N.M.R. data is shown in Table 9.

TABLE 9 - ^{13}C and ^{29}Si N.M.R. RESONANCES

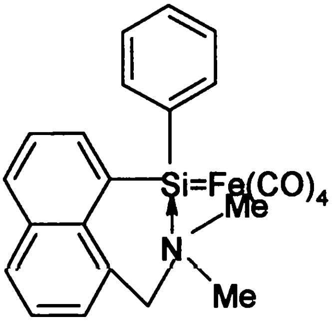
Compound	^{13}C (ppm)	^{29}Si (ppm)
A	54.4 50.3(NMe$_2$)	+101.1
B	48.0 45.0(NMe$_2$)	+124

A =



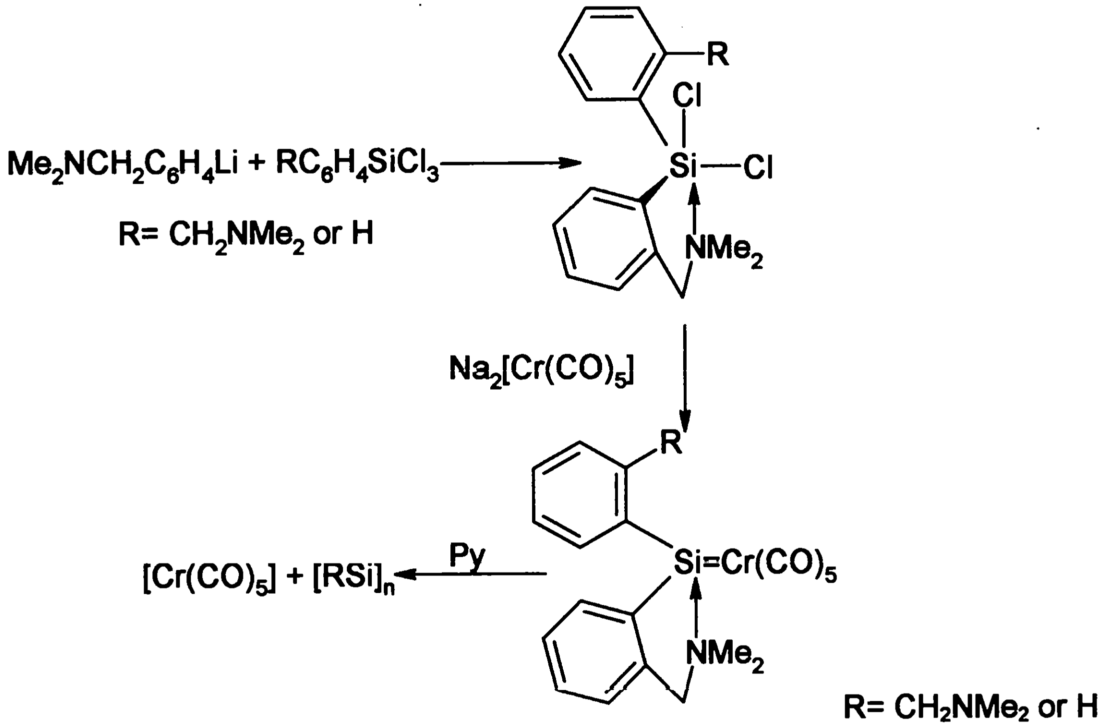
Cp' = Methylcyclopentadienyl

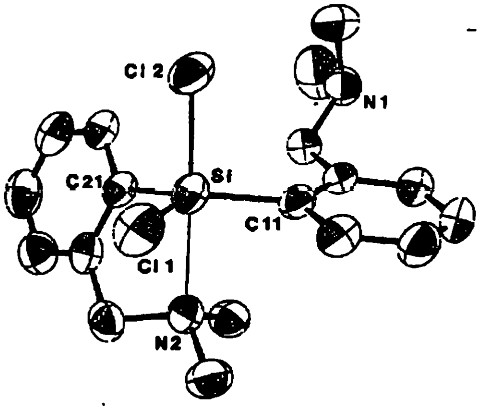
B =

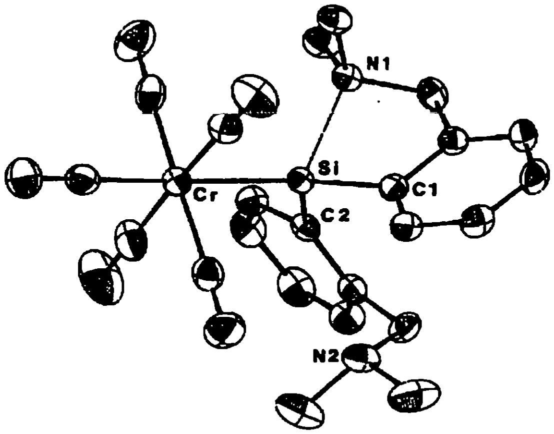


The absence of a Si-H bond was shown by the application of the pulse techniques DEPT and INEPT. Both of the above compounds are unreactive to nucleophiles although the Si=Fe compound will react with oxygen.

Auner (1991)[80] used the Corriu methodology to produce a compound containing a Si=Cr group. The outline of the synthesis is shown on page 51. The ^{29}Si N.M.R. chemical shift was found to be 129.4ppm at 22°C, which indicates a small Si-N interaction. The ^{29}Si N.M.R. does show strong temperature dependence and shifts to 138.8ppm at 58°C. The ^{1}H N.M.R. indicates that the dimethylamido protons are equivalent when R=H but when R=CH_2NMe_2 the signal is split into an AB pattern. This is due to the hindered rotation of the phenyl substituent and to the co-ordination of the nitrogen to the silicon. Above 58°C, the NMe_2 groups are equivalent indicating that the phenyl group is rotating fast and that the nitrogen is not coordinated to the silicon. The value of the rotational barrier was found to be 54.2 kJ/mol in R=CH_2NMe_2. The crystal structure of the last mentioned compound was obtained and a representation is shown on page 50. It is worth noting that the Si=Cr bond length is very short at 240.8pm compared to the calculated Si-Cr bond length of 270pm.

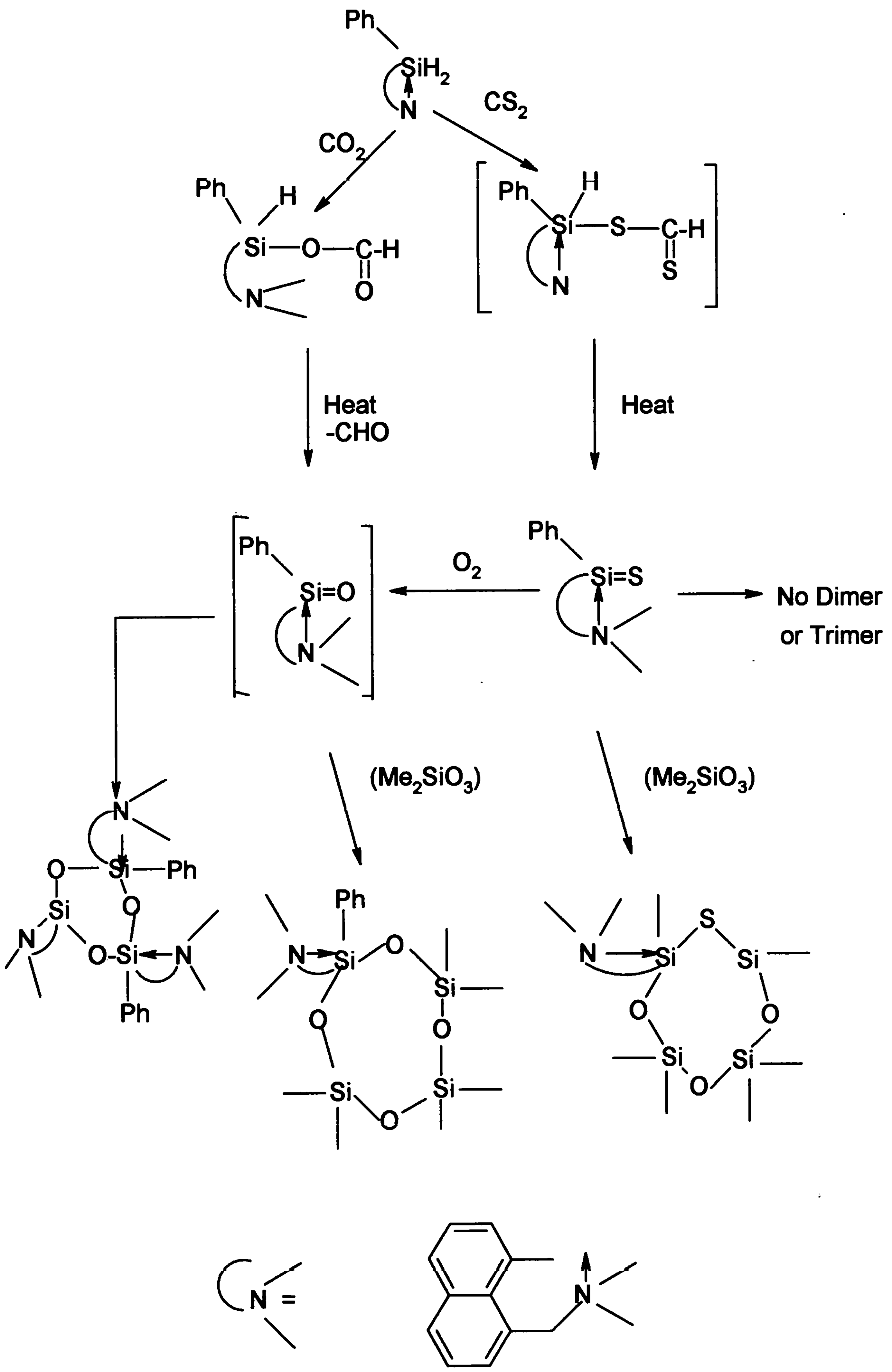




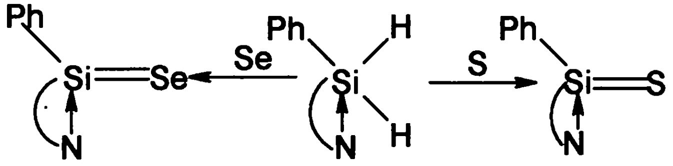


Auner and co-workers (1991)

A series of papers were produced by Corriu (1986)[81], (1988)[82] and (1987)[83] which described the reactions of hypervalent silanes with carbon dioxide, acyl chlorides and carboxylic acids. Some of the reactions are summarized in the diagram below:


CO2
CS2
Heat
-CHO
Heat
O2
No Dimer or Trimer
(Me2SiO3)
(Me2SiO3)

The Corriu group (1989)[84] have described the reaction of the parent hypervalent silane with CS_2, S_8 and Se which produced stable Si=S and Si=Se bonds:



The thio compounds may also be produced by direct reaction with S_8. The products were both found to be air and moisture sensitive. The infrared of the thio compound exhibited a new band compared to the hypervalent parent at 645cm^{-1}. This may be due to the Si=S stretch. Thompson (1987)[85] have synthesized a transient compound containing a Si=Se bond. Some data relating to the compounds synthesized by Corriu (1989)[84] is shown in the Table 10:

TABLE 10 - SELECTED PHYSICAL DATA

	Si=S	Si=Se
% Yield	67	84
^{29}Si	+22.3	+29.4
$^{13}C(NMe_2)$	46.3	47.23
FAB	321	-
m/e	321	369
MP(°C)	170-1	80 (decomp)

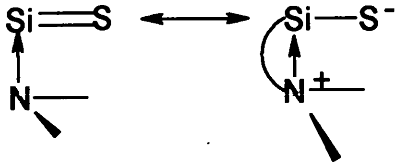
The reactivity of the thio compound was found to be low with respect to nucleophiles. The crystal structures of the thio compound, where a naphthyl group replaces the phenyl group, was obtained. The main structural features are as follows:

1) The Si=S bond length is 2.013Å which is significantly shorter than the Si-S single bond (2.16Å).

2) The dative Si-N bond is 1.96Å and is slightly longer than other Si-N bonds (1.79Å).

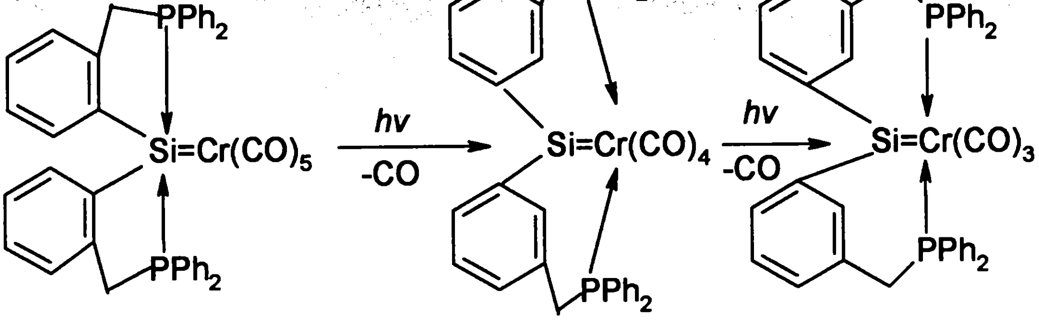
3) The sulfur atom is located outside the plane of the Si-naphthyl unit.

The low reactivity of the silanethione may be explained by the following resonance:



The more polar form making a greater contribution.

The Corriu group (1993)[86] has prepared additional transition metal complexes containing donor-stabilized hydrosilanediyl. These were prepared photochemically by a reaction between $Fe(CO)_5$, $Cr(CO)_6$ and $RCpMn(CO)_3$ in the presence of $ArSiH_3$. The presence of N,N-dimethylimidazolidinone (DMI) allowed the conversion of $[Fe_2(CO)_8(SiPh_2)_2]$ to $[Ph_2Si(DMI){=}Fe(CO)_4]$.In addition, further compounds were prepared by photolysis and a scheme is shown below:



Spectroscopic data including ^{29}Si N.M.R. spectra were also reported. In the above case, the intramolecular stabilisation was expected, based on the previously mentioned earlier work of Corriu and co-workers (1989)[86]. This work involved a similar reaction with silanethione in which stabilisation was achieved using an intramolecular coordinated aminoaryl group.

1.6 - DYNAMIC STUDIES OF HYPERVALENT SILICON COMPOUNDS

An increasing interest has been shown in the dynamic aspects of pentacoordinate species of silicon. The Damrauer group (1989)[42] have measured the ^{19}F exchange barriers for compounds of the type $[RR'SiF_3]^-$. Eight new silicates were prepared as K^+-18-crown-6 salts. The ^{19}F N.M.R. data is shown in Table 11:

TABLE 11 - ROTATIONAL BARRIER DATA

R	R'	^{19}F	Rotational barrier(kJ/mol)
4-Methylphenyl	4-Methylphenyl	-110	43.8
2-Methylphenyl	2-methylphenyl	-96.3	40.59
p-Nitrophenyl	p-Nitrophenyl	-110.5	36.0
α-Naphthyl	α-Naphthyl	-89.9	38.1
Phenyl	2,6-Dinitrophenyl	-101.5	46.71
Phenyl	Tert-butyl	-114.5	42.64
2,6-Dimethylphenyl	2,6-dimethylphenyl	-76.3 and –125	13-14 BB
2-Methylphenyl	2,6-Dimethylphenyl	-95.3	11.3

No ^{29}Si N.M.R. data were reported but along with the ^{19}F the ^{1}H spectra were reported. The compounds were prepared by the following reaction:

$$KF + 18\text{-crown-6} + RR'SiF_2 \text{ ---------> } [RR'SiF_3][K^+18\text{-crown-6}]$$

The yields were high and reported to be between 70-90%. All compounds showed two peaks in the low temperature ^{19}F and coalescence was obtained which allowed the value of the exchange barrier to be obtained. However, (2,6-dimethylphenyl)$_2$SiF$_3^-$ showed two resonances over a very large temperature range and it proved difficult to determine the coalescence point due to the presence of small amounts of impurity. Exchange barrier data are also presented in Table 4 and data originating from Damraurer (1986)[42] is shown in Table 12:

TABLE - 12 Exchange Barrier Data

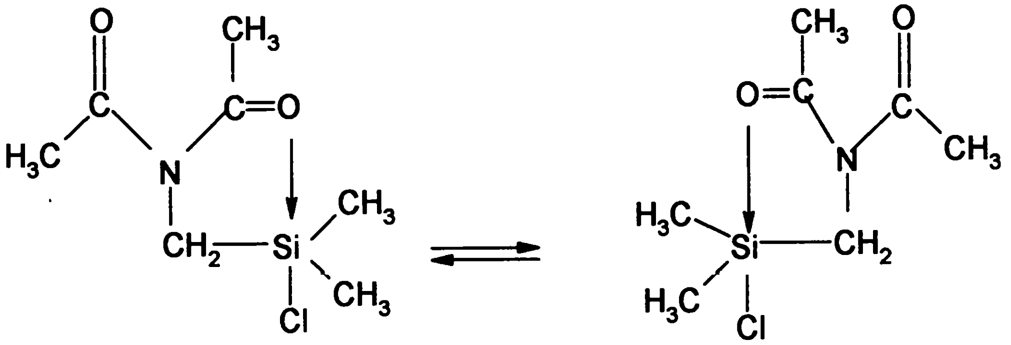
Compound	**Exchange Barrier (kcal/mol)**
$[(phenyl)_2SiF_3]^-$	11.7
$[(phenyl)(methyl)SiF_3]^-$	9.9
$[(phenyl)SiF_4]^-$	Rapid exchange
$[(phenyl)_3SiF_2]^-$	No exchange

In Table 12, the compound $[(phenyl)_3SiF_2]^-$ has all the phenyl groups located in the equatorial position and hence the rotational barrier is very high. Earlier studies by Martin (1985 and 1986)[87] looked at substituent effects in cyclic silicates of the type $[Ph(CF_3)_2O)_2SiY]$ where Y=CN, n-Butyl, F, OC_6H_5, alkyl, and aryl. The rotational energy barrier was found to range from 16.8kcal/mol in the case of CN to 28.6 kcal/mol in n- butyl. Very good Hammett correlations were obtained.

Not all the compounds undergo a simple dynamic process. Farnham and co-workers (1981)[88] have shown that similar compounds may undergo intermolecular and dissociative steps. Voronkov (1983)[89] has shown that (aroyloxy)methyl)trifluorosilane is pentacoordinated in both the solid and liquid state. The energy barriers were reported to be between 28 - 43 kJ/mol.

The Klebe group (1985)[90] have synthesized $(C_{12}H_{11}N_2)SiX_3$ where X=F and Cl using their own previously published method (Klebe group 1981 and 1983)[91]. The ^{19}F N.M.R. was studied at various temperatures. At room temperature, a singlet was observed whereas at -90°C a doublet and a triplet was obtained. The use of line shape analysis indicates that the energy barrier is about 30.75 kJ/mol. Rearrangement is thought to occur via an intramolecular process. The Si-N bond is longer in the fluoro compound compared to the chloro compound (Klebe group 1983)[91]. The barrier of 30.75 kJ/mol has been attributed to the total energy necessary for the positional change of the fluorine atom.

The Pestunovich group (1988)[92] have studied the effects of substituent on the strength of intramolecular Si=O coordinated bonds in compounds of the type CH_3-CO-$N(COCH_3)CH_2SiX(CH_3)_2$ where X=Cl, Br, I, $OC(O)CH_3$, $OC(O)CF_3$. These workers studied the effects using ^{13}C and ^{29}Si N.M.R.. The dynamic process under consideration is shown below in the case where X=Cl:



The process allows the migration of the Si-O co-ordinate bond between the oxygen atoms of the two acetyl groups and involves the dissociation and rotation by 180° of the silyl methyl group and the two acyl fragments about the N-C bond and the formation of a new Si-O bond involving the oxygen of the other acyl group. It was found that the strength of the Si-O bond weakens with the increasing electronegativity of the substituent X. The free energy of activation was found to be in the range 31.5-43.0 KJ/mol. This data was found using the Eyring equation. This is a significant barrier to rotation. The ^{29}Si N.M.R. data is shown in Table 13:

TABLE 13 - ^{29}Si N.M.R. RESONANCES

X	^{29}Si(ppm)
Cl	-24.2
Br	-29.2
I	-14.9
$OC(O)CH_3$	-11.3
$OC(O)CF_3$	-30.1

These values significantly exceed the values for model tetra co-ordinate compounds of the type $Me_2(ClCH_2)SiX$, which has a group of similar electronegativity attached to the central silicon atom. For the majority of compounds, a decrease in temperature brings about an increase in the shielding of the central silicon atom and results in an upfield shift in the ^{29}Si N.M.R. However, compounds in which the silicon is displaced from the plane of the equatorial ligands towards the ligand X constitute an exception (Pestunovich group, 1986[93] and Kalikhman, 1985[94]). The ^{13}C N.M.R. data supports the ^{29}Si N.M.R. data. The $^1J(^{13}C\text{-}^{29}Si)$ coupling is higher than the tetra co-ordinate analogues. This suggests that there is a significant increase in the 's' character of the Si-C bond. The silicon uses the sp^2 hybrid orbitals for bonding the equatorial ligands.

Further work has been carried out by the Mozzhukhin group (1992)[95] on the changes in the interatomic distances in $O...SiC_3\text{-}Cl$ fragments were examined. A study of several derivatives allowed a new relationship to be proposed between the changes in the Si..O and the Si-Cl distances. In addition, it was shown that the overall order of the hypervalent bond is constant and differed from unity. Often it was found to be greater than one. In this paper all the compounds studied contained an N-CO group and hence the possibility of delocalisation of electron density. This could possibility lead to a more ionic character of the Si-Cl bond. The relationship proposed in this paper between bond order and bond distance is based on the work of Pauling (1947)[96] and takes the following form:

$$\text{Bond Order} = 10^{-(d-do)/C}$$

where C = a constant; do bond length of bond with a bond order of one and d is the observed bond length. The constant may be calculated from the Burgi relationship (Burgi, 1973)[97]. Such relationships could be of use in interpreting structural data.

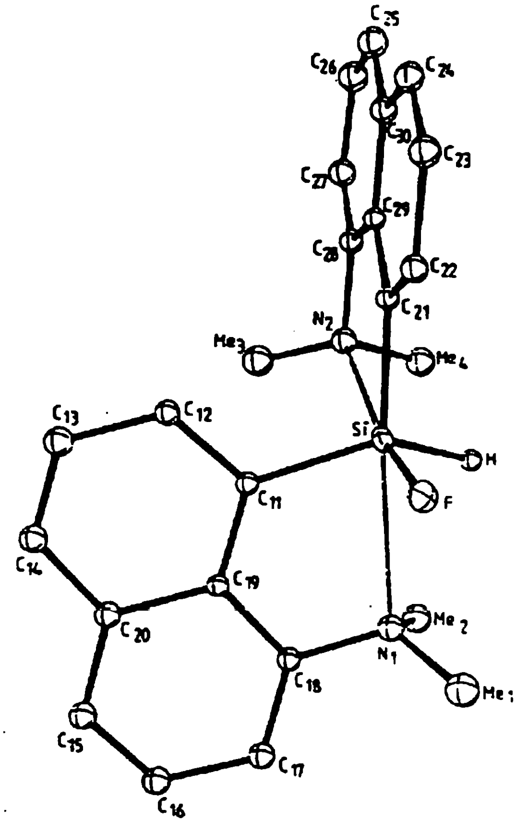
Voronkov and co-workers (1989)[98] have used infrared and dielectric constant measurements to look at =C=O-Si dative bonds. At room temperature, compounds such as 2-benzoyloxyethyl and 3-benzoyloxypropyl trifluorosilanes in non-polar solvents exist as rotational isomers containing tetrahedral Silicon. A decrease in temperature resulted in the formation of penta coordinated species in which the silicon forms part of a six membered ring. The stability constant for the increase in co-ordination was found to increase with decreasing temperature and with increasing polarity of the solvent. Compounds of the type $X'C_6H_4C(O)OCH_2SiF_nMe_{3-n}$ are capable of forming intramolecular Si-O, the strongest being formed when n=3. An increase in the number of (CH_2) groups separating the phenyl substituent from the silicon also decrease the strength of the dative Si-O bond. The enthalpy of formation of a six membered ring containing a Si-O dative bond changes little when X=Cl or X=F. The values for ΔH being 3.8 and 5kJ/mol respectively.

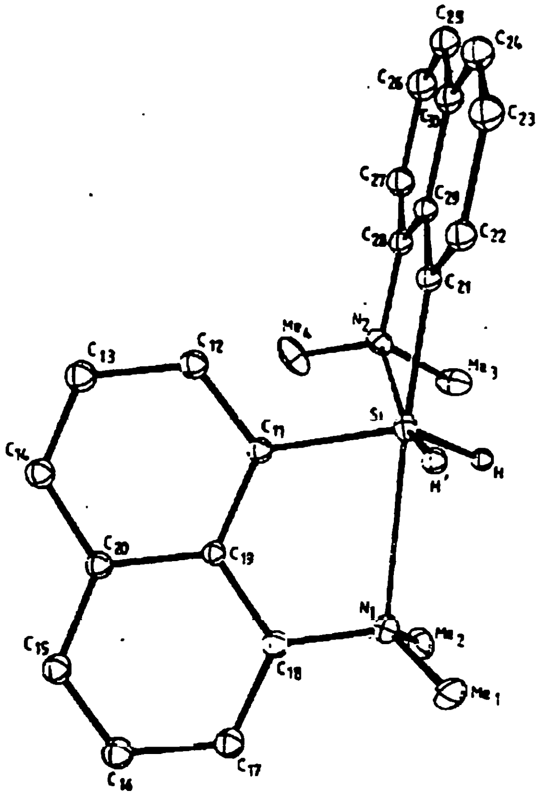
The ^{19}F NMR was recorded and showed a resonance at δ-64.04 ppm. The single crystal X-ray diffraction pattern was determined . The complex had a trigonal bipyramidal structure but the significant feature was the long apical $Si-CF_3$ (205.6 pm) and the considerably shorter $Si-CH_3$ bond length (188.2 pm).

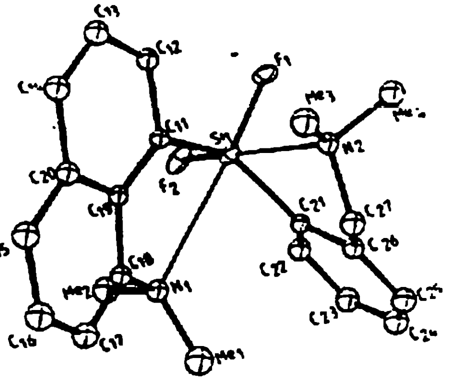
1.7 - HEXA COORDINATED SPECIES CONTAINING SINGLE Si-L BONDS.

All the reviews mentioned above also contain significant references to this group of compounds. Like penta co-ordinate compounds, hexa co-ordinate silicon compounds have attracted interest since they possibly serve as a model compounds for the study of reaction intermediates. The Corriu group (1974[99] and 1980[100]) has proposed hexa co-ordinate species as intermediates.

Corriu (1989)[101] prepared several hexa coordinated silicon compounds and characterized them by x-ray diffraction. Representations of the crystal structures of bis-(8-(dimethylamino)naphthyl)fluorosilane (35), bis(8-(dimethylamino)naphthyl)silane (36) and (2-(dimethylamino)methyl)-(phenyl)-(8-(dimethylamino)naphthyl)difluorosilane (37) are shown on page 64.


C25
C26
C24
C30
C23
C27
C29
C28
C22
C21
N2
Me3
Me4
C13
C12
Si
H
C11
F
C14
C19
Me2
C20
N1
C18
Me1
C15
C17
C16


C25
C24
C26
C30
C23
C27
C29
C28
C22
C21
Me4
N2
Me3
C13
C12
C11
Si
C14
H'
H
C20
C19
N1
Me2
C15
C18
Me1
C16
C17



37

The second compound mentioned (36) does not exhibit any polar groups. In compound (35), the lone pairs of both nitrogen atoms are directed towards the central silicon and have a bond lengths of 2.680Å and 2.646Å respectively, and are similar to pentavalent species (2.44 - 2.66Å). With respect to compound (36), the significant feature is the non-equivalence of the methyl hydrogen atoms. The strongest Si-N interaction involved the nitrogen atoms, which are opposite the aryl carbon. Compound (37) shows two different conformations in the solid state that involves a slight difference in the Si-N interaction. In all these compounds, the silicon maintains a largely tetrahedral arrangement, which is similar to a bi-capped tetrahedron, in which the tetrahedral silicon is undergoing nucleophilic co-ordination.

Additional studies of hexa coordinated silicon using chelating nitrogen donor ligands have been carried out by Corriu (1989)[102]. The studies of these compounds showed that several of them existed as a pair of enantiomers in fluctional equilibrium. N.M.R. studies indicate that isomerization does not involve bond cleavage. The compounds studied are indicated in Table 14 including additional ^{29}Si N.M.R. data.

TABLE 14 - SELECTED ^{29}Si N.M.R. DATA

Compound	^{29}Si
bis(8-(dimethylamino)naphthyl)fluorosilane (38)	-37.33
bis(8-(dimethylamino)naphthyl)methoxysilane (39)	-27.43
bis(8-(dimethylamino)naphthyl)methylsilane (40)	-26.79
bis(8-(dimethylamino)naphthyl)methylphenylsilane (41)	-12.08

Evidence for the hexa co-ordination also comes from the temperature dependent ^{1}H N.M.R. studies. At low temperatures two distinct naphthyl groups were observed. The use of selective saturation in the case of compound (38) and (39) have shown that isomerization by the naphthyl groups and NMe_2 groups are successively in equivalent positions and toward the functional group. All the compounds show that the compounds undergo a non-dissociative isomerization. A full mechanism was not provided at this stage.

An earlier paper produced by the Corriu group (1984)[103] has demonstrated an easier way to produce a dianionic hexa co-ordinate compound using catechol as the ligand. The compound produced were formulated as $M_2[(C_6H_4O_2)_3Si]$ where M=Na and K. The potassium analogue was found to be highly reactive and useful as a precursor for other compounds.

A new method for the synthesis of hexa co-ordinate compounds has been developed by Evans and co-workers (1991)[104]. The method involves the reaction between $SiCl_4$, $Si(OEt)_4$ and ligands such as Chrysin (chrH), maltol (malH), 3-hydroxypyridine-2-one (dhpH) and 8-hydroxyquinoline-N-oxide (dqoH). The method of preparation of is represented by the following equations:

$$Si(OEt)_4 + 3LH + HX \longrightarrow SiL_3^+[X^-] + 4EtOH$$

$$SiCl_4 + LH \longrightarrow SiL_3^+[Cl^-] + 3HCl$$

where X = HSO_4^-, $CF_3SO_3^-$, Cl^-, CF_3COO^-.

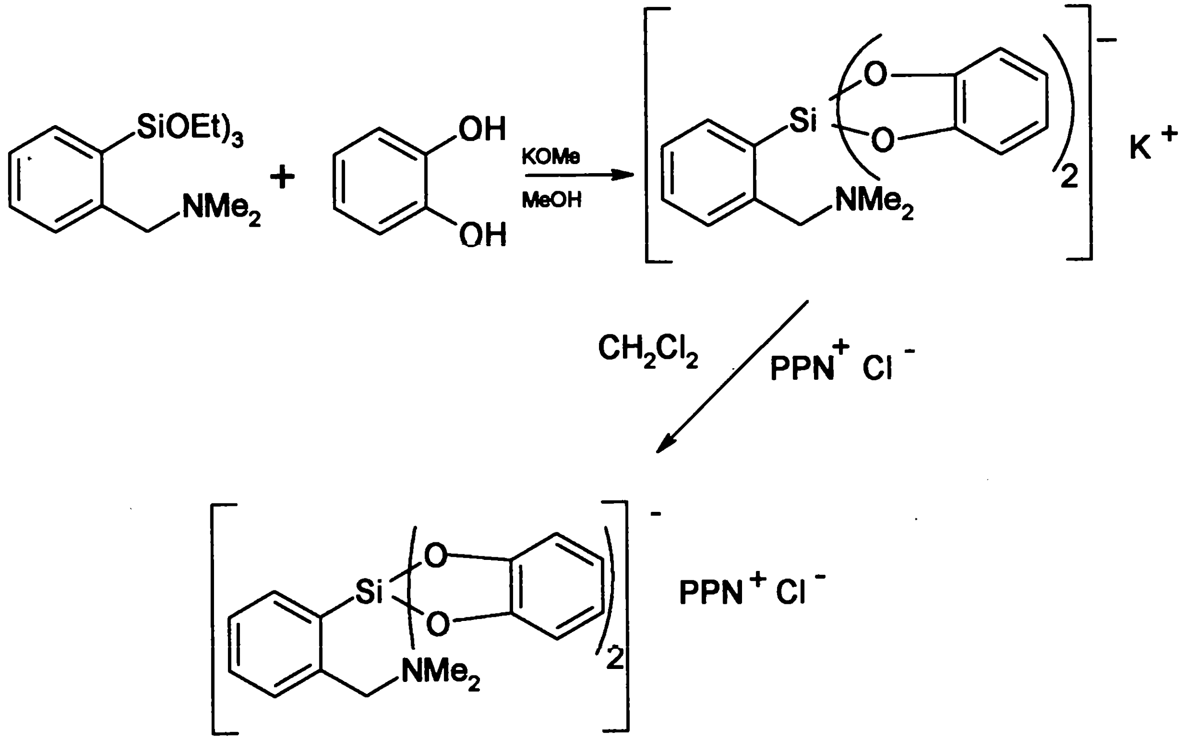
The ^{29}Si and ^1H N.M.R. were recorded and some of the ^{29}Si N.M.R. data is shown in Table 15:

TABLE 15 - SELECTED SPECTROSCOPIC DATA

Compound	^{29}Si	Yield (%)	MS(FAB)m/z
$Si(dmp)_3^+$	-135.3	89	442
$Si(mal)_3^+$	-134.9-134.4	50	403
$Si(dhp)_3^+$	-141.6	75	358
$Si(chr)_3^+$	-193.1	-	787
$Si(hmq)_3^+$	-192.3-192.7	90	550

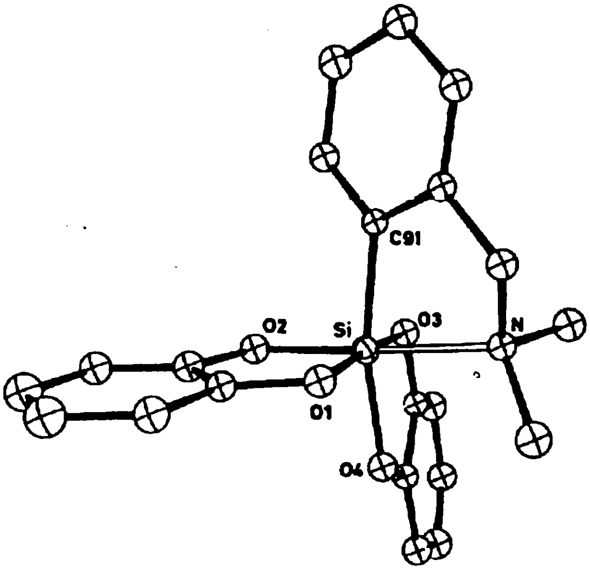
It can be seen from the above table that several of the compounds show two ^{29}Si resonances. This may be due to the presence of the fac and mer isomers. In addition the ^{29}Si chemical shifts appear to be independent of the nature of the co-ordinating oxygen, the nature of the counter ion and the charge on the complex. However, the ^{29}Si chemical shifts do depend on the chelate ring size. It would thus appear that the shielding of the silicon depends on the symmetry around the silicon. Williams (1983)[105] has suggested that in compounds where the symmetry is reduced the N.M.R. active nucleus becomes sensitive to changes in the electronic properties of the ligands.

As part of their continuing work on hypervalent compounds, Corriu (1989)[106] reported the synthesis of a (PPN)silicate where PPN = bis(triphenylphosphoranylidene)ammonium. This compound was prepared according to the following reaction:



Where PPN = $Ph_3P=\overset{+}{N}=PPh_3$

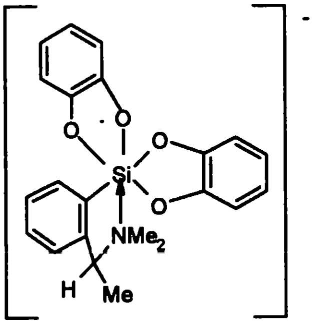
A molecular structure was obtained, and a representation is shown on page 70.



The compound adopts the expected octahedral configuration. The Si-C (to the phenyl group) is very long (1.917 A) while the Si-O distances are equal at 1.781Å. Again, these are long when compared with analogous penta coordinated compounds. The Si-N distance is consistent with being coordinated and similar to the silatranes at 2.15Å. The ^{29}Si N.M.R. shows a resonance at -121.2ppm, which is similar to other hexa-coordinated species.

The compound is chiral and in principle, it should be possible to show diastereotopism using ^{1}H N.M.R. However, only a single resonance was observed at low temperatures. This suggests that a rapid equilibrium exists between the open and closed form about the silicon -nitrogen bond, which allows rotation and inversion. Alternatively an intramolecular process such as a Bailar twist (Bailar, 1958)[107] and Corriu and co-workers(1987)[108] may be in operation.

In order to see which mechanism was operating in this case, another compound containing a chiral benzylic group was synthesized. The presence of the benzylic group has the effect of making the NMe_2 group diastereotropic when the nitrogen is coordinated. A representation of the compound is shown below:



PPN$^+$

The one coalescence point for the benzylic carbons and the single NMe_2 resonance is presumed to be indicative of an intramolecular non-dissociative mechanism in operation. The ^1H N.M.R. also allowed the determination of the ΔG activation of Si-N bond breaking. This was found to be 44.2 kJ/mol.

The Corriu group (1988)[109] have been looking for a way to prepare hypervalent compounds from silica. Corriu depolymerized silica by reacting it with catechol in the presence of sodium methoxide, which resulted in the formation of a hexa coordinated $[Si(o\text{-}O_2C_6H_4)_3]^{2-}$. The method for the depolymerization, in water, had been previously described by Rosenheim (1931)[60], Barnum (1970)[61] and the Weiss group (1961)[110]. This compound was found to react with Grignard reagents to give R_4Si or $R_3SiO\text{-}C_6H_4\text{-}(o\text{-}OH)$ depending on the R group.

Yoshikawa and co-workers (1992)[111] have achieved the complete optical resolution of

$[Si(phen)_3]^{4+}$ and $[Si(bipy)_3]^{4+}$. The former complex was synthesized from SiI_4 and 1,10-phenanthroline using the method of Kummer (1979)[112]. The resolution was achieved using a chromatographic method involving the use of sodium ((+)-tartrato)antimonate as eluent. The absorption, circular dichromism, and ^1H N.M.R. spectra were recorded. The results of these do indicate that complete resolution had been achieved. This paper is significant in that very little work has been reported on the resolution of optical six co-ordinate silicon compounds.

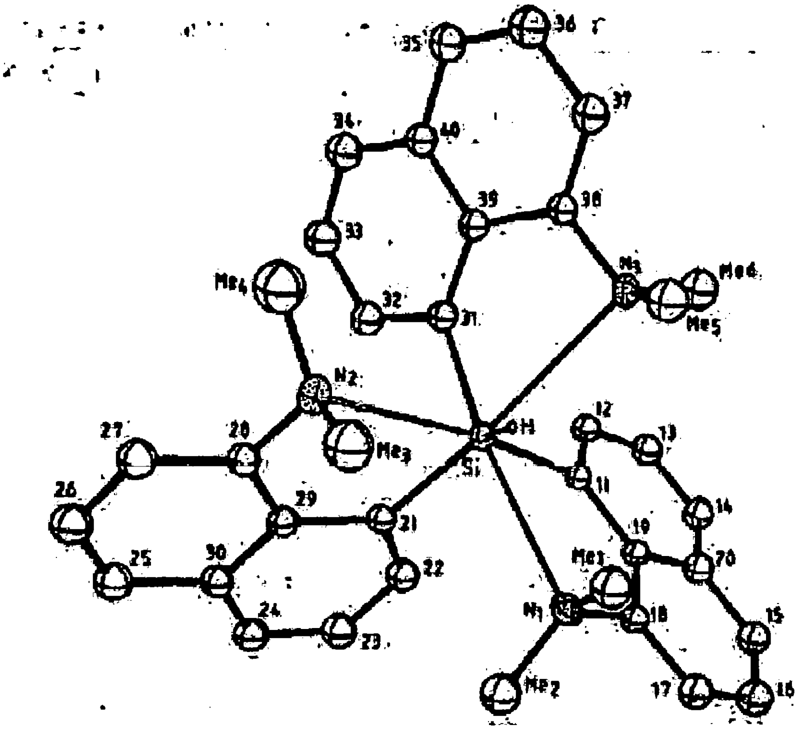
An interesting paper by the Corriu group (1988)[113] is worth noting because it contains reference to hepta coordinated silicon and germanium species. The only other report of hepta coordinated silicon has been reported by the Roddabasanagoudar group (1985)[114] on mechanistic studies of hexa coordinated species. The compounds obtained were of the form $(2\text{-}Me_2NCH_2C_6H_4)_3MH$ (where M = Si or Ge). The silicon compound was prepared by the following reaction:

$$3\ 2\text{-}Me_2NCH_2C_6H_4Li + SiHCl_3 \longrightarrow HSi(2\text{-}Me_2NCH_2C_6H_4)_3 + 3LiCl$$

A crystal structure was obtained for the germanium analogue. This compound was shown to be seven co-ordinate. However, it was only possible to obtain a powder pattern and thermal analysis for the silicon analogue. However, the results are similar for both compounds, which suggests that the silicon is also seven co-ordinate. The ^{29}Si N.M.R. showed a resonance at -35.3ppm ($^1J(SiH)$ = 229.3Hz).

Corriu (1994)[115] has extended the range of hepta coordinate compounds with the synthesis and characterization of tris[8-(dimethylamino)naphthyl]silane and tris[2-

(dimethylamino)methyl)phenyl]fluorosilane. A representation of the X-ray crystal structure is shown below:



The structure shown is known as tri-capped tetrahedron and the symmetry is C$_3$. It should be noted that the three Si-N interactions appear weak with a bond distance between 2.87Å and 3.47Å It appears that steric hindrance prevents the close approach of the nitrogen lone pairs. Spectroscopic data was recorded for each of the compounds including the ^{29}Si N.M.R. In the case of tris[2-((dimethylamino)methyl)phenyl]fluorosilane the resonance was observe at -9.86ppm while in tris[8-(dimethylamino)naphthyl]silane the resonance was observed at -25.86 ppm.

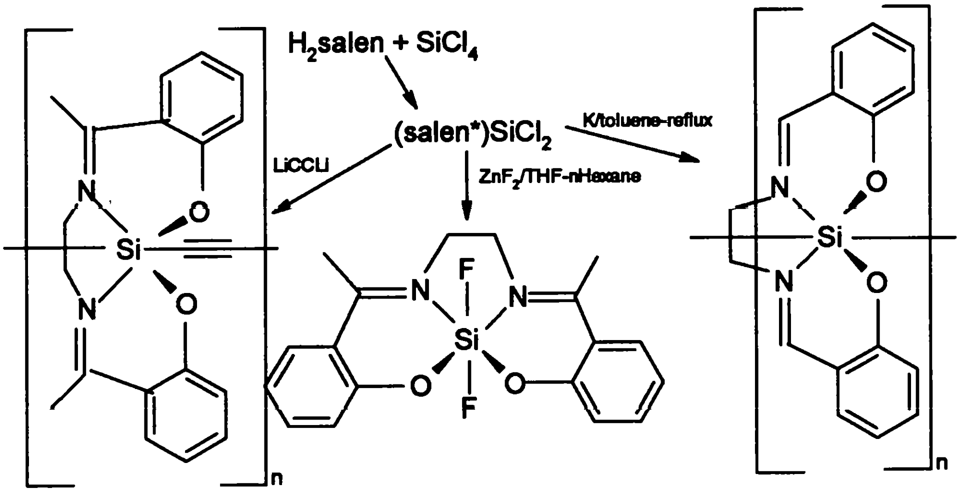
The crystallographic data provide certain points of interest:

a) In one case the Si-N donor bond is co-linear with the opposite Si-Ph bond despite the steric hindrance.

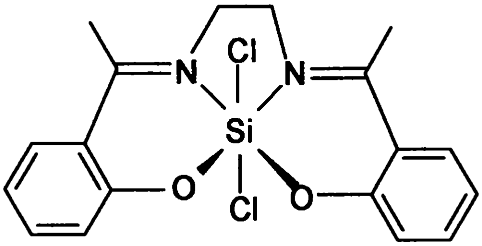
b) In general, penta or hexa co-ordinate fluoro compounds are formed by the additional ligands bonding opposite to the fluorine. In this case there is frontal co-ordination at the Si-F bonds by the three equivalent amino groups.

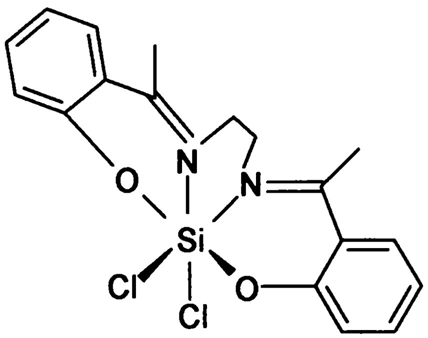
The synthesis of such hepta co-ordinate compounds provides evidence for the possible existence for heptacoordinate intermediates in the nucleophilic substitution of hexa co-ordinate compounds.

Recently, Rower and co-workers (1998)[116] have synthesized several novel six co-ordinate organosilicon compounds from $SiCl_4$, Si_2Cl_6 and N,N-ethylenbis(2-oxyacetophenoneiminate (salem*). This ligand has methyl groups, in place of hydrogen atoms, attached to the azomethine group. The six co-ordinate compounds were prepared according to the following scheme:

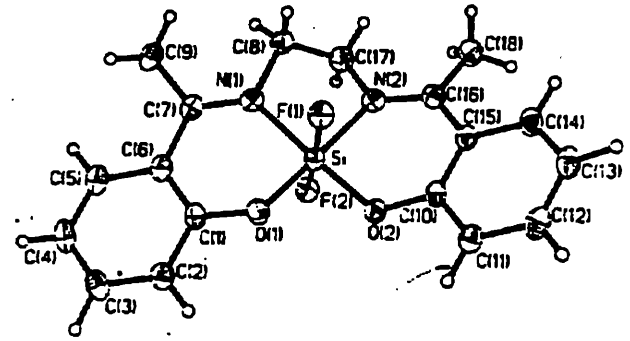


It should be noted that the ^{29}Si NMR of the chloro derivative, Si(salem*)Cl_2, showed two peaks at -186.1 ppm and -188.0 ppm respectively. These were due to the presence of the two isomers:





The single crystal X-ray diffraction pattern was obtained for the fluoro derivative and this is shown below:



The key feature is that the Si-O distances of 1.721 A and 1.724 A and Si-N distances of 1.931A and 1.937 A were short compared to other hexaco-ordinate species. The Si-F distances were 1.677 and 1.670 were within the normal range of 1.60A-1.73 A. The distortion from the octahedral geometry is probably due to the conformational requirements of the chelating salem* ligand.

As noted in the above synthetic scheme, polymer formation was achieved. These compounds are the subject of continuing study as they may have novel optical and electronic properties. Polymers with bridging acetylene ligands have already been prepared by Shim group (1984)[118].

The Douglas group (1998) [118a] have prepared poly(aryleneethynylenesilylene) compounds of general formula $(C_2SiR_2C_2X)_n$ (where X= 9,10-anthrylene) These polymers contain both penta and hexa co-ordinated silicon. The absorption spectra is consistent with Si conjugation along the polymer backbone. The electronic properties are such that these compounds could find application in the electronic industry.

The Corriu group (1996)[118b] have studied the acid/base chemistry of hexa-coordinate {2,6-bis-[(dimethylamino)methyl]phenyl}bis(1,2-benzenediolato)silicate and showed that it has a very high basicity. This was shown when this compound reacted with methanol. The result was a zwitterion. The compound had a higher p*Ka* (16.7) than the proton sponge 1,8-bis(dimethylamino)naphthalene. The Corriu group suggest that the high basicity was due to the greater stability of the zwitterion the geometry of which was nearer to a perfect octahedron than the parent compound.

CHAPTER 2: THE REACTIVITY OF SILICON COMPOUNDS

2.1 - THE REACTIVITY OF HYPERVALENT ORGANOSILICON COMPOUNDS

The aim of the next few sections is to obtain an explanation of the observed enhanced reactivity of penta and hexa coordinated silicon towards nucleophiles. In many ways these observations are counterintuitive since, it would not be expected that hypervalent neutral or anionic species would have such enhanced reactivity towards nucleophiles. The mechanism of nucleophilic substitution has been a major area of debate since the late 1970's. It would be useful to consider the content of the debate as a starting point to the discussion.

Recently the Janzen group (1997)[118c] has employed *ab-initio* molecular orbital calculations to look at the cleavage of the Si-F and Si-C bonds. Previously this group had studied Si-F bond cleavage using ^{19}F NMR in four and six co-ordinate silicon species (Janzen group 1977)[118d] . The current work suggests that Si-F bond cleavage occurs via the F- -Si- - F intermediate which Janzen had previously considered in 1994[126]. As a result of their calculations, it was concluded that the cleavage of the Si-C bond in $PhSiF_3$ takes place in the presence of F^- and oxidizing agents with the formation of $PhSiF_4^-$ and $PhSiF_5^{2-}$. Subsequent oxidation to $PhSiF_5$ radical anion occurs. The latter species was predicted to decompose to give SiF_5^- and a phenyl radical. The Janzen group further suggest that their work is in agreement with available experimental data. In addition they further contend that given the lack of thermodynamic and kinetic data associated with the reactive intermediate, that calculated bond lengths may be used and that using a quote from the the Perkin group (1980)[126] that the longer the bond, the faster it breaks.

Several other mechanisms for nucleophilic substitution have been proposed. Modena and co-workers (1957)[119] have proposed a mechanism for the hydrolysis of silylchlorides which utilizes base catalysis. Corriu group (1978)[120] have criticized this proposition on the basis that it does not explain the change in stereochemistry that occurred in some reactions. In addition, Frye (1984)[121] has shown that the rate of reaction does not depend on basicity but on the nucleophilicity of the nucleophile.

Another mechanism has been proposed by the Chojnowski group (1978)[122]. These workers have isolated a HMPA adduct of trimethylbromosilane which was shown by conductivity experiments to be ionic. Chojnowski argued that the reaction involved an intermediate consisting of four co-ordinate silicon and a phosphonium cation. Retention of configuration was achieved by two consecutive inversions. Similar substituents were studied by Beattie and co-workers (1966)[123] using trimethyliodosilane, but the stereochemical changes could not be studied in this reaction.

A crucial point was noted by the Corriu group (1980)[124]. They observed that the Sn and Ge analogues underwent racemization much faster than the silicon analogue and that these compounds did not give ionic adducts. In addition he notes that the above mechanism does not account for nucleophile induced epimerisation of chlorosilacyclobutane. Corriu suggests that this double displacement mechanism may be confined to silanes with labile Si-Br and Si-I bonds.

The most favoured mechanism currently available was the one put forward by Corriu (1977)[125]. This mechanism involves increasing the co-ordination number of the silicon to five or six depending on the nature of the silane. However, this mechanism has not gone unchallenged. Frye and co-workers (1984)[121] have suggested that the Corriu mechanism is unlikely because:

1. Increase in steric bulk on increasing co-ordination.

2. Penta coordinated silicon will have an increase in negative charge due to the formation of the dative bond from the nucleophile.

However, there are several pieces of strong evidence for the Corriu mechanism:

1. The kinetic data for racemization shows a second order dependence on the nucleophile and for alcoholysis shows a first order dependence on the nucleophile and the alcohol. This suggests that there is a common mechanism involving a pre-equilibrium intermediate (five co-ordinate) and the subsequent attack by the nucleophile on the intermediate.

2. Small enthalpies of activation and large negative entropies of activation indicate a highly associated state.

3. The Corriu group (1974)[127] has shown the presence of the CF_3 substituent on a phenyl group of Ar(1-naphthyl)EtSiCl reduces the rate of racemization by making

the silicon less electropositive and reducing the length of the Si-Cl bond.

4. X-ray fluorescence spectra show clearly that the silicon has a higher positive charge in penta coordinated $XSi(O\text{-}CH_2CH_2)_3N$ than in the tetra coordinated $XSi(O\text{-}CH_2CH_3)_4$ (Voronkov co-workers (1984)[128].

5. Molecular orbital calculations by Baybutt (1975)[129] also indicate that the positive charge on the silicon increases on going from four to five co-ordinate by 0.16 - 0.20e.

6. The Corriu group (1983)[130] has shown that $H_2Si(C_6H_4\text{-}CH_2NMe_2)$Naphthyl undergoes alcoholysis rapidly compared to H_2SiPhNaphthyl which does not undergo this reaction.

2.2 - THERMODYNAMIC AND KINETIC ASPECTS OF REACTIVITY

Before going into the details of the reactivity of hypervalent silicon compounds it is worth reviewing the key areas concerning reactivity-namely thermodynamic and kinetic functions.

The thermodynamic quantity which most readily affects a chemical reaction is ΔG. In general ΔG may be defined as follows:

$$\Delta G = \Delta H - T\Delta S \qquad -(1)$$

$$\Delta G = -RT\log_e K_c \qquad -(2)$$

$$\Delta G = -nFE \qquad -(3)$$

In redox reactions, the importance use of the standard reduction potential is that it can be used to calculate other thermodynamic functions. For example ΔH:

$$\Delta G = \Delta H - T\Delta S$$

$$dG/dT = -\Delta S$$

$$\text{now } -nFE = \Delta H - T\Delta S$$

$$\text{therefore, } nF\, dE/dT = -\Delta S$$

Substituting into equation (1) and rearranging we obtain:

$$\Delta H = -\Delta G + T\Delta S$$

$$\Delta H = nFE + TdE/dT + \mu F$$

A favourable reaction will give a negative ΔH and a positive ΔS.

However, it is equally important to look at kinetic parameters when considering reactivity.

Various theories of rates of reaction have been developed and reviewed elsewhere. Details of the simple collision model may be found in Moelwyn-Hughes (1957)[131] and Laidler (1969)[132]. Many of the theories may be classified under the following headings:

1. Simple Collision theory.

2. Modified Collision theory.

3. Semi-empirical methods.

4. Bond energy bond order (Johnson, 1966)[133].

5. Activated complex theory.

6. Statistical treatments (Rice and co-workers, 1927)[134].

A useful approach has been the development of the activated complex theory using a thermodynamic approach. This approach may be stated as follows:

The rate expression may be given by:

$$K = (kT/h)\, Q/\, Q_a Q_b \exp{-E_a/RT}$$

where Q is the partition coefficient of the species involved. This can be reduced to:

$$K = (kT/h)\, K_c$$

and since:

$$K_c = (Q/Q_aQ_b)\, \exp\text{-}E_a/RT\ .$$

Now-RTlog$_e$ $K_c = \Delta G$ and substituting into 2 and manipulating we obtain:

$$K = (kT/h)\, \exp\text{-}\Delta G/RT$$

now $\Delta G = \Delta H - T\Delta S$

therefore:

$$K = (kT/h)\, \exp\text{-}(\Delta H\text{-}T\Delta S)/RT$$

$$= (kT/h)\, \exp\text{-}\Delta S/R\exp\text{-}\Delta H/R$$

For an experimental determination of the above it can be shown that:

$E\exp = RT^2\ (d\log_eK_c)/dT$

$$=(RT^2/h)\,d\log_e/dT(kTK_c/h) = RT + RT^2(d\log_e K_c)/dT$$

given that $d\log_e K_c/dT = \Delta E/RT^2$

$E_{exp} = RT + \Delta E_0$

$\Delta H = \Delta E + (P\Delta V)$

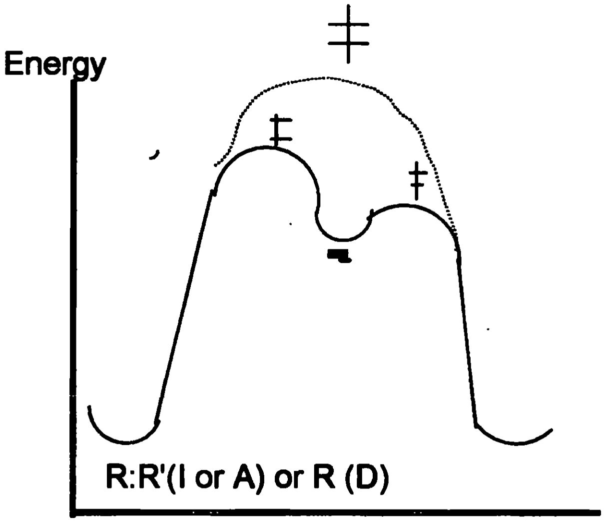
therefore $E_{exp} = \Delta H_0 + RT$

1.81 - TYPES OF MECHANISM

Several types of reaction mechanism are available and these may be classified as:

1) Interchange (I) mechanism
2) Associative (A) mechanism
3) Dissociative (D) mechanism

The reaction profile for each type is shown below:



▬ - = intermediate for A or D only

‡ =Activated complex for A, D or I

A reaction energy profile illustrating the formation of an intermediate characteristic of A and D process (▬) and the formation of an activated complex characteristic of an I process (- - - -).

(From Kotz group, 1977)[135]

The substituents can affect the value of the mechanism of reaction and the rate constant. Qualitative data is shown in Table 16:

TABLE 16 EFFECT OF ENTERING AND LEAVING GROUP ON RATE CONSTANT

MECHANISM	LEAVING GROUP	ENTERING GROUP
D	LARGE	NONE
A	SMALL	LARGE
Id	SIGNIFICANT	LESS SIGNIFICANT
Ia	LESS SIGNIFICANT	SIGNIFICANT

The only certain way to differentiate between D or A mechanisms is to observe the intermediate. The difficulties associated with this have recently been reviewed by Williams (1993)[136]

A great deal of information may be obtained from the rate equation. The rate equation is usually expressed in the form of a rate law:

$$\text{Rate} = K[A]^m[B]^n$$

The n and m refer to the respective orders and m+n give the overall order. The rate equation may be defined as any order and must be determined from experiment. For a first order the differential equation has the form:

$$-d[A]/dT = K[A]$$

which integrates to $[A]=[A_o]\exp{-kt}$. Second order rate equations are found in silicon and the rate equations are more complex. In fact as the order increases the complexity of the integrated form also increases. For a second order reaction where the concentration of the reactants are the same the differential equation takes the form:

$$-d[A]/dt = k[A]^2 \text{ where } [A]=[B]$$

which integrates to $1/[A]-1/[A]_o = kt$.

Where the concentrations are not equal, and the above cannot be integrated, it may be useful to use the decrease in concentration x. Given that the reactants are consumed in equal amounts, it can be said that at time t, the concentration of A and B respectively are $[A]=[A]_{o-x}$ and $[B]=[B]_{o-x}$ therefore we may write:

$$dx/dt = k([A]_{o-x})([B]_{o-x})$$

which upon integration by parts produces, $1/([A]_o-[B]_o)Ln[B]_o[A]/[A]_o[B] = kt$. Chemical reactions show a temperature dependence defined by the Arrhenius equation:

$$k = Aexp\text{-}E_a/RT$$

This will produce a linear plot when ln k is plotted against 1/T except when competitive reactions are occurring or at very low temperatures where quantum effects are being apparent.

The majority of reactions do not take place as a result of a single collision but have a series of consecutive or concurrent reactions. Consequently a great deal of care needs to taken when interpreting kinetic data.

The solvent may have a profound effect on the rate of reaction, for example the reaction between 4-fluoronitrobenzene and the azide ion proceeds two million times faster in $O{=}P(NMe_2)_3$ than in water. A change from one solvent to another will cause, among other effects, an alteration in the relative free energies of the reactants and the activated complex. An increase in the free energy of the reactants and a reduction in the free energy of the activated complex will favour an increase in the rate of reaction.

Parallel with the theoretical developments is the improvement in experimental procedures. In particular the Alibrandi group (1994)[137] has recently developed kinetic methods which will speed up the obtaining of kinetic data.

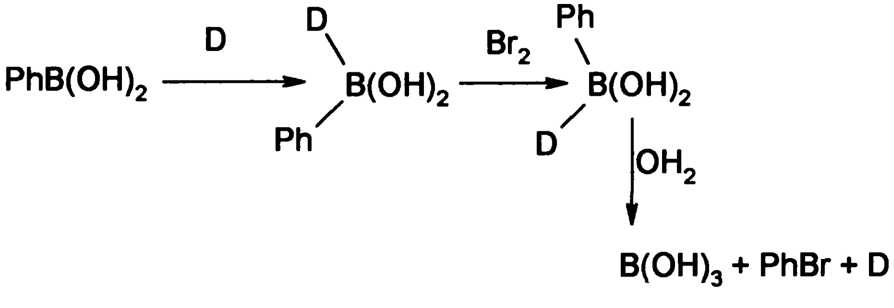
CHAPTER 3: NUCLEOPHILIC SUBSTITUTION OF SILICON AND RELATED ELEMENTS

3.1 - NUCLEOPHILIC SUBSTITUTION IN BORON AND RELATED COMPOUNDS

Although boron is a group 3 element it has certain similarities to silicon via the diagonal relationship. It is worth considering reactivity of the tetra coordinate adduct. Kuivila (1951)[138] and co-workers have noted that the bromination of arylboronic acids is facilitated by the presence of oxygen donor solvents. The rate equation for such reactions was shown to be as follows:

$$\text{Rate} = k[\text{PhB(OH)}_2][\text{Donor}][\text{Br}_2]$$

A possible mechanism is as follows:



However, it should be noted that the last stage may not be a substitution at the bromine but electrophilic substitution at the phenyl group.

The exchange reactions of four co-ordinate boron compounds have been extensively studied. The exchange reaction between NMe_3 and $Me_3N\text{-}BMe_3$ have been shown to be first order in adduct and an activation energy of 74kJ/mol which is about the same as the B-N bond energy. The entropy of activation was found to be negative which is indicative of an associative mechanism. Early studies by the DeRoos group (1965)[139] on In and Ga found them to be too fast for the various parameters to be determined.

Extensive studies on the substitution reactions of boron amine adducts have been reported by Buddle (1971)[140] and Walmsley (1971)[141]. They found that the rate law progresses from first to competitive first and second when BH_3 is compared with BH_2R. Substituents have been shown to have a profound effect on the reaction rates. For example, the reaction between $Me_3N\text{-}BH_3$ and PH_3, the attack by the latter is the rate-determining step. However, when H is replaced by butyl or aryl groups, several effects are observed. These include the appearance of a competitive first order reaction. This appears to have its origin in the bulk of the butyl group and electronic stabilisation of the transition state in the case of the aryl substituted compound.

Blackborow (1968)[142] has studied the elimination of hydrogen halide in BCl_3 and BBr_3 using amines in acetonitrile:

$$RNH_2 + D\text{-}BX_3 \text{ -------> } RHN\text{-}BX_2 + HX + D$$

Where R= 2,4-dinitrophenyl, 2-nitrophenyl and 2,4-dinitroanthracene.

The rate equation was found to take the form:

$$\text{Rate} = k_{obs}[RNH_2]$$

The k_{obs} was shown to be proportional to the concentration of the D-BX_3.The rate equation being:

$\text{Rate} = k[DBX_3][RNH_2]$

This rate law could arise in two ways:

1) I interchange mechanism

$$\text{D-BX}_3 \xrightleftharpoons{k_2a} \text{D} + \text{BX}_3$$

$$\text{BX}_3 + \text{RNH}_2 \xrightleftharpoons[k_2b]{k_{-2}a} \text{RH}_2\text{N-BX}_3$$

2) Apparent D process

3) D elimination of HX from $RH_2N\text{-}BX_3$

The data gives rise to the following rate law:

$$\text{Rate} = K_{2a}k_{2b}[\text{D-BX}_3][\text{RNH}_2]/k_{-2a}[\text{D}]+k_{2b}[\text{RNH}_3]$$

This rate law could be reduced to a second order law if $k_{-2a}[\text{D}]>k_{2b}[\text{RNH}_2]$. This means that the mechanistic choice is reduced to:

I mechanism: $\text{D-BX}_3 + \text{RNH}_2 \text{ -----> } \text{RH}_2\text{N-BX}_3 + \text{D}$

D Mechanism: $\text{D-BX}_3 \text{ -----> } \text{D} + \text{BX}_3$

$\text{BX}_3 + \text{RNH}_2 \text{ --------> } \text{BX}_3\text{NRH}_2$

followed by elimination:

$$\text{RH}_2\text{N-BX}_3 \text{ ----> } \text{RHN-BX}_2 + \text{HX}$$

The entropy of activation was again found to be negative which is suggestive of an associative pathway. The enthalpy of activation also suggests this. Replacement of Cl by phenyl does not affect the rate law. Studies carried out by the Heaton group (1966)[143] on pyridine adducts suggests that hydrolysis occurs via a dissociative mechanism.

Halogen exchange in co-ordinatively saturated boron trihalides require a dissociative step or associative interaction which is different from the halogen bridged intermediate found in three co-ordinate boron halides. It follows that where the adduct is the source of the halide, dissociation of the adduct is the rate determining step:

$$\text{D-BX}_3 \text{ -----> } \text{D} + \text{BX}_3$$

The rates of fluorine-chlorine redistribution show an inverse relationship with respect to the strength of the boron-donor bond. In general, the breaking of the boron-donor bond is a rapid process compared to the redistribution process. A small amount of boron trihalide that does not recombine with the donor probably undergoes a redistribution reaction via an associative mechanism possibly involving the following intermediate:

Cl
B B
Br

Uncomplexed boron trihalides undergo rapid redistribution reactions, which are too fast to allow individual mixed halide species to be isolated. It was only in the late 1960's that the application of N.M.R. allowed detailed study. Many adducts of boron are in fact stable with respect to halogen disproportionation.

With respect to halogen exchange in tetrahaloborates, a dissociative mechanism appears to operate with the degree of dissociation being in the order I > Br > Cl :

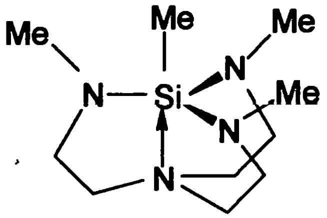
$$BX_4^- \text{ --------> } BX_3 + X^-$$

Hartman (1972)[144] has proposed the following possible mechanisms:

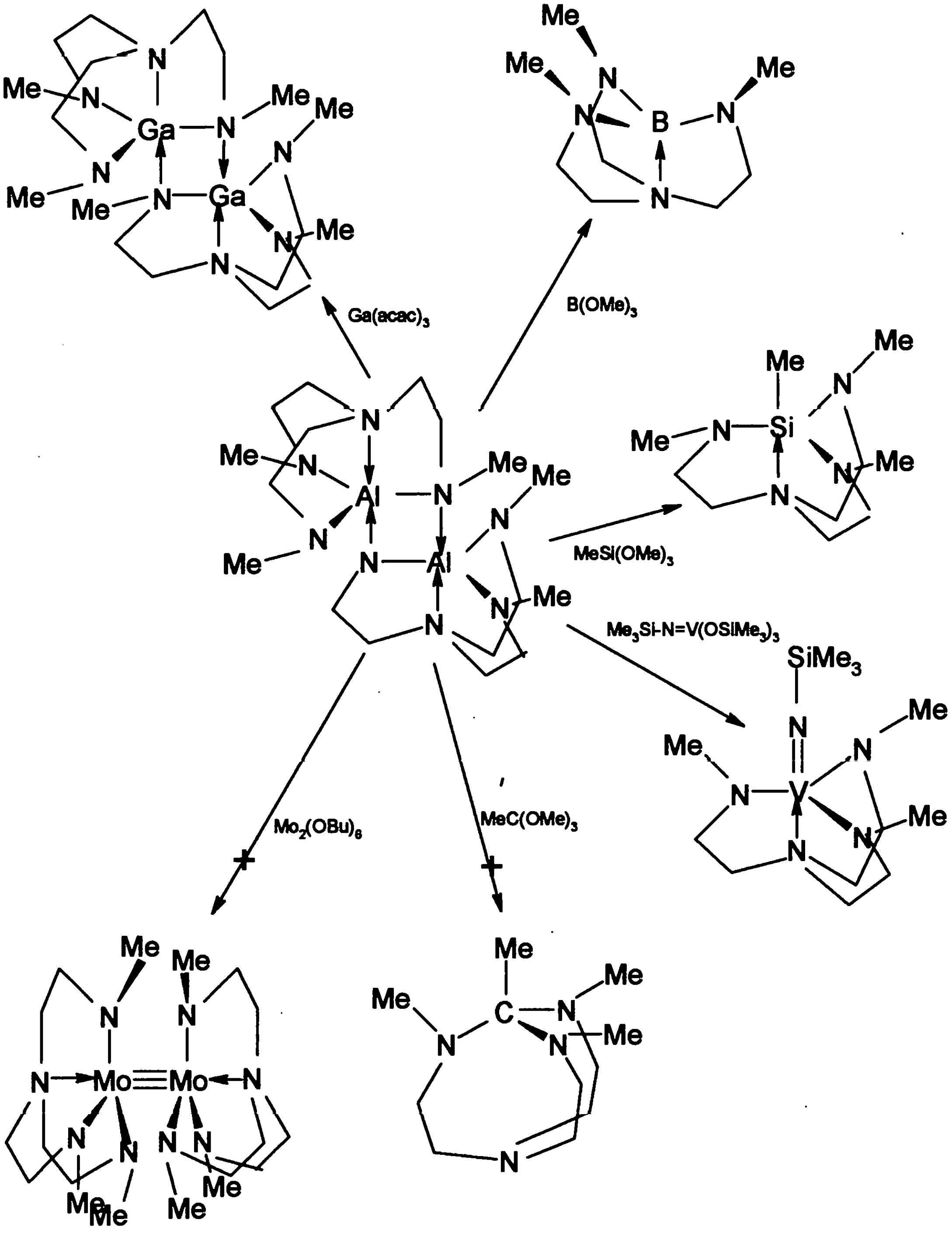
1) Recombination of BX_3 with a different halide.

2) Exchange via a halogen bridged intermediate such as $B_2F_7^-$.

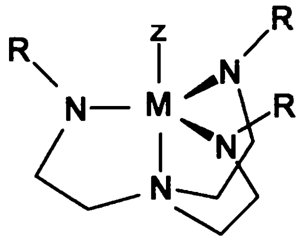
More recently a limited study of azatrane derivatives of group 13 elements in terms of reactivity and structure were carried out by the Verkade group (1994)[145]. These workers have synthesized several compounds such as trimethylazaalumatrane and trimethylazaboratrane. The former compound is a dimer which when reacted with $MeSi(OMe)_3$ yielded the following compound:



and $[Al(OMe)_3]_n$ in 40% yield. The spectroscopic data, including ^{29}Si N.M.R., was found to be in accordance with that of Wonning (1991)[146]. Other reactions of the trimethylazaalumatrane compound is shown on page 94.


Ga(acac)$_3$
B(OMe)$_3$
MeSi(OMe)$_3$
Me$_3$Si-N=V(OSiMe$_3$)$_3$
Mo$_2$(OBu)$_6$
MeC(OMe)$_3$
Ga
Al
B
Si
V
Mo
C
N
Me
SiMe$_3$

The reaction of trimethylazaboratrane with O=V(O-i-Pr)$_3$ and Ti(O-i-Pr)$_4$ was also studied. In both cases the following compounds were formed:



MZ = V=O or Ti-iso-Pr
R = Me

In the former case the reaction took 40 hours and in the latter case 9 months.

In these cases there was no systematic study of the rates of reaction. However, the data is suggestive that these hypervalent compounds did not show any rate enhancement. This of course may be due to steric effects of the bulky ligand that prevents the approach of the nucleophile ($^{-}$OMe). However, more data is required in order to reach a firm conclusion.

Toyota and co-workers (1995)[147] have studied the facile exchange between intramolecularly coordinated ligands in 2,6-bis(N,N-dimethylaminomethyl)phenylborates. These were studied by using N.M.R. and X-ray diffraction. The facile ligand switching is attributed to a S$_N$2 mechanism with the assistance of the uncoordinated ligands. The trigonal bipyramidal structure of the transition state shows the boron to be in a hypervalent state. *Ab-initio* calculations and kinetic studies suggest that fast switching of the amine ligand will only take place via penta co-ordinated boron.

The data suggest that the rate enhancement seen in hypervalent silicon is observed to some extent in boron compounds but its size and significance remains unclear. The literature with respect to gallium and aluminium does not indicate any rate enhancement effect for hypervalent compounds. Early work on the kinetics of substitution reactions of gallium suggested an associative mechanism may operate (Fait group, 1968)[148]. However recent work on gallium and aluminium suggest that they both utilize a dissociative mechanism (Saito group, 1990)[149]. The chemistry and reactivity of aluminium compounds have recently been reviewed (Robinson 1994)[150].

3.2 NUCLEOPHILIC SUBSTITUTION OF TETRA CO-ORDINATE SILICON

It is worth, at this stage, briefly reviewing the factors, which influence the reactivity of 4 co-ordinate silicon species, as hypervalent intermediates appear to play a significant role. Prior to 1958, virtually no work was reported on the kinetics of nucleophilic substitution of silicon. The first major monograph in this area appeared in 1965 (Sommer, 1965)[151] Since then a vast quantity of work, both experimental and theoretical, has been carried out in this area. A recent review of nucleophilic substitution in functional siloxanes has been produced by Ruhlmann (1992)[152]. This concentrated on deriving the Taft parameter σ^* from ^{29}Si N.M.R. data. They derived the Taft equation in the following form:

$$\sigma^* = 0.571d - 4.28 \quad \text{where } d = {}^{29}\text{Si chemical shift}$$

This goes some way to allowing quantitative predictions to be made about the steric and kinetic factors involved in the nucleophilic substitution of these industrially useful compounds.

A comparison of the rate laws for racemization and nucleophilic attack is instructive. Substitution in the case of phosphorus is similar in form to the rate equation racemization and substitution of silicon (Corriu group, 1978 and 1980)[153/154]:

$$\text{Rate (rac)} = k_{rac}[\text{A-X}][\text{Nu}]^2$$

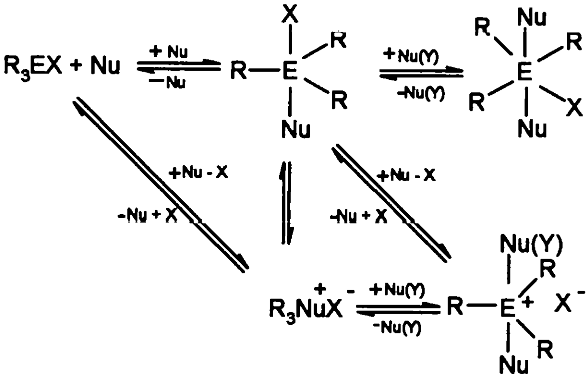
$$\text{Rate (sub)} = k_{sub}[\text{A-X}][\text{Nu}][\text{Y}]$$

Where X = halogen, Y = substituent, A = Si or P

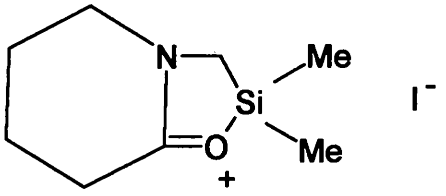
The relative rate of reaction depends on the nature of X, and it was found to be in the following order:

Br > Cl > > F

The enthalpy of activation tends to be approximately zero or positive. The entropy of activation was found to be negative for both types of reaction, which indicates that, the



formation of the penta co-ordinate intermediate (Corriu,1989)[155]. This is followed by the rate-determining step, which involves the nucleophile. Such a reaction which involves a negative entropy is indicative of a symmetrical intermediate. The details of each reaction have not often been determined. The penta co-ordinated species is more sterically hindered than the tetra co-ordinate species (3). This has led to the suggestion by West 1965[156] that the rate enhancement will only be achieved if the intermediate is cationic. Evidence to support this proposition has not been easy to find. Macharashvili (1988)[157] has obtained the following compound:



The fluoro and chloro analogues are however, not ionic. Solvents such as acetonitrile are not sufficiently nucleophilic to displace I^-. In general, silicon shows a great reluctance to form R_3Si^+ in solution (Lickiss, 1992)[158].

Attempts have been made to extend the Westheimer (1968)[159] concept to substitution reactions of silicon. This was originally applied to the hydrolysis of phosphonates and phosphates. This concept states that a nucleophile enters in an apical position in the phosphorus intermediate and the leaving group is also suggested to be displaced from the apical position. This is required by the principle of microreversibility.

Martin (1985)[160] has shown that the energies involved in pseudorotation of silicon are the same as or lower than in the case of phosphorus.

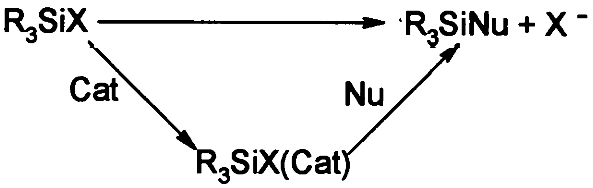
Corriu (1986)[161] has pointed out that the S_N2 reaction of the Si-F bond is sensitive to the nature of the nucleophile. For example, R_3SiF will give retention in the case of OMe^- but inversion in the case MeLi. This has led to the application of electronic treatment to $S_N2(Si)$ processes as outlined below. In general, phosphorus chemistry can be explained using Westheimer concept [159]. However, Corriu (1986)[161] points out that the work of Westheimer on the hydrolysis of phosphate esters is a special case applicable only to nucleophiles and leaving groups which give rise to P-O bond cleavage. Corriu (1986)[161] does suggest that there is analogous behavior between silicon and phosphorus and proposes the hypothesis that whether retention or inversion occurs depends on the symmetry of the trigonal bipyramidal intermediate.

In this paper, the Corriu group (1986)[161] compared:

1) Nucleophilic substitution at the P-X bond with the Si-X bond.

2) Hydrolysis reactions of the cyclic alkoxysilanes similar in structure to the phosphonates studied by Westheimer (1980)[161a].

An older review by Corriu (1982)[162] examined the nucleophilic substitution of tetra coordinated silicon. In this paper, he examined the evidence for the formation of a pre-equilibrium penta coordinated intermediate. The intermediate acts like a nucleophilic catalyst. This intermediate is then subjected to nucleophilic attack during the rate determining step:



Additional theoretical studies have been carried out by Anh and co-workers (1980)[162a] using pertubation theory. They have proposed that the frontier orbital interaction between the nucleophile HOMO and the substrate LUMO. A frontside attack will result in retention in which the large lobe of the silicon is used. This will be opposed by an unfavourable out of phase overlap between the nucleophile and the leaving group. An attack which results in inversion involves a backside attack and the small lobe of the silicon, with no unfavourable interaction. A comparison was made with carbon and they proposed that only inversion was observed in S_N2 reactions for the following reasons:

1) The Si-X bond is long and hence reduces unfavourable interactions between the leaving group and the incoming nucleophile during a frontside attack.

2) The 3s and 3p orbitals are more diffuse than the carbon 2s and 2p orbitals. These orbitals can therefore overlap with the orbitals of the incoming nucleophile at greater distances.

3) Silicon has an enhanced contribution, in terms of electron density, to the substrate LUMO whilst that contribution to the leaving group is diminished.

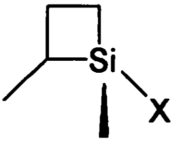
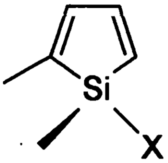
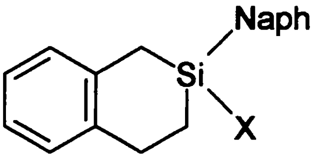
This analysis does allow one to take account of the hardness of the nucleophile. For example, a hard nucleophile has contracted orbitals and hence unfavourable interactions with the leaving group is reduced during a frontside attack. Soft nucleophiles however, have more diffuse orbitals and as a consequence a frontside attack is more unfavourable.

Several factors have an effect on the reactivity of organosilicon compounds and it is worth reviewing some of the work on this area.

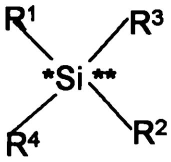
The work of Sommer (1973)[163] indicates that the structure of the phenyl and alkyl groups will have very little effect on the stereochemical nature of the product. However, if the silicon becomes part of a strained ring, stereochemical effects may be observed. Some data are presented in Table 17 (Bassindale group 1989)[164]:

TABLE 17 - STEREOCHEMICAL OUTCOMES

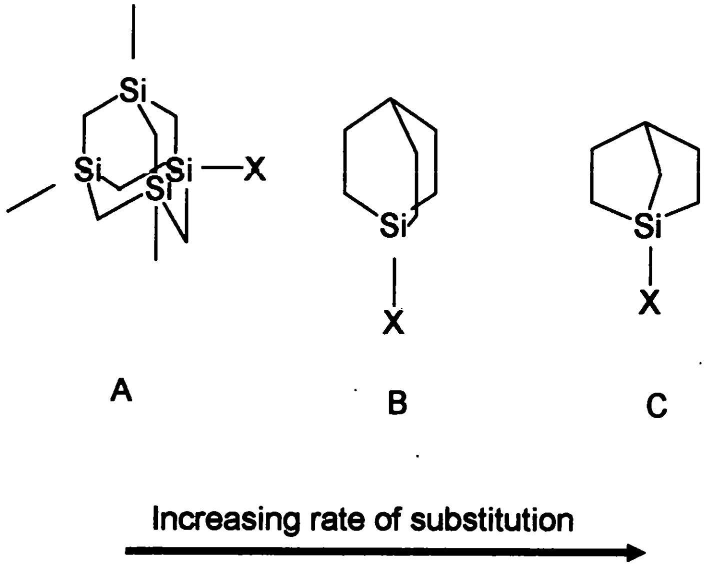
Stereochemical outcomes for the reaction between exocyclic organosilicon compounds and $LiAlH_4$

COMPOUND	ANGLE	X=Cl	X=F
	90	RET	RET
	93-96	INV	INV
	105	INV	RACEMIC
R_3SiX	109	INV	INV

Anh and coworkers (1980)[162] have put forward an explanation for the observed effects:



If R1 and R2 are part of the strained ring system, angle * will become smaller while angle ** will become bigger. This means that the Si-X has more 's' orbital character and thereby increasing the favourable interaction between the reaction centre and the incoming nucleophile. Where the Si-X group is part of the strained system, the 's' character is decreased and thereby decreasing the overlap between the reaction centre and the nucleophile and inversion is favoured. This accounts for the increasing rate going from A to C below (Corriu 1980)[154]:



An extensive study has been carried out by Swain (1974)[165] who was looking at the hydrolysis of aryloxytriphenylsilanes in acetonitrile/water mixture. It was found that the reaction was second order with respect to $[OH^-]$ when the hydroxide ion concentration was low, while first order when the hydroxide concentration was high. The reaction may be specified by the following reaction:

$$OH^- + Ph_3SiOAr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ph_3Si(OH)(OR)]^- \overset{k_2}{\rightleftharpoons} \text{Products}$$

When $k_2[OH^-] << k_{-1}$ the reaction is second order in hydroxide ions. When $k_2 >> k_{-1}$, it is first order with respect to OH^-. The rate equation may be stated as follows:

$$k_{obs} = k_1k_2[OH^-]/ k_{-1}+k_2[OH^-]$$

In the case of methyltriphenylsilane is second order in $[OH^-]$ over the whole range. Eaborn (1975)[168] has suggested that this observation was due to acid impurities which reduced the concentration of OH^-. By the removal of the impurities Eaborn obtained first order kinetics. These results were consistent with the following:

1) Concerted S_N2 mechanism.

2) Involvement of a five coordinated intermediate.

Another area of research is the geometry of the intermediate and the transition state. A simple model for inversion involves a distorted TBP where both the entering group and the leaving group are both apical. In both cases they have a 3-centred 4-electron hypervalent bond. This has been confirmed by the Martin group (1985)[160], where x-ray diffraction has shown that the Si-O bond lengths are longer when compared to the tetra coordinated species.

The reactions of silicon are significantly different from carbon with respect to stereochemistry. In the latter case a similar reaction will always take place with inversion at a chiral centre. Early work by Corriu (1982)[162] have indicated that the degree of retention increases along the series: OCOR< Br< Cl< SR< F< OR< H

In his review, Corriu (1982)[162] looked at the factors which controlled the stereochemistry. They identified the following factors:

1) Stereochemistry and the nature of the leaving group.

2) The nature of the nucleophile.

With respect to (1), the following points may be made:

a) The Si-H reacts only with retention except when the reaction involves Ph_2CHLi or alcohols in the presence of Raney nickel. The latter involves a different mechanism from the former. The Si-H bond is postulated to be activated via absorption on to the surface, which results in a penta coordinated species.

b) Chloro and bromosilanes undergo mainly inversion.

c) Si-F and Si-SR undergo inversion or retention depending on the nucleophile.

d) Si-OR reacts mainly with retention except when charge delocalised ligands, such as benzyl, are involved.

Various bifunctional compounds of the form 1-NpRSi(X)(Y), where R=phenyl or ferrocenyl have been studied to look at the relative reactivity of X and Y. Some examples are shown in table 18:

TABLE 18 - STEREOCHEMICAL OUTCOMES FOR BIFUNCTIONAL COMPOUNDS

Substrate	**Reagent**	**Products**	**Stereochemical outcome**
1-NpPhSiClOMe	RLi/RMgX	1-NpPhSiROMe	INV
1-NpFcSi(F)Cl	RLi/RMgX	1-NpFcSiFR	INV
1-NpFcSi(H)F	Rli	1-NpFcSiHR	RN
1-NpFcSi(H)F	RMgX	1-NpFcSiHR	INV

From the above data, the following points may be made:

1) Hydrogen is the poorest leaving group.

2) Chlorine is the best leaving group.

3) When chlorine is considered, inversion occurs.

The data shows the relative ease of displacement as:

Cl>F>OR>H

The order of displacement is similar to the monofunctional compounds (Corriu, 1973)[167] Corriu also noted that the rate constant $k_F/k_{OMe} > 10^3$. An explanation provided for this effect was based on the Sommer classification (Sommer 1965 and 1973)[151/163] of leaving groups which in itself was based on the relative basicity of the leaving group. A good leaving group, such as Cl, has a pK_a less than 5 and this favours inversion of configuration. The poor leaving groups such as OR and H have pK_a's of the conjugate acids greater than 10. However, as pointed out by Corriu(1973)[167] the Si-SR bond cleavage should occur with retention. Experimental results, however, show both retention and inversion depending on the nucleophile.

An analysis involving the polarizability of the leaving group has been proposed. The highly polar Si-Cl and Si-SR bonds are always displaced with inversion as in the case of Si-F. The order of polarization and ability for inversion are:

Br> Cl >> F,SR >> OR

The difficulty in producing a relationship based on the physical properties of the leaving group, led Corriu (1978)[120] to produce the following sequence in terms of the ability of the Si-R bond to be cleaved, where R is in the order:

OTs, OCOR, Br, Cl > SR, F > OR, H

The above can be extended to acyclic organosilicon compounds and the dominant effect of the leaving group is not changed. Inversion is mainly observed when the Si-X bond is able to stretch under the influence of a leaving group.

The review by Corriu (1982)[162] also considers N.M.R. studies of apophilicity and the formation of penta co-ordinate species. It was found that the formation of penta coordinated species was not due to the electronegativity of the substituents but by the tendency of the Si-X bond to stretch.

As previously noted, the inversion/retention ratio is heavily influenced by the incoming nucleophile. The following points may be made:

1. Nucleophiles with localized negative charges react mainly with retention (e.g. BuLi). However, when good leaving groups are present, such as Cl and Br, inversion may well occur.

2. Where the negative charge is delocalised over an sp^2 carbon, such as in benzyl lithium, inversion will result, except where the poorest leaving groups are involved (e.g. hydrogen).

3. Where the counter ion changes as in the case when Mg^{2+} is substituted for Li^+, there is a significant shift towards inversion.

In addition the displacement at tetracoordinate silicon may be rationalized in terms of the Frontier-Orbital approximation. In this it is assumed that the major interaction during the interaction is the HOMO of the nucleophile and the LUMO of the σ^*_{Si-X}. A front side attack, results on an attack on the big lobe of the silicon and leads to retention. However, when this is an unfavourable interaction, an out of phase interaction between the nucleophile orbitals and the leaving group predominates Nucleophillic attack at the rear of the molecule (opposite to the Si-X bond) will result in inversion. It is possible to regard retention as a balance between in phase and out-of-phase interactions.

The shape of the σ^*_{Si-X} orbital is sensitive to the leaving group. An X group with a high electronegativity such as F increases the 's' character around the silicon. This results in a large lobe between the Si-X bond and hence retention is favoured. The influence of the nucleophile may be explained in a similar way. As Pearson (1970)[168] pointed out a hard reagent is usually small and has small contracted valence orbitals. This suggests that the unfavourable overlap with the leaving group will be small and hence a front side attack with retention will be favoured.

Soft nucleophiles are larger and hence have diffuse valence orbitals with a sizeable out-of-phase overlap and therefore inversion will result. The main features of this approach may be summarized as follows:

1. The major interaction between the nucleophile and the R_3Si-X occurs via the HOMO of the nucleophile and the LUMO of the R_3Si-X group the σ^*_{Si-X} orbital.

2. The shape of the σ^*_{Si-X} directs the stereochemical outcome. A group with high electronegativity increases the 's' character at the silicon. This means that a bigger lobe is between the Si-X group. Therefore increasing the electronegativity of the leaving group will favour retention.

3. There is a balance between in-phase and out-of-phase interaction between the nucleophile and the σ^*_{Si-X}.

Corriu (1987)[169] has further examined the mechanism of nucleophillic activation of silicon. The nucleophilic substitution of R_3SiX with Nu^- is considered to proceed by an addition-elimination process:

$$R_3SiX + Nu^- \xrightarrow{RDS} R_3SiNuX \xrightarrow{-X^-} R_2SiNu + X^-$$

The rate-determining step (RDS) involves the formation of the penta coordinated species. Early studies on SiF_5^- performed by Klanberg (1968)[170] have shown the equivalence of the fluorine atoms using ^{19}F N.M.R.. Janzen (1973)[171] has pointed out that the equivalence is due to pseudo rotation or hexa co-ordination.

There is no significant Si-F cleavage since the ^{29}Si-^{19}F couplings are always present. The work of Martin which compared phosphorus compounds with silicon and found that ΔG_{act} is similar or lower than the phosphorus compounds.

Corriu went on to examine Si-H, Si-C, Si-O and Si-Cl activation using F^-. He found that the presence of F^- resulted in the Si-H bond behaved like a silicon hydride and the addition to carbonyl groups took place. When F^- is added to allyl and benzyl silanes it results in the activation of Si-C bonds and this will allow the formation of C-C bonds when reacted with carbonyl groups. The activation of Si-O bonds by F^- results in the ability to undergo the Michael reaction. The Si-Cl activation can be achieved by using

DMF and DMSO. These reagents increase the rate of hydrolysis by a factor of a 1000. The rate law was found to be:

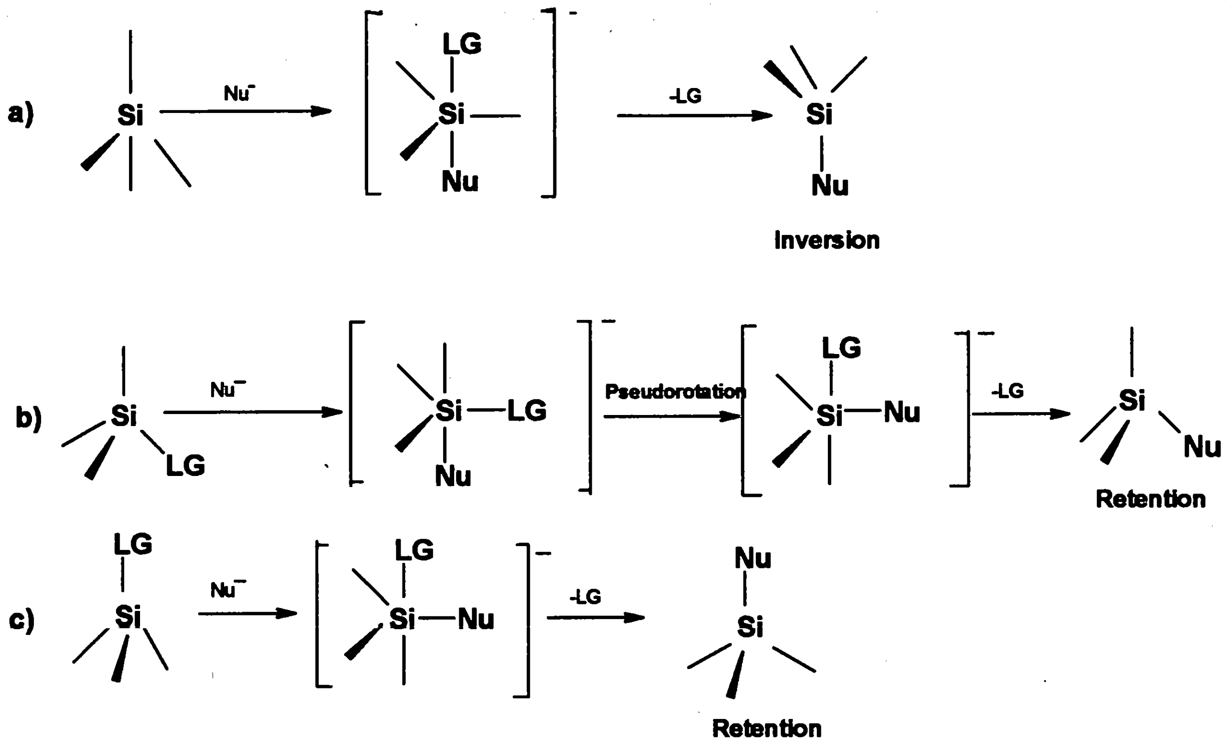
$$v = k[\text{HMPA}]_0 [R_3\text{SiCl}][H_2O]$$

The reaction was also found to be controlled by the entropy of activation, which was found to be in the range -50 to -70 entropy units. However, the enthalpy of activation was found to be low. The effect of this is that the rate of reaction increases when the temperature decreases. When the activation agent (HMPA, DMF and DMSO) is not present, inversion occurs but retention occurs in the presence of an activating agent. In effect the activation has been achieved by what has been termed nucleophilic activation.

A major review of nucleophilic activation has been produced by Holmes (1990)[172] The review deals with both experimental and theoretical aspects. In the experimental part of the review it was noted that the evidence for the following leaving group sequence:.

INV Cl, Br, OAc > F, SR > OMe, H RET

The intermolecular S_N2 reactions are also considered in both silicon and phosphorus. The entering group and leaving group leave via the apical position, which is in line with the Westheimer mechanism. The basic mechanism of nucleophilic substitution is shown below:



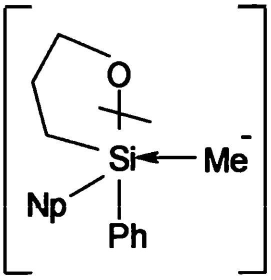
Mechanism of nucleophilic attack:

a) Inversion

b) Retention with axial attack and pseudorotation to give axial departure.

c) Retention involving equatorial attack and axial departure

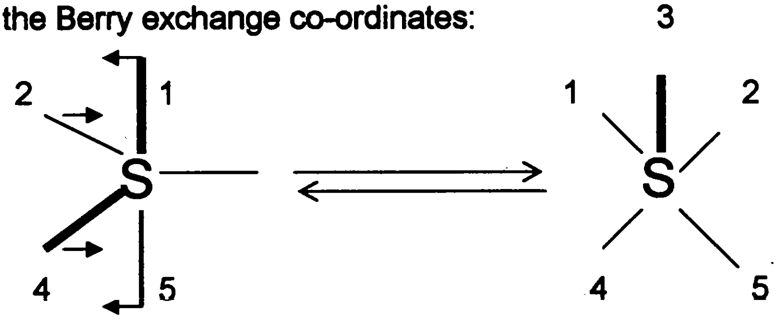
The intermediates are a result of a facial attack on the tetra co-ordinated silicon. Where retention has taken place, pseudorotation must have taken place. Holmes also considered the structure and reactivity of various activated states. For example the Si-O bond in:



Retention

would require pseudorotation in order for the leaving group to be in the apical position. The above intermediate may be kinetically facile if the Np group sterically blocks the approach of the nucleophile opposite to the endocyclic groups. Pseudorotation would allow the Si-O bond to take up the apical position. Corriu (1986)[161] has suggested that the high rate of hydrolysis and inversion of Si-O bonds are attributable to the symmetry of the intermediate which give rise to one Si-O bond being replaced by another.

As part of the review by Holmes (1990)[172], mention was given to the structural characterization of the 5-coordinated species which provided useful information about the structural preference of the activated state. Noting that the structure of 5-co-ordinated species run from TBP to SP. A useful analysis was provided by the use of the trans basal angle of the RP which are axial and equatorial angles with reference to the TBP structure d_{24}. The latter angle is the dihedral angle formed between the normals to the TBP face 123 and 245, which have a common edge 24 and are directly associated with the Berry exchange co-ordinates:



The dihedral angle is 53.1° in TBP and 0° in the forming SP due to the disappearance of edge 24.

Apophilicity is defined as the change in energy when an apical substituent changes position with an equatorial position in a TBP structure. Thus the energy difference is a measure of the degree to which a substituent prefers a given position. The apicophilicity depends on a number of factors:

1) Electronegativity of the substituent.

2) Inductive effects operating.

3) Electronegativity of the substituent.

4) Π bonding effects.

At this point it is worth considering the relationship between apophilicity and nucleophilic substitution.

Corriu and co-workers (1986)[161] have examined the stereochemical behaviour during nucleophilic substitution. The work indicates that retention/inversion of configuration is controlled by frontier orbitals. The stereochemical outcome also depends on the nature of the nucleophile. Subtle changes in the nucleophile can have profound changes on the outcome of a reaction. Some data is shown in the Table 19:

TABLE 19 - REACTION OUTCOMES FOR NUCLEOPHILIC SUBSTITUTION

Substrate	Reagents	Products	Steriochemical outcomes
1-NpPhSiClOMe	RLi/RMgX	1-NpPhSiROMe	INVERSION
1-NpFcSi(F)Cl	RLi/RMgX	1-NpFcSi(F)R	INVERSION
1-NpFcSi(H)F	RLi	1-NpFcSi(H)R	RETENTION
1-NpFcSi(H)F	RMgX	1-NpFcSi(H)R	INVERSION

Corriu attempted to rationalise the results by considering an extension of the frontier orbital approach derived from carbon chemistry. In this approach, the $S_N2(Si)$ reaction the σ^* of the Si-X constitutes the LUMO. The HOMO constitutes the highest occupied molecular orbital of the nucleophile. The σ^* is associated with the big lobe located in side the Si-X bond. This means that a favourable attack would take place via the front side which will involve retention of configuration. Where the repulsion between the leaving group and the incoming nucleophile predominates and hence inversion predominates.

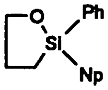
Another factor, which is significant, is the delocalisation of the charge, the out of the plane overlap increases and hence inversion becomes a more favourable process. This essentially means that any process, which effects these parameters, will affect the stereochemical outcome of a reaction. When the nucleophile does not contain oxygen, such as $LiAlH_4$ and RLi, the stereochemistry is predominantly retention as is often expected for Si-O.

The rate of reaction increases when the five membered rings are reacted with methanol but not when nucleophiles such as RLi are used. This suggests that the increase in the rate when using five membered rings is due to the symmetry of the intermediate. This is particularly apparent when oxygen replaces oxygen at the silicon. Westheimer (1980)[161a] has shown that compounds which contain Si-S hydrolyze much faster than compounds containing Si-O bonds. However, when in the form of a five membered ring, Si-O hydrolyses 10^2 times faster than the Si-S bond. Some results are shown in Table 20 on page 117.

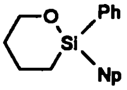
TABLE 20 - KINETICS OF THE HYDROLYSIS OF Si-O AND Si-S COMPOUNDS

Nucleophile	Compound A	Compound B	$t_{1/2}(A)/t_{1/2}(B)$
H_2O	60	3×10^5	5×10^3
MeOH	30	5×10^5	1.6×10^4
MeLi	180	600	3.3
MeMgBr	120	300	2.5

Compound A=

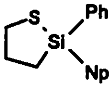


Compound B=

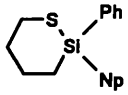


Nucleophile	Compound C	Compound D	$t_{1/2}(C)/t_{1/2}(D)$
MeOH	3×10^{10}	1×10^5	33

Compound C=



Compound D=



The Bassindale group (1995)[173] have carried out a detailed study on the ΔH and ΔS activation for the racemization of $PhCHMeSiMe_2X$, where X= Cl or Br. The data was analyzed by the Eyring equation:

$$k = BT/h\exp - \Delta H/RT + \Delta S/R$$

where ΔH = enthalpy of activation, R = Gas constant and ΔS = entropy of activation.

A plot of $Log_e(k/T)$ v $1/T$ gives a straight line of intercepts of $Log_e(B/T) + \Delta S/R$.

The value of ΔH, from the gradient, was found to be approximately 45kJ/mol. The entropy of activation was found to be in the range of -15 to -50J/kmol.

This data was consistent with the nucleophile displacing the halide ion in the first step and the rate determining step is the attack by the halide ion on the halosilane. When the experiments were repeated using $PhCHMeSiMe_2X$ in the presence of hexamethylphosphamide(HMPA) a curved plot was observed. This suggests two competing mechanisms. At low temperatures the halide/halosilane mechanism predominated. However, at high temperature, a double displacement mechanism is dominant. The rate determining step in this case was the attack of the nucleophile on $PhCHMeSiMe_2(HMPA)^+$. The thermodynamic parameters for the latter were found to be:

$$\Delta H = 0\text{kJ/mol and } \Delta S = -180\text{J/kmol}$$

However, the data does not allow for a distinction between nucleophilic activation at a hypercoordinated silicon or that of a tetra co-ordinate silicon.

3.3 NUCLEOPHILIC SUBSTITUTION OF HYPERVALENT ORGANOSILICON

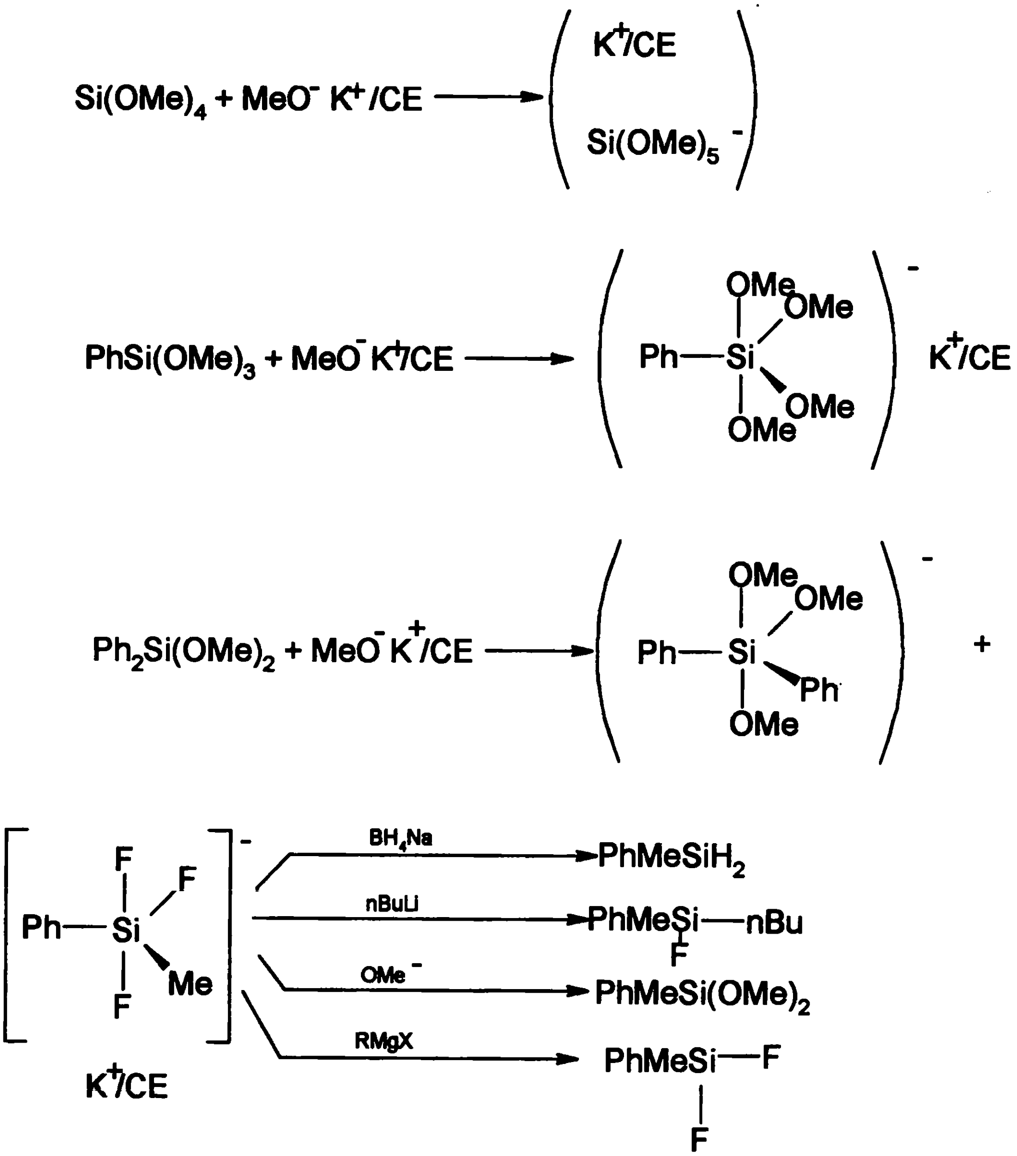
As pointed out by Corriu (1982)[162], it is difficult to understand why an acceleration should take place at a crowded and less electrophilic silicon. Corriu (1988)[174] has studied the 18-crown-6-potassium salts of $PhF_3CH_3Si^-$, $F_2(CH_3)_2PhSi^-$, $F_2Ph_3Si^-$ and $(MeO)_2Ph_3Si^-$ with various strong nucleophiles such as RLi. RMgX, H^- and RO^-. These were compared to the rate of reaction of the tetra co-ordinate species (Table 16). A comparison was also made between the reactivity of tetra coordinated compounds containing Si-H bonds and the penta coordinated species. It was found that R_2SiH_2 does not react with R-OH, RCOOH or carbonyl groups. However, the pentavalent species reacts readily with the above.

TABLE 21 - COMPARISON OF THE RATES OF REACTION

Compound	**Reagent**	**$t_{½}$ (minutes)**
$PhMeSiF_3^-$	PrMgBr	<5
$PhMeSiF_2$	PrMgBr	800
$Ph_3SiF_2^-$	PrMgBr	32
Ph_3SiF	PrMgBr	300

The above data is consistent with the results obtained by Boudin (1986)[175] and Corriu (1986)[176].

The penta co-ordinate compounds were also found to react with the sterically hindered t-BuMgBr within ten minutes. Other reactions are summarized below:



R= Pr or Bu

Further evidence for the enhanced reactivity of hypervalent compounds was obtained by Corriu (1991)[177]. They studied the hydrolysis and methanolysis reaction of $Si(OR)_3X/KOR$ (X=H or OR), $K[Si(OR)_4X]$ (X=H) and [K,18-crown-6]$[XSi(OR)_4]$ (X=OR) and observed the following:

1) Formation of intermediates via nucleophilic activation of silicon

2) The rate-determining step is the co-ordination of ROH to the penta co-ordinate intermediate.

3) When $K[H_2Si(OR)_3)]$ and $K[HSi(OR)_4]$ are subjected to stepwise nucleophilic substitution, using OR^-, penta coordinated $K[HSi(OR)_4]$ and [K,18-crown-6]$[Si(OR)_5]$ are produced.

The reaction between $K[HSi(OR)_4]$ and ROH, confirms the enhanced reactivities found by the Corriu group (1989)[178]. The obtaining of a new penta coordinated species from the above reaction is also confirms that the mechanism occurs via an intermediate as originally proposed by Corriu and co-workers (1978)[153].

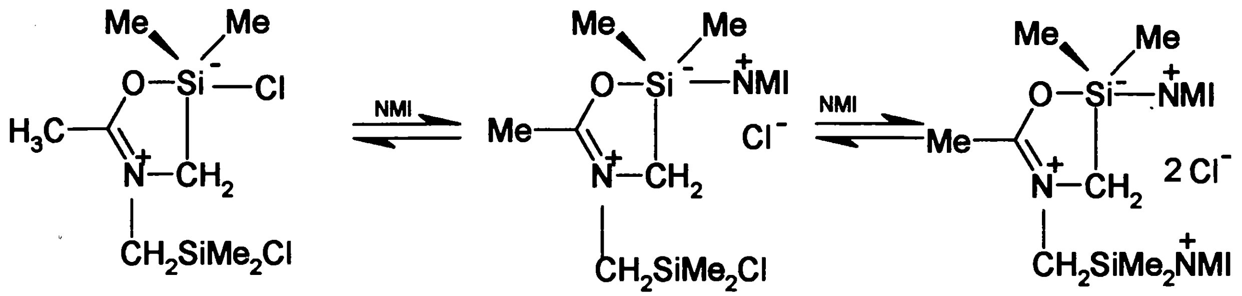
A very significant study was carried out by the Bassindale group (1993)[179], on N,N-bis(chlorodimethylsilylmethyl)acetamide as a dynamic probe for the effects of co-ordination on reactivity. This is useful because it contains two silicon atoms in different chemical environments. This allows the investigation into the reactivity of the two types of silicon under identical conditions. The relative reactivities were examined using ^{29}Si N.M.R.. The N.M.R. was recorded for the reaction between the chloro derivatives and

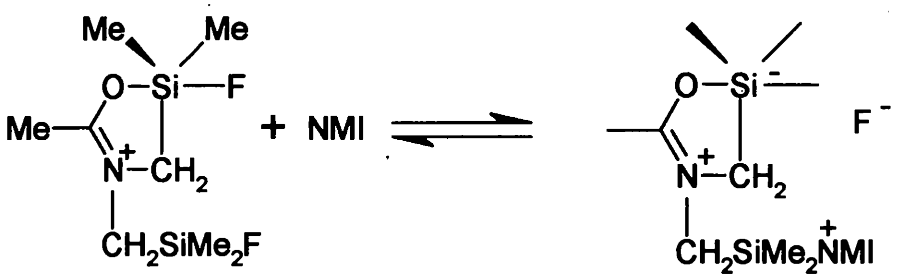
N-methylimidazole(NMI). The effects of the NMI on the ^{29}Si N.M.R. are shown in Table 22:

TABLE 22 - EFFECTS Of NMI ON ^{29}Si N.M.R. RESONANCES

Concentration of NMI (mol/dm^3)	^{29}Si (tetra)	^{29}Si(penta)
0	26.8	-39
0.5	26.8	-39
1	26.8	-54
2	18.4	-54

The data may be presented by the following scheme:





The results are significant in that they do confirm the proposition that penta coordinate species are more reactive than the tetra coordinate species.

However, the fluoro derivative showed a different reactivity. In this case it would appear that the N-methylimidazole (NMI) attacked the tetra coordinate species first. This suggests that in this case the tetra coordinate species is more reactive than the penta co-ordinate species.

The last result may be explained in terms of the proposal made by Gordon and co-workers (1989)[180]. They have suggested that coordination of two axial ligands in a five co-ordinate species share electron density. The strongest hypervalent bonds are those which are formed by atoms from the same period. In complexes where the atoms are from different co-ordinating groups, then the stronger bonds will be formed by the atom from the higher period, and this will repel ligands such that something akin to an anion dipole complex results. This has the effect of activating the Cl and Br to attack nucleophiles such as NMI and F$^-$. The data in these papers again provides evidence for the enhanced reactivity of hypervalent silicon.

Using the limited examples shown in Table 2, it can be seen that the hypervalent species react more rapidly. Two reasons were advanced by the Voronkov group (1986)[13]:

1) Increase in the bond lengths, and hence weakening, on increasing co-ordination.

2) Increasing the electrophilicity of the silicon atom.

3.4 - THEORETICAL STUDIES

Much of the work in this area has been done involves ab-initio calculations.

An early study carried out by Baybutt (1975)[129] who used ab-initio calculations to consider the nucleophillic attack of H$^-$ and F$^-$ upon silanes and fluorosilanes. A particular emphasis was the determination of the reaction barrier and the polarization function contributed to this. A comparison was made with carbon. This showed that the silicon intermediates are of lower energy than carbon. In addition, it was also found that there were only limited changes in the bond lengths compared to carbon. In the discussion, Baybutt, considered the difference between the activation energy and the barrier height. The former is a quantity determined by the Arrhenius equation, while the latter is the energy difference between the reactants and the lowest pass (saddle point) across the potential energy surface to the products. In general there is no equality between the two quantities. This paper examined the possibility of the penta coordination and the involvement of d orbitals in the transition state.

Nucleophillic substitution at silicon was found to be significantly different from that of carbon. The barrier for CH_4 + H^- and H^- + SiH_4 were calculated and found to be 61.2kcal/mol and 18.6kcal/mol respectively. The main drawback of these calculations is that they are not as exact as the current computer systems allow. For example the calculations apply to in-vacuo rather than in solution, and neglect the relativistic contribution to the molecular energy.

All these results do indicate that reactivity has more to do with the lability of the ligands than an increase in the positive charge on the silicon.

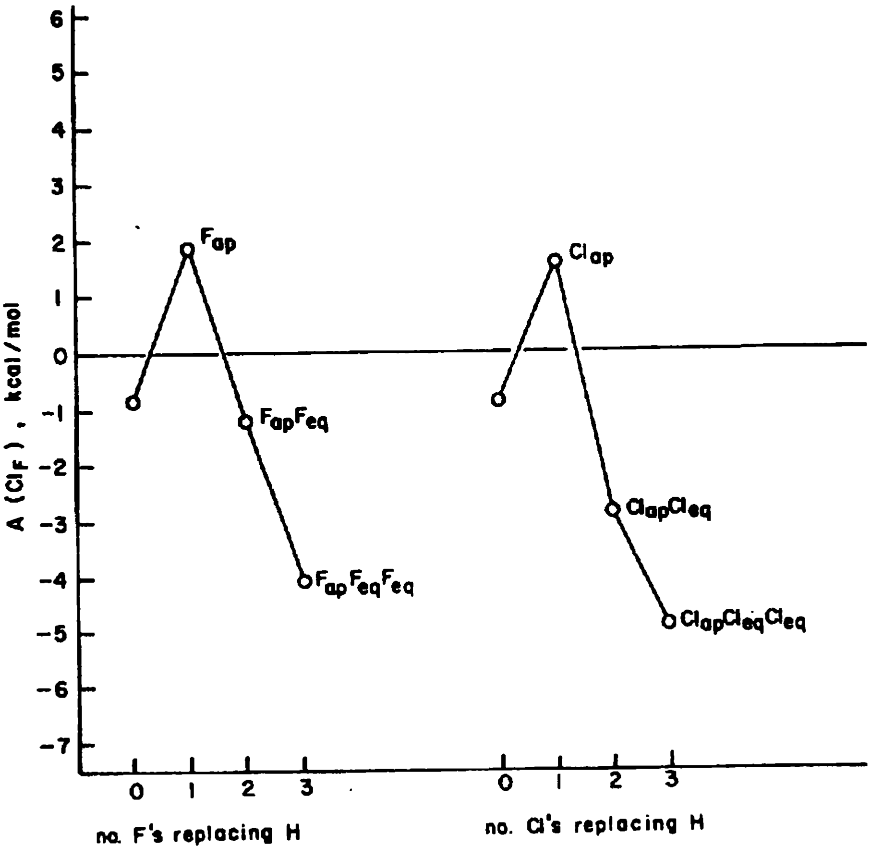
The Holmes group (1987)[181] have used molecular quantum mechanical calculations to determine the minimum strain energy and conformational energy. This approach is designed to model the inversion and retention of configuration during nucleophilic substitution. The relative energies of the pathways were compared for fluorine and chlorine. It was shown that the attacking nucleophile prefers an axial entry. The retention pathway occurs via a pseudorotation which is of lower energy than via axial attack. In addition, the calculations show that chlorine is a better leaving group and prefers retention over inversion. In the case of fluorine, the energies involved in inversion and retention are nearly equal. This is in agreement with experimental evidence.

Holmes (1988)[182], has carried out a theoretical study using *ab-initio* molecular orbital calculations with respect to penta coordinated species of silicon and phosphorus. These calculations were used to establish the apicophilicities of some TBP molecules composed of combinations of ligands (H, Cl and F). The method of calculation involved SCF Gaussian 82. It was found that Cl is more apophilic than F or H except when the sum of the electronegativities of the apical atoms increases sufficiently.

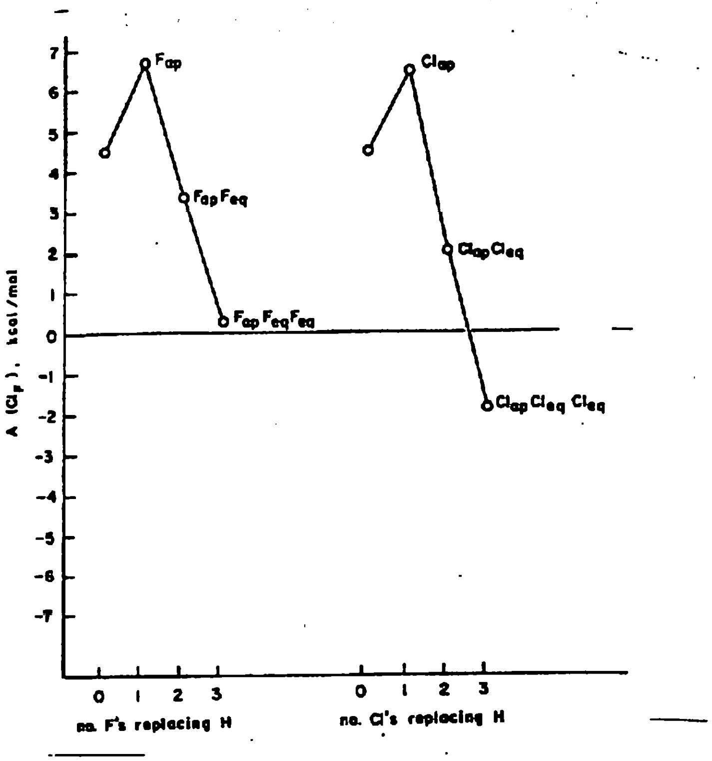
The apicophilicity of fluorine relative to hydrogen is lowest when hydrogen occupies the opposite apical position and the equatorial positions have chlorine atoms. The chlorine was found to be the highest when opposite an apical chlorine. The replacement of hydrogen in an apical position raises the apophilicity in the opposite apical position. The introduction of a chlorine or fluorine atom in place of a hydrogen atom in the apical position raises the apicophilicity of the atom in the opposite apical position. However, the only exception observed was the replacements of an apical hydrogen atom by a fluorine atom, when all the equatorial positions were filled with H. In general, the calculations established that the effectiveness of an apical atom increases in the order:

$$H < F < Cl$$

A plot of apicophilicity of Cl relative to F is shown below for Si and P:



Effect of halogensubstitution on apicophilicity of Cl relative to F in $SiH_3Cl_{ap}F_{eq}$]



Effect of halogen substitution on apicophilicity of Cl to F in $[SiH_3Cl_{ap}F_{eq}]^-$

The presence of a positive value indicates that Cl>F, but negative values suggest that F>Cl. The diagram shows a crossover point, except in the case of SiH_nClF_{4-n} where Cl>F even when H=0 as for example in $SiClF_4^-$. In silicon molecules, which contain highly electronegative groups, the reverse occurs that is, F>Cl. As the equatorial F is replaced by H a crossover point occurs where Cl>F.

The reason for these results may be rationalized by considering ligand charge (q). A decrease in apicophilicity is correlated with a decrease in the difference between the q_{eq}- q_{ap}. The difference appears to become smaller as the sum of the equatorial charges approaches the sum of the apical charges. With silicon, fluorine equatorial substitution does not affect the apical charge distribution as much as chlorine equatorial substitution.

Ab-initio calculations are able to give meaningful relative energies of substituted organosilicon compounds. Holmes (1990)[172] work in this area gives the order which is predicted by Corriu (1980)[154]. In addition the review considers the reactivity of the penta coordinated species which have been shown experimentally to be more reactive than the tetra coordinated species. Noting the work of Corriu (1988)[174] that species such as $PhMeSiF_3^-$ are more reactive than $PhMeSiF_2$ toward RMgBr and this is found to be examples of a general case. Corriu and co-workers (1988)[174] have suggested that the enhanced reactivity is due to the greater electropositive character of the silicon atom in such species.

The stereochemical aspects of nucleophilic substitution has been reviewed by Holmes (1990)[172]. Molecular orbital calculations carried out by Holmes (1990)[172] have compared the charge on the silicon and the bond length in compounds such as SiH_nF_{4-n} and $SiH_nF_{5-n}^-$ and the isoelectronic phosphorus compounds. It was shown that the bond lengths of the penta coordinated species are longer than in the tetra coordinated species and are particularly so at the axial positions. With respect to the charge on the silicon, the calculations indicate that the presence of the additional fluoride ion results in a slight increase in positive charge on the silicon atom of about 0.1 of an electron. In addition the bond overlap population for the penta coordinated silicon are less which is indicative of a significant weakening of the Si-F and Si-H bonds.

The result of this study is that the enhanced reactivity of the penta-coordinated species is due to having more loosely held ligands and in particular the apical ligands of the TBP species. This was further confirmed by considering the amount of energy required to remove a fluoride ion from a tetra coordinated species which was found to be much higher than the penta coordinated species in a similar series of compounds.

The results obtained by Holmes above confirm the results obtained by the Streitwieser group (1989)[182a] who looked at the SiH_4-SiH_4F^- system. There work produced geometries similar to Holmes (1987)[181], and the results in terms of charge on the silicon obtained by Streitwieser were 2.6 in the case of SiH_4 and 2.74 in the case of SiH_4F^-. However, the calculations were carried out on the basis of an ionic model.

A major study has been carried out on gas phase penta co-ordinate silicon species by Damrauer (1988)[183]. Several earlier studies have also been carried out by Dillard (1974)[184] and McNeil (1970)[185]. In this study, Damrauer (1988)[180], has used MNDO calculations to make predictions and flowing afterglow technique to detect gas phase pentacoordinate species. Damrauer (1987)[186] has reviewed the flowing afterglow technique.

Computational studies of silicates have shown that the penta coordinated species have a lower energy than either the reactants (Deiters 1987a+b)[187/188]. However it should be noted that the penta coordinated species may not be more stable than alternative species. Hajdasz (1986)[189] has discussed this with particular reference to SiH_5^- which is more stable than SiH_4 and H^- but not as stable as SiH_3^- and H_2.

The work of Damrauer looks in detail at the following:

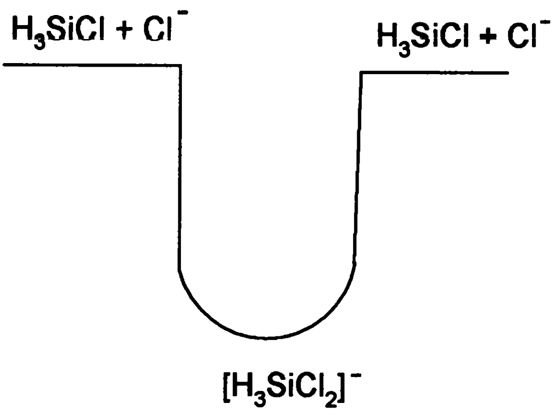
1) Energetics of the formation of silicates.

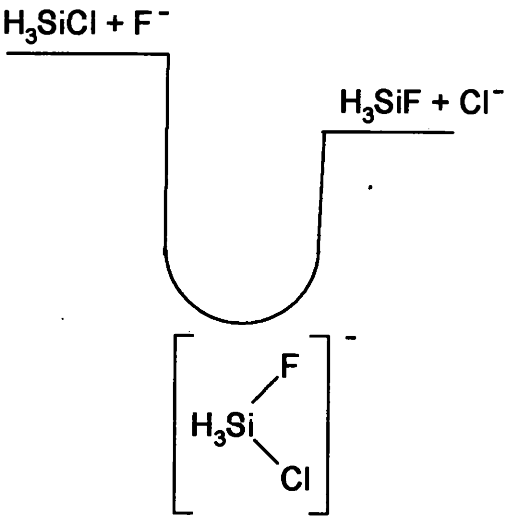
2) Computing examples, which can be experimentally verified.

3) Comparison of MNDP with *ab-initio* consistency.

The key point is that the propositions put forward by workers such as Corriu are based on kinetic data but those of Damrauer are based on thermodynamic data.

The computational studies confirm the Corriu order of ease of penta coordination and nucleophilic substitution. Various reaction profiles have been generated and an example is shown below:





The calculation indicates that the formation of silicates also control the ease of nucleophilic substitution. These are also consistent with the results of the fast afterglow technique on trimethylchlorosilane undergoing nucleophilic substitution which have shown that substitution takes place via a penta coordinated species (Damrauer 1983)[190]. However, MNDO calculations can seriously underestimate the stability of certain compounds such as H_3SiFX^- where X is OH, CH_3, and CH_3O-.

An interesting part of the study was a comparison between the ease of silicate formation compared to Si-X bond dissociation energy. For example, if the Si-X bond is strong and it would be reasonable to expect that the Si-F bond in silicates would be strong (Walsh 1981)[191]. However, the study indicates that this is only partly true and it also depends on the nature of Y.

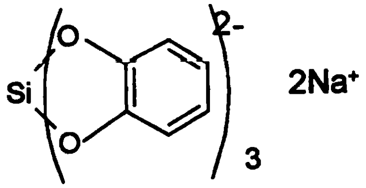
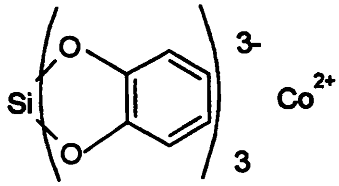
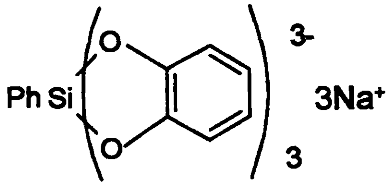
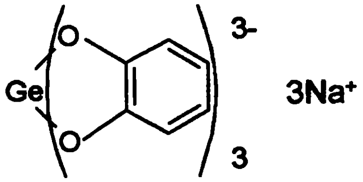
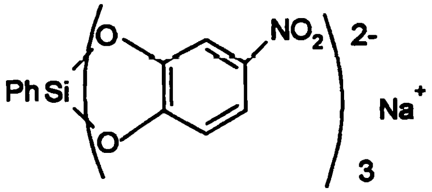
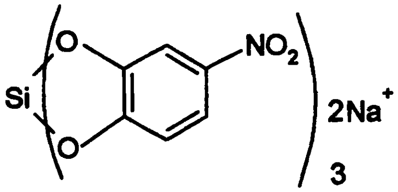
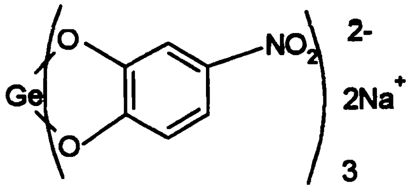
The usefulness of these calculations were tested by the preparation of $[Si(CH_3)_3N(CH_3)_2Cl]^-$ by the soft transfer of Cl^- from $Si(CH_3)_4Cl^-$ to $Si(CH_3)N(CH_3)_2$ in the fast after flow technique. The calculations indicate that the product of the soft transfer, $[Si(CH_3)_3N(CH_3)_2Cl]^-$, would be exothermic to a value of about 4.2 kJ/mol. A very weak signal was observed indication the formation of this product. This means that the calculations do have some utility in predicting the outcome of quite complex reactions. In general, where the MNDO calculations failed to agree with experimental results (i.e. the Corriu order), then *ab-initio* results gave a much better match to experimental results.

Streitwieser and co-workers (1989)[182a] have also made some useful comparisons with carbon. SiH_5^- has been observed in the gas phase by Hajdasz(1986)[189] and it has been found to be an effective hydride donor. Further, calculations carried out by Brandemark and co-workers(1984)[192] indicates that SiH_5^- is more stable than SiH_4 and H^-. Streitwieser (1989)[189] points out that the increase in bond length in silicon in terms of the Si-H and Si-F bonds of the penta coordinated species compared to the tetra coordinated species is less than 10%. However, in the case of carbon, the work of the Keil group (1976)[193] suggests that the value to be 35% and 75% respectively. This makes penta co-ordination in carbon very unfavourable.

Corriu (1989)[194] has reported the unexpected reactivity of hypervalent anionic organosilicon and germanium compounds with respect to single electron transfer. In the presence of some nucleophiles, compounds such as $[RSi(o\text{-}O_2C_6H_3R')_2]^-M^+$ and $[Ge(o\text{-}C_6H_3R)_3]^{2-}2M^+$ where R=H, undergo a single electron transfer. The ability to accept electrons depends on the ligands, the central metal atom and the nature of the nucleophile. The above compounds may be prepared by the depolymerization of silica and GeO_2 (Rosenheim group, 1931)[60]:

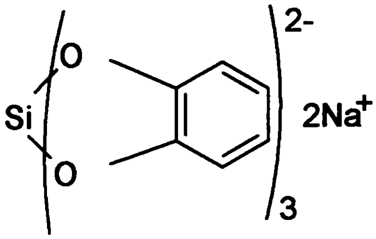
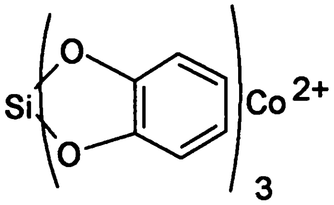
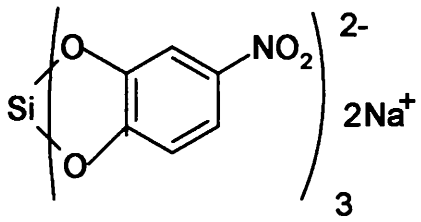
The reactions of some of these compounds are shown in Table 24 on page 134.

TABLE 24- SELECTED REACTIONS

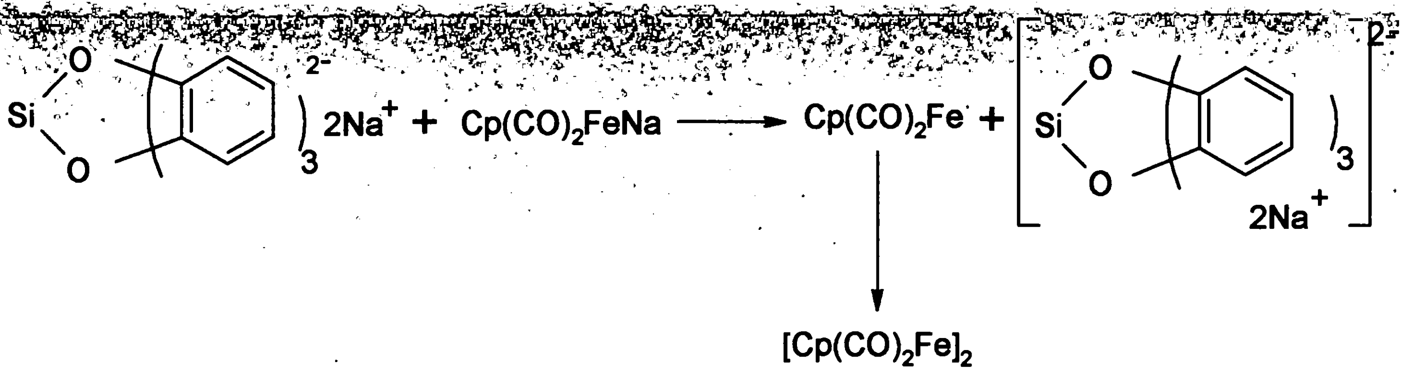
COMPLEX	Cp(CO)$_2$FeNa eq. consumed	[Cp(CO)$_2$Fe]$_2$ eq. formed	Li eq. consumed
	2	1	1
	4	2	6.6
	1	0.5	
	2	1	6
	6 (4)	3 (2)	
	9 (6)	4.5 (3)	9
	6 (3)	3 (1.5)	6

The fact that single electron transfer has occurred was shown by the reaction of the above compounds with Li/Me3SiCl/the towards compounds 1, 2 and 3 in Table 5. However, the products of the reaction have not been fully characterized. However, some details of the reaction are shown in Table 25.

TABLE 25 - SELECTED REACTIONS OF ORGANOSILICON COMPOUNDS

			
RMgX	Substitution R_3Si, R_4Si	Substitution + Electron Transfer Reaction	No substitution Side reaction on Nitro Group
Cp(CO)$_2$Fe$^-$	Electron Transfer Reaction	Electron Transfer Reaction	Electron Transfer Reaction
i/Me$_3$SiCl/THF	Electron Transfer	Electron transfer	Electron transfer

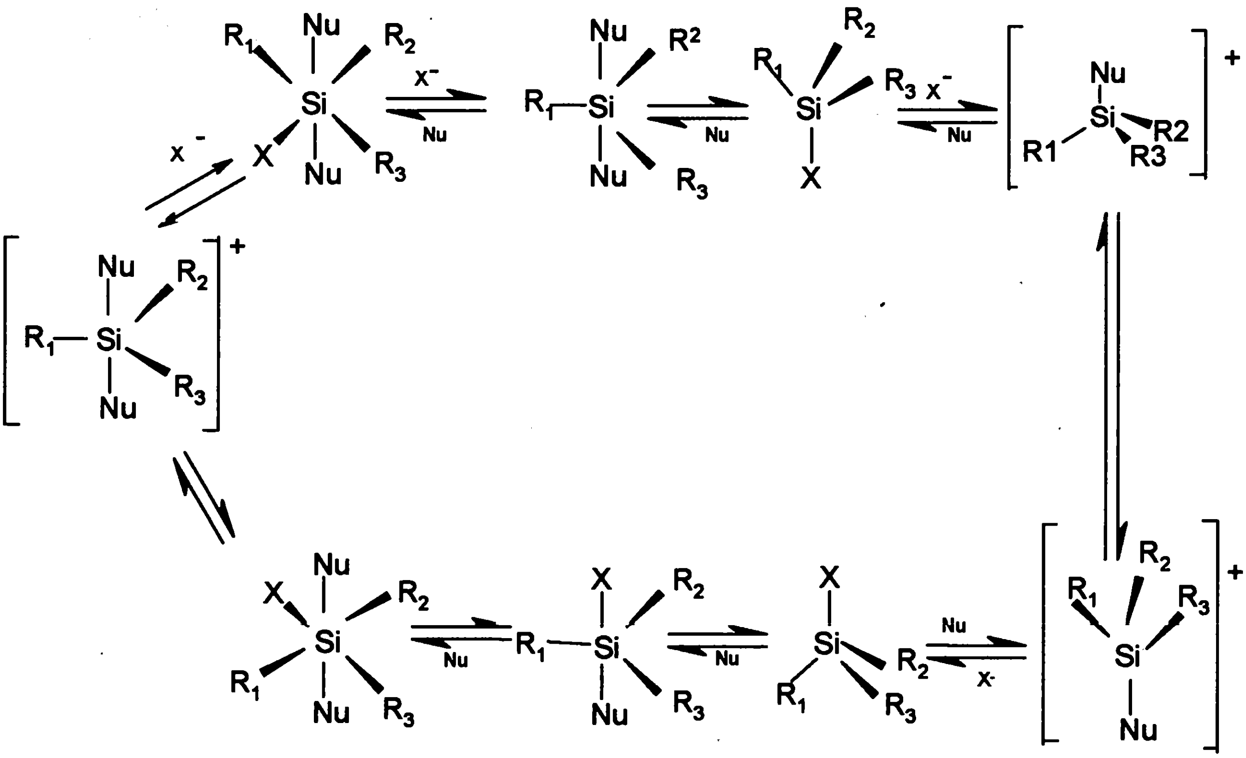
An example of one of the reactions is shown below between $[Si(O_2C_6H_4)_3]^{2-}$ and $CpFe(CO)_2Na$:



The reaction between nitro substituted phenyl rings show some enhancement in electron accepting properties of the complexes.

Corriu (1993)[195] has produced a major review of the reactivity and synthesis of hypervalent organosilicon compounds. He provides evidence for the involvement of penta-coordinate species in the nucleophilic substitution of tetra coordinate organosilicon compounds. However, when considering hexa coordinate species this area is relatively under developed and although nucleophilic substitution via a hepta coordinate intermediate has been suggested by Pearson and co-workers (1962)[196] , the evidence has been contradictory. For example, Pearson found that the hydrolysis tris(acetylacetonato)silicon cation was consistent with an S_n2 mechanism. However, Wright (1965a+b)[197/8] found that the attack of hydroxide ions on the tris(tropolonatosilicon) cation was more consistent with an attack on the ligand. It is of great importance that hepta coordinate species are synthesized and single crystal X-ray diffraction data obtained. To this end Corriu (1994)[199] has obtained such data. However, as the evidence is sparse on this mechanism we cannot rule out the generality of other mechanisms such as electron transfer.

Not all silicon reactions take place via a hypervalent intermediate. Bassindale and co-workers (1995)[173] have carried out a series of nucleophile induced racemization of $PhMeCHSiMe_2X$, where X = triflate, Br or Cl. Thirteen nucleophiles were involved and



the data produced could be interpreted in two ways, which are shown in the scheme below:

The rate of reaction with respect to the added nucleophile varies between 1st and 2nd order when using strong nucleophiles in polar solvents. On occasions, high orders were found using non-polar solvents. The latter may be due to the aggregation of the nucleophile. An important point is that the reactions involved good leaving groups and strong nucleophiles and there was no evidence of the involvement of hypercoordinated silicon other than as a transition state.

3.4 - CONCLUSION

The results of the above strongly indicate that there is an increase in reactivity in hypervalent compounds of silicon. This has been shown particularly strongly by the work of the Bassindale group on compounds containing two silicon atoms in different co-ordination environments within the same molecule. The reasons for this increased reactivity may be stated as follows:

1) Weakening of the silicon-ligand bond, which more than compensates for the increased steric crowding.

2) The contribution of the increased positive charge on the silicon atom in such compounds.

In addition the fact that an increase in reactivity of elements from other groups has been observed to some extent leads to conclusion that this is not just limited to silicon.

REFERENCES

1) Davy H, *J.Philos. Trans* 1812 2 352
Liebigs Ann. Chem. 1813 86 178

2) Gay-Lussac, J *Memories de Physique et Chemie de la Societe d'Arceuil,* 1809 2 307

3) Ghosh P, Shabat D and Kumar S, *Nature* 1996 282 339

3a) Tacke R,. and Pfrommer B, *Eur. J. Inorg. Chem.* 1998 415

3) Corriu R, Chevalier P, Delord P, Moreau J, Wong Chi Man,
New Chem. Journal 1998 22 423

4a) Akiba K, Yamamoto Y., Toyota Y and Wakisaka Y,
Heteroatom Chemistry 2000 11 42

5) Kudo H, *Nature* 1992 355 432

6) Williams E, in *Chemistry of Organic Silicon Compounds* Edt. S. Patai and Z. Rappoport Pub. John Wiley 1989

7) Lande A, Jakobsen H and Kimber B, *J. Am. Chem. Soc.* 1975 97 3219

8) Murphy P, Taki T, Sogabe T, Metzler R and Squires T,
J. Am. Chem. Soc. 1979 101 4055

9) Morris G. A. and Freeman R, *J. Am. Chem. Soc.* 1979 101 760

10) Jutzi P, Kanne D and Kruger C, *Angew. Chem.* 1986 98 193

11) Corriu R, Chuit C, Reyne C and Young C, *Chem. Reviews* 1993 93 1371

11a) Cella J A, Cargioli J D and Williams E, *J. Organometallic Chem* 1980 186 13

11b) Bassindale A R and Stout T J, *Chem. Soc. Chem. Comm.* 1984 1387

12) Lukevics E, Pudova O, and Sturkovich R, *Molecular Structure or Organosilicon Compounds* Pub. Ellis Harwood 1989

13) Voronkov M G, Alekseev N V, Tandura S N,
Top. Curr. Chem 1986 131 99

14) Kutzelnigg W, *Angew. Chem. Int Ed Engl* 1984 23 272

15) Rundle R, *J. Am. Chem. Soc* 1963 85 112
16) Musher J, *J. Angew. Chem. Int Edt.Engl.* 1969 8 54

17) Reed A. and Weinhold F, *J Am. Chem. Soc.* 1986 108 358

18) Gutman V, *Co-ordination Chemistry Review* 1975 15 207
Co-ordination Chemistry Review 1976 18 225

The Donor Acceptor Approach in Molecular Interactions Pub Plenum 1978

19) Adley A, Bird P, Fraser A. and Onyschuk M, *Inorg. Chem.* 1972 11 1402

20) Collins J, Schleyer P, Krogh-Jespersen M, Chandrasekhar J, and Wurthwein E, J. *Am. Chem. Soc.* 1980 102 2263

20a) Rottger D and Erker G, *Angew. Chem. Int. Ed. Engl.* 1997 36 812

21) Fransto da Silva, *J Chem Ed.* 1983 60 390

22) Bell F, *Metal Chelation Principles and Applications*
Pub Oxford Chemistry Series 1977

23) Lehn J M and Sauvage J, *J. Am. Chem. Soc.* 1975 97 6700

24) Sheldrick W, Chapter 3 in *Chemistry of Organic Silicon Compounds.* Edt Patai S and Rappaport. Pub John Wiley Ltd 1989

25) Holmes R and Deiters J, *J. Am. Chem. Soc.* 1977 99 3318

26) Voronokov M, Baryshok V, Pestunovich V, Bleidelis Ya, Klemme A, *Akad. Nauk. SSSR* 1978 243 688

27) Schomburg D, *Habilitationsschrift Braunschweig* 1985

28) Corriu R. and Young C, in *The Chemistry of Organic Silicon Compounds* Ed. Patai S and Rappoport Z 1989

29) Holmes R, *Progress in Inorganic Chemistry* 1984 32 119

30) Holmes R, Day R, Harland J, Holmes J and Sau A
Organometallics 1984 3 341

31) Holmes R, Day R, and Harland J., *Organometallic* 1984 3 347

32) Corriu R, Breliere C, Carre F, Poirier M and Royo G, *Organometallics* 1986 5 388

33) Royo G, Breliere C, Carre F, Corriu R, Kpoton A, Poirier M, Young J and Boyer J. J. Chem. Soc. Dalton Trans. 1989 43

34) Mislow K. Acc. Chem. Res. 1970 3 321

35) Stevenson W, Wilson S, Martin J and Farnham W. J. Am. Chem. Soc. 1985 107 6340

36) Onan K, McPhail A, Yoder Y,Hillyard R. J. Chem. Soc. Chem. Comm. 1978 209

37) Klebe G, Bats J. and Hensen K, *J. Chem. Soc. Dalton Trans.* 1985 1
Klebe G, *J. Organomet. Chem.* 1985 293 147

38) Britton D, Dunitz J, *J. Am. Chem. Soc.* 1981 103 2971

39) Voronokov M, *J. Organometallic. Chem.* 1983 244 5

40) Corriu R, Royo G, Zwecker J and Breliere C, *Organometallics* 1989 8 1834

41) Holmes R, Day R, and Johnson S, *Inorg. Chem.* 1989 28 3182

42) Damrauer R and Danahey S, *Organometallics* 1986 5 1490

43) Oldfield J and Janes N, *J. Am. Chem. Soc.* 1985 107 6769

44) Corriu R, Lanneau G and Mehta V, *J. Organomet. Chem.* 1991 419 9

45) Corriu R, Arya P, Boyer J, Carre F, Lanneau G, Lapasset J, Perrot M. and Priou C, *Angew. Chem. Int. Ed. Engl.* 1989 28 1016

46) Veith M, Becker S and Huch J, *Angew. Chem. Int. Ed. Engl.* 1990 28 1237

47) Veith M, Becker S and Huch J, *Angew. Chem. Int. Ed. Engl.* 1991 29 216

48) Lappert M and Prokai B, *Adv. Organometallic Chem.* 1967 5 243

49) Englehardt L, Junk P, Patalinghug, Sue R, Raston C, Skelton B and White A, *J. Chem. Soc. Chem. Comm.* 1991 930

50) Tacke R and Linoh H, Bioorganosilicon Chemistry in *The Chemistry of Organosilicon Compounds* ed by Patai S and Rappoport Z. Pub Wiley 1989

51) Lukevics E, Borisova L and Gevorgyan V, *J. Organomet. Chem.* 1991 418 C21

52) Machavariani A, Shklover V, Struchkov Y, Oleneva G, Kramarova E, Shipov A and Baukov Y, *J. Chem. Soc. Chem. Comm.* 1988 683

53) Mozzhukhin A, Antipin M, Struchkov Y, Shipov A, Kramarova E and Baukov Y, *Organometallics in the USSR* 1992 5 439

54) Gavrilova G, Chipanina N, Frolov Y and Voronokov M, *J. Organomet. Chem.* 1991 418 291

55) Orlova N, Shipov A, Baukov Y, Mozzhukhin A and Antipin M, *Organometallics in the USSR* 1992 5 323

56) Klebe G and Bats J, *J Chem Soc Dalton Trans* 1985 1

57) Corriu Boudin A, Cerveau G , Chult C and Corriu R, *Organometallics* 1988 7 1165

58) Muller R, *Z. Chem.* 1984 24 41

59) Laine R, Blohowiak K, Robinson T, Hoppe M, Nardi P, Kampf J. and Uhm J, *Nature* 1991 353 642

60) Rosenheim A, Raibmann B and Schendel G, *Z Inorg. Chem.* 1931 196 160

61) Barnum D, *Inorg. Chem.* 1970 9 1942 and 1970 11 1424

62) Ault B, *Inorg. Chem.* 1981 20 2817

63) Marsden C, *Inorg. Chem.* 1983 22 3177

64) Schaad L, Jiani H, and Hess B, *J. Am. Chem. Soc.* 1991 113 1463

65) Tamao K, Hayashi T, Ito Y and Shiro M, *Organometallics* 1992 11 182

66) Holmes R, Harland J, Payne J and Day R, *Inorg. Chem.* 1987 26 760

67) Damrauer R, O'Connell D, Danahey S and Simon R, *Organometallics* 1989 8 1167

68) Boudjouk P and Hong J, *Organometallics* 1995 14 574

69) Corriu R, Guerin C and Kolani B, *Bull. Soc. Chim. France* 1985 973

70) Corriu R, Guerin C, Henner B and Wang Q, *Organometallics* 1991 10 2297

Corriu R, Guerin C, Henner B and Wang Q, *Organometallics* 1991 10 3574

70a) Kolomeitsev A,Bissky G, Lork E, Movchun V, Rusanov E, Kirsch P and Roschenthaler G, *Chem. Comm.* 1999 1017

71) Lickiss P, *J.C.S. Chem. Soc. Rev.* 1992 271

71a) Zybil C and Muller G, *Angew. Chem. Int. Ed. Engl.* 1987 26 669
Zybil C and Muller G, *Organometallics* 1988 7 1368

72) Straus D, Tilley T.D, Rheinhold A, Geib S, *J. Am. Chem. Soc.* 1987 109 5872

73) Tilley T D, Strauss D, Rheingold A and Geib S, *J. Am. Chem. Soc.* 1987 109 5872

74) Ogino H, Ueno K, Tobita H and Shimoi M, *J. Am. Chem. Soc.* 1988 110 4092

75) Tilley T D, Grumbine S and Becard J, *J. Am. Chem. Soc.*1990 112 780

76) Woo L, Smith D and Young V, *Organometallics* 1991 10 3977

77) Colman J, Barnes C and Woo L, *Proc. Natl. Acad. Sci.* 1983 80 7684

78) Muller G, Zybill C, Wilkinson D, Handwerker H and Leis C, *Organometallics* 1992 11 514

79) Corriu R, Lanneau G, and Priou C, *Angew. Chem. Int. Ed. Engl.* 1991 30 1130

80) Auner N, Zybill C, Herdtweck E, Gamper S, Leis C and Probst R, *Angew. Chem. Int. Ed. Engl.* 1991 30 1132

81) Corriu R, Boyer J, Breliere R, Kpoton M, *J. Organomet Chem* 1986 311 C39

82) Corriu R, Lanneau G and Perrot M, *Tetrahedron Letters* 1988 29 1271

83) Corriu R, Lanneau G and Perrot M, *Tetrahedron Letters* 1987 28 3941

84) Corriu R, Arya P, Boyer J, Carre F, Lanneau G, Lapassi J, Perrot M and Priou C, *Angew. Chem. Int. Ed. Engl.* 1989 28 1016

85) Thompson D and Boudjouk A., *J. Chem. Soc. Chem. Comm.* 1987 1466

86) Corriu R, Lanneau G and Chauhan B, *Organometallics* 1993 12 2001

87) Stevenson W, Wilson D, Martin J and Farnham W,
J. Am. Chem. Soc. 1985 107 6340 and 1985 107 6352

88) Farnham W and Harlow R, *J. Am. Chem. Soc.* 1981 103 4608

89) Voronokov M, Albanov A, Gubanova L, Larin M and Pestunovich V,
J Organometallic Chemistry 1983 244 5

90) Klebe G and Hensen K, *J. Chem. Soc. Dalton. Trans* 1985 5

91) Klebe G and Hensen K, *J Organometallic Chem.* 1981 209 17
Klebe G, Hensen K. and Fuess H, *Chem. Ber.* 1983 116 3125

92) Kalikhman I, Bannikova O, Belousova G, Gostevskii G, Leipins E, Vyazankin O,
Vyazankin N and Pestunovich V, *Organometallic Chem. in the USSR* 1988 1 379

93) From Pestunovich V, *Doctoral Thesis USSR Academy of Sciences Irkutsk* 1986

94) Kalikhman I, Bannikova O and Gostevskii B,
Akad. Nauk SSSR Ser Khim 1985 7 1688

95) Mozzhukhin Z, Antipin M, Struchov Y, Shipov A, Kramarova E and Baukov Y,
Organometallics in the USSR 1992 5 445

96) Pauline L, *J. Am. Chem. Soc.* 1947 69 542

97) Burgi H. B, *Inorg. Chem.* 1973 12 2321

98) Chipanina N, Gavrilova G, Aksamentova T, Modonov V, Gubanova L, Sorokin M,
Chernov N, Frolov Yu and Voronkov M, *Organometallics in the USSR* 1989 3 369

99) Corriu R and Hanner M, *J. Organomet. Chem.* 1974 1 74

100) Corriu R, Martineau M and Dabosi G, *J Organomet. Chem.* 1980 25 18

101) Corriu R, Carre F, Breliere C, Poirier M, and Royo G,
Organometallics 1989 8 1831

102) Corriu R, Brelier C, Royo G and Zwecker J, *Organometallics* 1989 8 1834

103) Corriu R, Cerveau G, Chuit C and Reye C, *Fr Pat. 51308 1/YS* 1984

104) Evans D. and Wong C, *Polyhedron* 1991 10 1131

105) Williams E, Royal Society of Chemistry *An. Rep. NMR Spectrosc.* 1983 15 235

106) Corriu R, Carre F, Cerveau G, Chuit C. and Reye C, *Angew Chem Int Ed* 1989 28 489

107) Bailar J., *J. Inorg Nucl. Chem* 1958 8 165

108) Corriu R, Carre F, Colomer E, and Lheureux M, *J.Organomet. Chem.* 1987 331 29

109) Corriu R, Cerveau G, Boudin A and Reye C, *Organometallics* 1988 7 116

110) Weiss A, Reiff G, Weiss A., *Z. Anorg. Allg. Chem.* 1961 311 151

111) Yoshikawa Y, Kojima M, Kuroda Y, Namba M and Ohmori Y, *Inorg. Chem.* 1992 31 2300

112) Kummer D, Gaisser K, Seifert J and Wagner R, *Z. Anorg. Allg. Chem.* 1979 145 459

113) Corriu R, Carre F, Breliere C and Royo G, *Organometallics* 1988 7 1006

114) Biradar N, Roddabasanagouder V and Aminabhavi T, *Indian J. Chem. Sect A* 1985 24A 873

115) Corriu R, Breliere C, Carre F, Royo G and Mann M, *Organometallics* 1994 13 307

116) Roewer G, Mucha F, Bohme U, *Chem. Comm.* 1998 1289

117) Corriu R, Breliere C, Carre F and Royo G, *Angew. Chem. Int. Ed. Engl.* 1994 33 1097

118) Shim W and Risen W, *J. Organomet. Chem.* 1984 260 271

118a) Douglas W, Guy D,Kar A and Wang C, *Chem. Comm.* 1998 2125

118b) Chuit C, Corriu R, Mehdi A and Reye C, *Chem. Eur. J.* 1996 2 342

118c) Janzen A and OuX A, *Inorg. Chem.* 1997 36 392

118d) Janzen A and Morat R, *Can. J. Chem* 1997 55 3845

119) Modena G and Allen A, *J. Chem. Soc* 1957 3668

120) Corriu R, Dabosi G and Martineua M, *J. Organomet. Chem.* 1978 150 27

121) Frye C, Chu H and Johnson M, *J. Organomet. Chem* 1984 271 327

122) Chojnowski M, Cypryk M and Michalski M, *J. Organomet Chem.* 1978 161 C31

123) Beattie I and Parrett F, *J. Chem. Soc. A* 1966 1784

124) Corriu R, Dabosi G and Martineau M, *J. Organomet. Chem.* 1980 186 25

125) Corriu R, Larcher F and Royo G, *J. Organomet. Chem.* 1977 129 299

126) Janzen A , *Coord. Chem. Rev.* 1994 130 355

127) Corriu R and Henner M, *Bull. Soc. Chim. France* 1974 1447

128) Voronkov M, Shevchenco S, Elin V, Dolenko G, Baryshok V, Feshin V, Frolov Y and Mazalov L, *Dakl. Akad. Nauk SSR* 1982 264 373

129) Baybutt P, *Mol. Phys.* 1975 29 389

130) Corriu R, Henner B, West R, Poirier M, Royo G and De Saxce A, *J. Organomet. Chem.* 1983 251 295

131) Moelwyn-Hughes E, *Physical Chemistry* Pub. Pergamon Press 1957

132) Laidler K, *Theories of Chemical Reaction Rates* Pub. McGraw-Hill 1969

133) Johnson H, *Gas Phase Reaction Rate Theory* Pub. Ronald Press 1966

134) Rice O and Ramsperger M, *J. Am. Chem. Soc.* 1927 49 1616

135) Kotz T and Purcell k , *Inorganic. Chemistry* Pub. Holt Saunders 1977

136) Williams I, *Chem. Soc. Reviews* 1993 277

137) Alibrandi G, *Chem. Comm.* 1994 2709

138) Kuivila H and Easterbrook E, *J Am Chem Soc* 1951 73 4626

139) DeRoos J and Oliver, *J Inorg. Chem.* 1965 4 1741

140) Buddle W and Hawhorne M, *J. Am. Chem. Soc.* 1971 93 3147

141) Walmsley D J Am Chem Soc, *J. Am. Chem. Soc.* 1971 93 3150

142) Blackburrow J and Lockhard C, *J. Chem. Soc. A* 1968 3015

143) Heaton G and Railey P, *J. Chem. Soc. A* 1969 925

144) Hartman J and Schrobilgen G, *Inorg. Chem.* 1972 11 940

145) Pinkas J, Wang T, Jacobson R and Verkade J, *Inorg. Chem.* 1994 33 5244

146 Woning J and Verkade J, *J. Am. Chem. Soc.* 1991 113 944

147) Toyota T, *J. Chem. Soc. Chem. Comm.* 1995 2491

148) Fait D and Connick R, *J. Am. Chem. Soc.* 1968 90 608

149) Saito K and Nagasawa N, *Polyhedron* 1990 9 215

150) Robinson G, *Co-ordination Chemistry of Aluminium* Pub. VCH 1993

151) Sommer L, *Stereochemistry,mechanisms and silicon* Pub McGraw Hill 1965

152) Ruhlmann K, Scheim U, Kappler K and Gewald R, in *Frontiers of Organosilicon Chemistry* Edt Bassindale A and Gaspar P Pub. RSC 1991

153) Corriu R, Dabosi G and Martineau M, *J Organomet. Chem.* 1978 150 27

154) Corriu R, Dabosi G and Martineau M, *J Organomet. Chem.* 1980 186 25

155) Corriu R and Joung G, in *Chemistry of Organosilicon Compounds* Edt. Patai S and Rappoport Z Pub. John Wiley 1989

156) West R, *International Symposia on Organosilicon Chemistry Sci. Com.* 1965

157) Macharashvili A, Schklova V, Yu T,Baukov I, Kramarova P and Oleneva G J *Organomet. Chem.* 1987 327 167

158) Lickiss P, *J.C.S. Chemical Soc. Reviews* 1992 271

Lambert T, Schultz W, McConnell J in *Silicon Chemistry* Edt. By Corey J, and Schilf W Pub. Ellis Harwood 1988

159) Westheimer F, *Acc. Chem. Res.* 1968 1 70

160) Martin J, Wilson S, Stevenson W and Farnham W, *J. Am. Chem. Soc.* 1985 107 6340

161) Corriu R, *Phosphorous and Sulfur* 1986 27 1

161a) Westheimer F, in *Rearrangements in the ground and excited state* Edt by De Mayo P Pub Academic press 1980

162) Corriu R and Guerin C, *Adv. in Organomet. Chem.* 1982 20 265

162a) Anh H and Minot C, *J. Am. Chem. Soc.* 1980 102 103

163) Sommer L, *Inter-sci Chem Rep* 1973 7 1

164) Bassindale A and Taylor P, in *Chemistry of Organosilicon Compounds* Edt by Patai S and Rappoport Z_Pub John Wiley 1989

165) Swain C, Porshcke W, Ahmed W, *J. Am. Chem. Soc.* 1974 96 4700 and Schowen R

166) Eaborn C, Eidenschink R and Walton D, *Chem. Comm.* 1975 388

167) Corriu R and Henner B, *Chem. Comm.* 1973 116

168) Pearson R, *J. Chem. Ed.* 1975 45 581

169) Corriu R, *Recent Advances in Mechanistic and Synthetic Aspects of polymerisation* 1987 49

170) Klanberg F and Muetterties L, *Inorg. Chem.* 1968 7 155

171) Janzen A, Ibott D and Gibson J, *Canad. J Chem.* 1973 51 3203

172) Holmes R, *Chem. Review* 1990 90 17

173) Bassindale A, Lau J and Taylor P, *J. Organomet. Chem.* 1995 449 137

174) Corriu R, Guerin C, Henner B, Wong C and Man W, *Organometallics* 1988 7 237

175) Boudin A, Cerveau G, Chuit C and Corriu R, *Angew Chem Int Ed Engl* 1986 25 473

176) Corriu R, Boyer J, Breliere R, Kpoton M, and Royo G *J Organomet Chem* 1986 311 C39

177) Corriu R, Guerin C, Henner B, Wong C and Man W. *Organometallics* 1991 10 3200

178) Corriu R, Becker B, Guerin C, Henner B and Wang Q, *J Organomet Chem* 1989 368 C25

179) Bassindale A and Borbaruah M, *Chem. Comm.* 1993 362

180) Gordon M, Davis L and Burggraf L, *Chem. Phys. Letts.* 1989 163 371

181) Holmes R and Deiters J, *J. Am. Chem. Soc.* 1987 109 1686

182) Holmes R, Holmes J and Deiters J, *J. Am. Chem. Soc.* 1988 110 7672

182a) Streitwiester A, Glaser R and Gronert S, *J. Am. Chem. Soc.* 1989 111 3111

183) Damrauer R, Burggraf L, Davis L and Gordon M, *J. Am. Chem. Soc.* 1988 110 6601

184) Dillard J, *Inorg. Chem.* 1974 13 1491

185) McNeil K and Thynne J, *Int J Mass Spectrom. Ion Phys* 1970 3 445

186) DePuy C.H, Damrauer R, Bowie J and Shelton J, *Acc. Chem. Res.* 1987 20 127

187) Deiters J and Holmes R, *J. Am. Chem. Soc.* 1987 109 1692

188) Deiters J and Holmes R, *J. Am. Chem. Soc.* 1987 109 1686

189) Hajdasz D and Squires R, J. Am. Chem. Soc. 1986 108 3139

190) Damrauer R, DePuy C, Bierbaum V, *Organometallics* 1983 98 4787

191) Walsh R, *Acc. Chem. Res.* 1981 14 246

192) Brandemark U, and Siegbahn P.E.M, *Theor. Chim. Acta* 1984 66 233

193) Kiel F and Ahlrichs R , *J. Am. Chem. Soc.* 1976 98 4787

194) Corriu R, Gerbier L and Cerveau G, *Phosphorous, Sulfur and Silicon* 1989 42 115

195) Corriu R, Chuit C, Rayer C and Young J, *Chem. Review* 1993 93 1371

196) Pearson R, Edgington D and Basola P, *J. Am. Chem. Soc.* 1962 84 3233

197) Wright C and Muetterties E Muetterties E, *J. Am. Chem. Soc.* 1965 87 21

198) Wright C and Muetterties E Muetterties E, *Pure and Applied Chem.* 1965 10 53

199) Corriu R, Carre F, Breliere C, Royo G and Man M, *Organometallics* 1994 13 307