Reactivity of Penta- and Hexacoordinate Silicon Compounds and Their Role as Reaction Intermediates

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I. Introduction

Compounds of silicon with coordination number greater than four have been known since the beginning of the 19th century, when Gay-Lussac[1] and J. Davy[2] first observed, independently, the formation of the $[SiF_6]^{2-}$ ion and of the adduct of SiF_4 with ammonia.

The formation and structure of hypervalent silicon compounds continue to be an area of lively interest[3-5] and has been regularly reviewed,[6,7] most recently by the Russian school of Voronkov[8,9] and the Latvian school of Lukevics.[10]

Alongside these studies, another aspect of the chemistry of hypervalent silicon compounds has elicited considerable interest in the last 20 years, as it has been realized that these compounds have a distinctive reactivity of their own.[11,12] One impetus for these studies arises from the widespread use of nucleophilic activation and catalysis in the application of organosilicon compounds as intermediates in organic synthesis.[13-16] Another derives from the studies of Müller,[17,18] subsequently greatly extended by Kumada,[19] on the formation and reactivity of organofluorosilicates $[RSiF_5]^{2-}$.

It is the purpose of this review to survey comprehensively the literature, up to the end of 1992, on the chemical reactivity of penta- and hexacoordinate silicon compounds, including their interconversion, with respect to their applications in organic synthesis, and as reagents for the preparation of organosilicon compounds. Recent results in the area of nucleophile-catalyzed reactions will also be considered (this topic was comprehensively reviewed in 1988[20]) and a general mechanism for such reactions proposed.

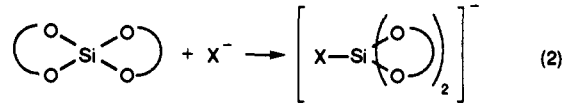
These sections will be preceded by a survey of the general methods available for the preparation of hypervalent compounds of silicon, and of their main structural characteristics which are particularly relevant to their reactivity. The stereochemical nonrigidity of penta- and hexacoordinate complexes will also be discussed in view of the significance for stereochemistry.

II. Preparation of Pentacoordinate Silicon Compounds

Pentacoordinate silicon species may be prepared according to the following general methods:

(1) By addition of an anion to an organosilane (eq 1) or to a spirosilane (eq 2) to give an anionic pentacoordinate silicon complex.

$$R_nSiX_{4-n} + X^- \longrightarrow [R_nSiX_{5-n}]^- \quad (1)$$



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(2) By inter- or intramolecular coordination of a neutral donor to silicon, giving a neutral or a cationic pentacoordinate silicon complex, depending on the nature of the substituents.

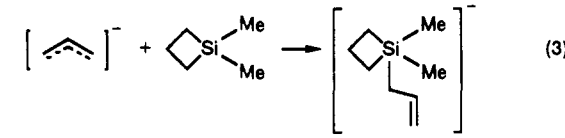
(3) By substitution of a trifunctional organosilane: (a) by a bidentate ligand to give an anionic or a cationic pentacoordinate complex according to the nature of the bidentate ligand or (b) by triethanolamine or another trialkanolamine to give silatranes, or by tris-(2-aminoethyl)amine to give triazasilatranes.

Illustrative examples for each of these methods follow.

A. Coordination of Anions to Tetracoordinate Silicon Compounds

1. Fluoride Donation to an Organosilane

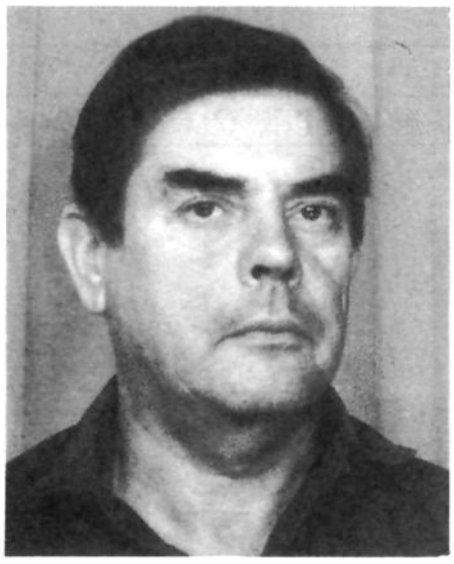
The fluorosilanes SiF_4, $RSiF_3$ (R = Me, Ph), and Ph_2SiF_2 react with tetraalkylammonium fluorides in a 1:1 ratio to yield stable ionic compounds.[21,22] NMR[21,23] and vibrational spectroscopic data[24,25] strongly suggest that the anions in these compounds are pentacoordinated at silicon. Attempts to isolate trialkyl- and triaryl-substituted complexes by this method were not successful. Some years later, Damrauer et al. reported[26] that in the gas phase, using a flowing afterglow system, a large number of organic pentacoordinate silicon anions, including one with five carbon substituents, could be generated cleanly by addition of anions to cyclic or acyclic silanes (eq 3). Of particular interest



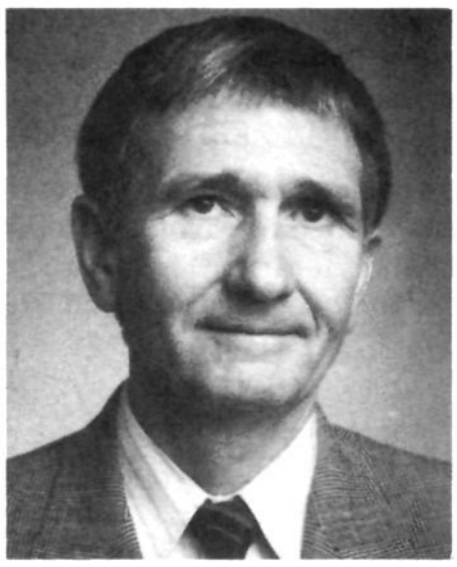
(3)

are the reactions of F^- with cyclic silanes, (for example eq 4), not only because they shed light on the energies of formation of pentacoordinate anions, but also because some novel cleavage reactions producing α-silyl carbanions occur.

The need to reinvestigate the dynamic behavior of pentacoordinate silicon species led Damrauer and Danahey[27] to prepare stable and nonhygroscopic pen-



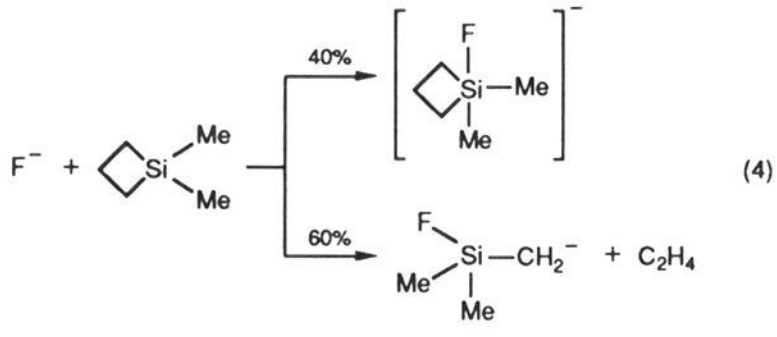
Claude Chuit was born in Paris. He received his doctorat d'Etat in 1970 from the Université d'Orsay. After a year of postdoctoral study at the University of Stirling (Scotland), he spent 10 years in Professor J. F. Normant's laboratory at the Université P. et M. Curie in Paris. In 1980 he joined Professor Corriu's group where he became Directeur de Recherche at the C.N.R.S. in 1990. At present his main research interest involves the chemistry of hypercoordinated species of silicon, germanium, and phosphorus.



Robert Corriu was born in France (Pyrénées Orientales) in 1934. He obtained the degree of Docteur ès Sciences Physiques in 1961 from the Université de Montpellier. He became Associate Professor at the Université de Poitiers in 1964 and Professor at the Université des Sciences et Techniques du Languedoc (Montpellier) in 1969. His research interests involve organometallic chemistry: organosilicon and organogermanium compounds, transition metal complexes, hypercoordinated silicon and phosphorus compounds. The chemistry of organometallics polymers as precursors to new materials and the sol–gel process are now his new research interests. He has obtained awards from the French Chemical Society (1969 and 1985), from the CNRS (silver medal in 1982), and from the American Chemical Society (1984). He was elected to the French Academy of Sciences in 1991.

Catherine Reyé was born in France (Deux Sèvres). She received her Ph.D. degree in chemistry from the University of Montpellier II under the supervision of Professor R. J. P. Corriu. Since 1976 her principal research interest has focused on hypercoordinated silicon chemistry. First she worked in the area of nucleophile-catalyzed reactions involving hypercoordinated silicon intermediates, and then she studied the structure and the reactivity of penta- and hexacoordinate silicon compounds. Her most recent research interest is in hypercoordinated phosphorus chemistry and its use in organic synthesis. In addition to her research she teaches (maitre de conferences) in the University Institute of Technology in Montpellier.

Colin Young was born in London, but brought up in Norwich, before going up to the University of Cambridge where he obtained his B.A. and Ph.D. degrees. His interest in silicon chemistry, particularly that of silyl free radicals, was kindled by his research with R. N. Hazeldine for his doctoral thesis. He was for 25 years a lecturer at the University College of Wales, Aberystwyth, before the untimely closure of the Chemistry department there led to a return to Montpellier to continue his collaboration with Robert Corriu, in whose laboratory he had earlier spent a year of study leave. He is now easing himself into retirement.



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tacoordinate organofluorosilicates, so that subsequent NMR studies could be done without ambiguity. They found that the presence of 18-crown-6 ether greatly stabilizes potassium salts of pentacoordinate fluorosilicates $[R_nSiF_{5-n}]^-$ (n = 1–3). Shortly after, this method was used to prepare other organotetra- and organotrifluorosilicates $[RSiF_4]^-$ [28] and $[R_2SiF_3]^-$ [29–31] as their 18-crown-6 potassium salts and also the triaryldifluorosilicate $[Ph_2(\alpha Np)SiF_2]^-[S(NMe_2)_3]^+$.[32]

2. Alkoxide Donation to an Organosilane

The use of potassium ion complexed by 18-crown-6 ether as counterion to stabilize pentacoordinate anionic silicates, as developed by Damrauer and Danahey,[27] has been extended to the preparation of alkoxy- and aryloxysilicates. The phenylmethoxysilicates **1** (eq 5) were isolated[33] as white crystalline powders. In analogous reactions, the salts of $[MeSi(OEt)_4]^-$ [33] and

$$Ph_nSi(OMe)_{4-n} + MeO^-[K,18\text{-crown-6}]^+ \rightarrow \quad (n = 1\text{–}3)$$

$$[Ph_nSi(OMe)_{5-n}]^-[K,18\text{-crown-6}]^+ \quad (5)$$

1

Table 1. Reaction of Potassium Hydride with Trialkoxysilanes

entry	$HSi(OR)_3$	solvent	reaction time (h)	products (%)[a] $[H_2Si(OR)_3]^-K^+$ (2)	$[HSi(OR)_4]^-K^+$ (3)
1	$HSi(OMe)_3$	THF	2	0	100
2	$HSi(OEt)_3$	THF	6	40	60
3	$HSi(OEt)_3$	THF	24	0	100
4	$HSi(OEt)_3$	THF(18-crown-6)	26	55	45
5	$HSi(OEt)_3$	DME	2	0	100
6	$HSi(OBu^n)_3$	THF	4	50	50
7	$HSi(OPr^i)_3$	THF	6	100	0
8	$HSi(OPh)_3$	THF	2	0	100
9	$HSi(OPh)_3$	THF(18-crown-6)	2	15	85

[a] Relative ratio of reaction products determined by ^{29}Si NMR.

$[PhSi(OCH_2CF_3)_4]^-$ [34] were similarly isolated, the former arising from aryl–silicon bond cleavage (eq 6).

$$MePhSi(OEt)_2 + EtO^-[K, 18\text{-crown-}6]^+ \rightarrow [MeSi(OEt)_4]^-[K, 18\text{-crown-}6]^+ \quad (6)$$

In the case of the $[Si(OR)_5]^-$ series,[34] the formation of pentacoordinate oxysilicates in solution was inferred from the upfield shift of the ^{29}Si NMR resonances.

The direct reaction of alkoxy (or aryloxy) silanes with the corresponding potassium alkoxide (or aryloxide) afforded the anionic pentacoordinate hydridosilicates[35,36] $[HSi(OR)_4]^-$ (eq 7) in good yield, even in the absence of crown ether.

$$HSi(OR)_3 + ROK \xrightarrow[DME]{THF\ or} [HSi(OR)_4]^-K^+ \quad (7)$$
$$(R = Me, Et, Bu^n, Pr^i, Ph)$$

3. Hydride Donation to an Organosilane

Potassium hydride reacts with various trialkoxy (or triaryloxy) silanes to yield the pentacoordinate anions[37] **2** and **3** (eq 8). The formation of **3**, in addition to the

$$HSi(OR)_3 \xrightarrow{KH} \underset{\mathbf{2}}{[H_2Si(OR)_3]^-K^+} + \underset{\mathbf{3}}{[HSi(OR)_4]^-K^+} \quad (8)$$
$$(R = Et, Pr^i, Bu^n, Bu^s, c\text{-}C_6H_{11})$$

expected product **2**, was observed in all cases except with $HSi(OPr^i)_3$ and can be explained by the disproportionation of $[H_2Si(OR)_3]^-K^+$ according to eq 9.

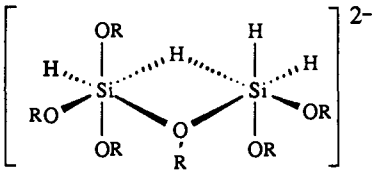
$$4[H_2Si(OR)_3]^-K^+ \rightarrow 3[HSi(OR)_4]^-K^+ + SiH_4 + KH \quad (9)$$
$$(R = Me, Et, Bu^n)$$

Evolution of SiH_4 was always observed [except with $HSi(OPr^i)_3$]. $[H_2Si(OPr^i)_3]^-K^+$ was isolated as white crystals in 82% yield after recrystallization.

The ratio of **2** to **3** was determined by ^{29}Si NMR.[37b] As indicated in Table 1, the proportion of $[HSi(OR)_4]^-$ diminishes with the steric bulk of the OR group. Moreover the disproportionation of **2** occurs less readily with increasing solvating power of the solvent (see entries 2, 3, and 5, Table 1). The presence of 18-crown-6 ether seems also to stabilize greatly the dihydridosilicate **2** (see entries 3 and 4, 8 and 9).

The migration of OR and H groups from one pentacoordinate silicon species to another could take place through a dimeric hexacoordinate intermediate (Scheme 1). This interpretation is supported by the

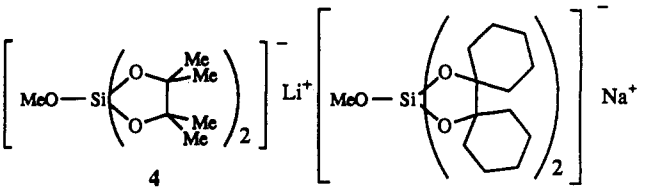
Scheme 1



effect of the steric hindrance of the OR groups, since no disproportionation occurs when R = Pr^i.

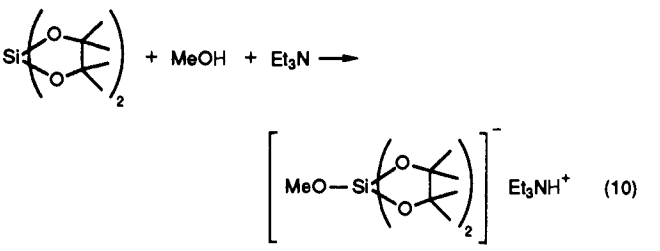
4. Coordination of an Anion to a Spirosilane

The literature contains few examples of the formation of pentacoordinate silicon derivatives from spirosilanes. In 1961 Müller and Heinrich[38] presented evidence for the formation of the two silicates **4** and **5** isolated from



4 **5**

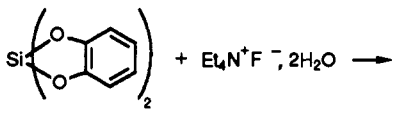
the reaction of the corresponding spirosilanes with lithium and sodium methoxide respectively. Later, C. L. Frye[39] found that simple amines were sufficiently basic to afford similar silicates (eq 10).



$$+ MeOH + Et_3N \quad (10)$$

This method for the preparation of pentacoordinate silicates has not been extensively developed[40,41] since only spirosilicates derived from highly alkyl-substituted 1,2-diols can be prepared. Holmes et al.[42] synthesized tetraethylammonium bis(1,2-benzenediolato)fluorosilicate (**7**) by reaction of spirosilane **6** with $Et_4N^+F^-$, $2H_2O$ (eq 11). Other attempts to prepare anionic pentacoordinated silicon species from **6** and an anion proved unsatisfactory.

Recently, Holmes et al.[43] reported the reaction of some spirosilanes with potassium fluoride in the presence of 18-crown-6 ether to give new pentacoordinate



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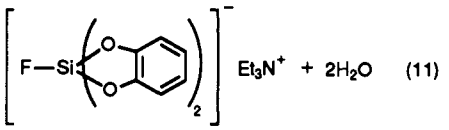

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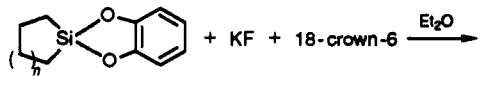
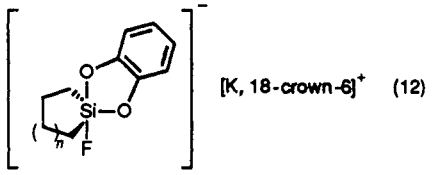
cyclic organofluorosilicates (eq 12). By contrast the spirosilane 8[44] has an exceptional ability to coordinate





a further ligand including organic, fluoride,[45] hydride,[46] and neutral donors.[47] The pentacoordinate silicon complexes 9,[44] 10,[45] and 11[48] were prepared in this way (Scheme 2).

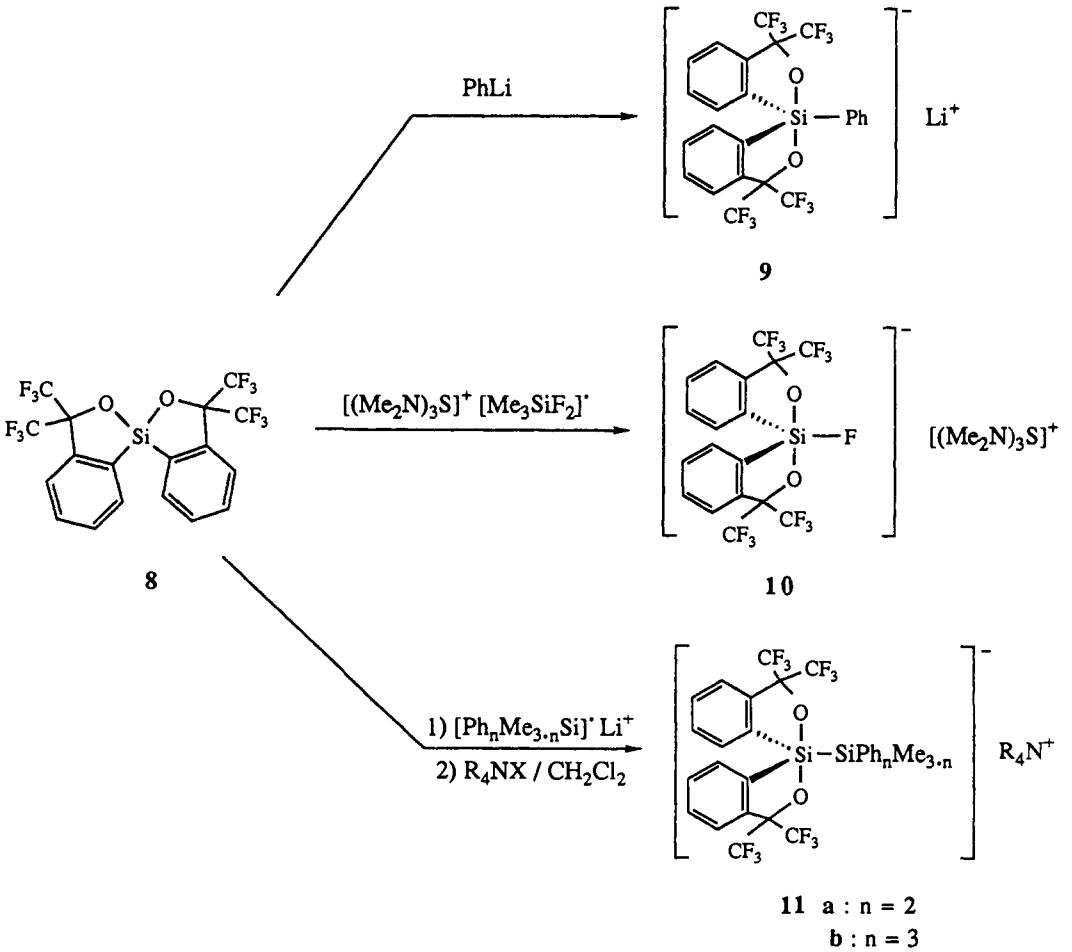
B. Intermolecular or Intramolecular Donation by a Neutral Donor to an Organosilane

1. Intermolecular Coordination to an Organosilane

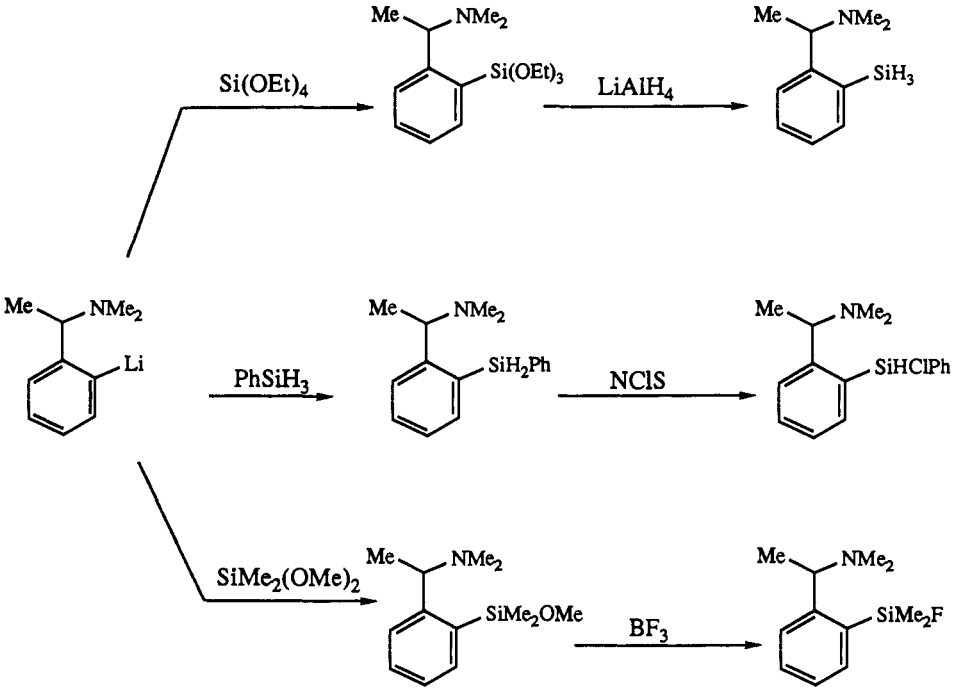
Neutral complexes of silicon can be formed from tetracovalent molecules by coordination of uncharged donors of groups 15 and 16. Although much of the early work which established the ability of silicon to expand its coordination sphere was concerned with the interaction of halogenosilanes with neutral donors,[6] there has often been considerable difficulty in fully characterizing the products. This is particularly the case of the adducts of 1:1 stoichiometry, where, depending on the nature of the silicon compound, interaction seems either to be relatively weak, or to result in complete displacement and the formation of ionic complexes.[49] In the latter case, the silicon atom therefore remains tetracoordinate, or by coordinating a second ligand gives a pentacoordinate cation. Some years ago, the 1:2 adducts of the compounds SiH_3X and $MeSiH_2X$ (X = Br, I) with pyridine were assigned[50] the ionic structure $[RSiH_2 \cdot py_2]^+X^-$ (R = H, Me; X = Br, I), and an ionic structure was also suggested[51] for the adduct 12 of iodotriphenylsilane with 2,2′-bipyridyl.

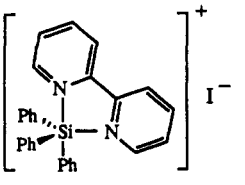
More recent studies have confirmed[52] that compounds of the trimethyl series Me_3SiX where X is halogen, perchlorate, triflate, etc. either form ionic adducts $[Me_3SiNu]^+X^-$ or do not react at all. Complexes in which the coordination at silicon is increased to five (or six) are formed only when there is more than one electronegative ligand bonded to the parent organo-

Scheme 2



Scheme 3





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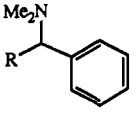
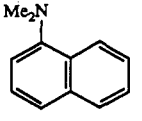
silicon compound, or when hydrogen is a ligand as well. Thus the formation[53] from Me_2SiHCl of $[(Me_2SiH(NMI)_2]^+Cl^-$ has been confirmed[54] by X-ray structural analysis, whereas NMR studies have shown[55] for example that $MeHSi(OTf)_2$ initially gives 1:1 molecular adducts with HMPA and NMI and that $PhSiF_3$ reacts[55] with HMPA to give $PhSiF_3$·HMPA which may then be converted to $[PhSiF_2(HMPA)_2]^+F^-$.

2. Intramolecular Donation to an Organosilane

Another way of achieving pentacoordination in silicon species is to prepare tetraorganosilicon compounds in which the silicon center may become pentacoordinate by intramolecular coordination. This strategy was used for tin compounds by van Koten et al.[56-60] in particular with ligands **13**[56-59] and **14**.[60]



13 a : R = H
b : R = Me



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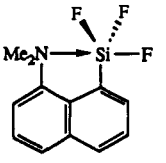
The preparation of silicon species containing such ligands is very easy. Indeed the presence of the dimethylamino group facilitates the lithiation of these ligands in a single position (ortho lithiation from **13**, perilithiation from **14**). Further reaction of these lithio derivatives with a functional organosilane affords directly the corresponding organosilane (Scheme 3) containing the potentially intramolecularly coordinating NMe_2 group.[61]

Intramolecular coordination from a donor group in **15**[62] and **16**[63] is facilitated by the rigid geometry of the ligand in which the donor group is always held in close proximity to the Si center. Intramolecular coordination is also possible with ligands for which there exists a favorable conformation allowing interaction between the Si center and the donor atom, as in compounds **17**,[64,65] **18**,[66] **19**,[67] and **20**.[68] In these cases the extent of



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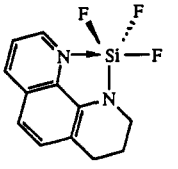

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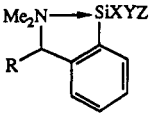
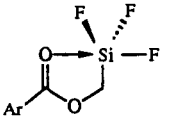


17 a : R = H
b : R = Me



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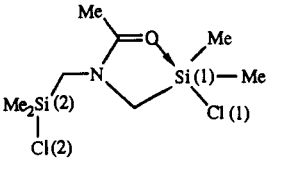

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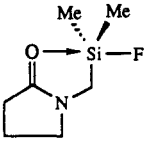

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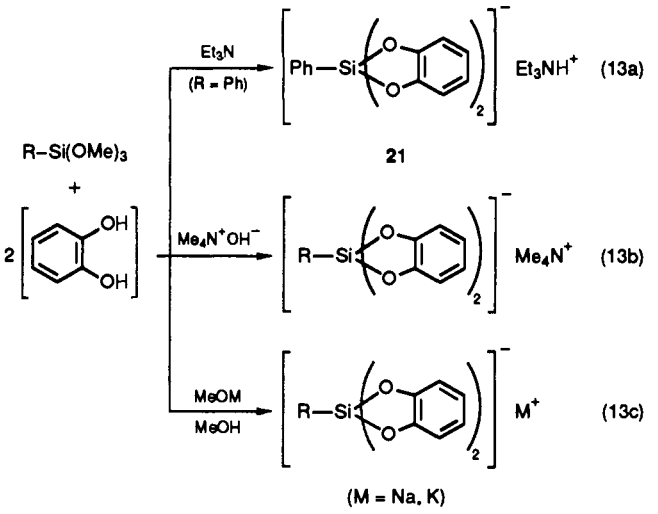
the intramolecular coordination is more dependent on the remaining substituents on the silicon atom. It may be inferred in the solid state from crystallographic data which give donor atom–silicon distances and in solution from NMR data. In a significant publication Yoder et al.[67] reported as early as 1978 the X-ray crystal structure of compound **19**. It was at that time one of few compounds known in which pentacoordination at silicon resulted from an intramolecular dative bond.

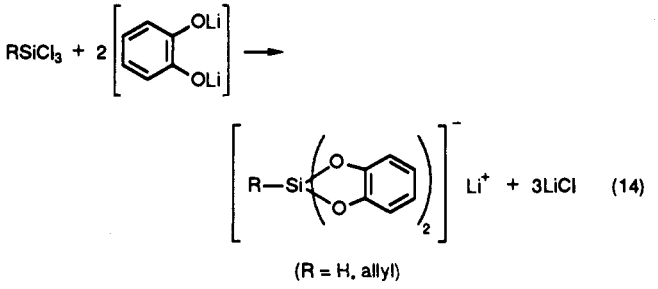
C. Substitution in a Trifunctional Organosilane

1. Substitution by a Bidentate Ligand

Complexes in which oxygen is directly bound to silicon within a cyclic bidentate ligand are formed readily and have been known for a long time. C. L. Frye[69] found that $PhSi(OMe)_3$ reacts with catechol in the presence of triethylamine to give quantitatively **21** (eq 13a). Boer et al.[70] subsequently determined the structure of the tetramethylammonium salt, which confirmed the presence of a pentacoordinate silicon anion. This reaction is general. It was shown that trialkoxysilanes $RSi(OMe)_3$ also react readily with catechol in the presence of bases such as tetraalkylammonium hydroxide or sodium or potassium methoxide (eqs 13b and 13c).[71]



These complexes can also be prepared from trichlorosilanes $RSiCl_3$ and alkali metal catecholates (eq 14).

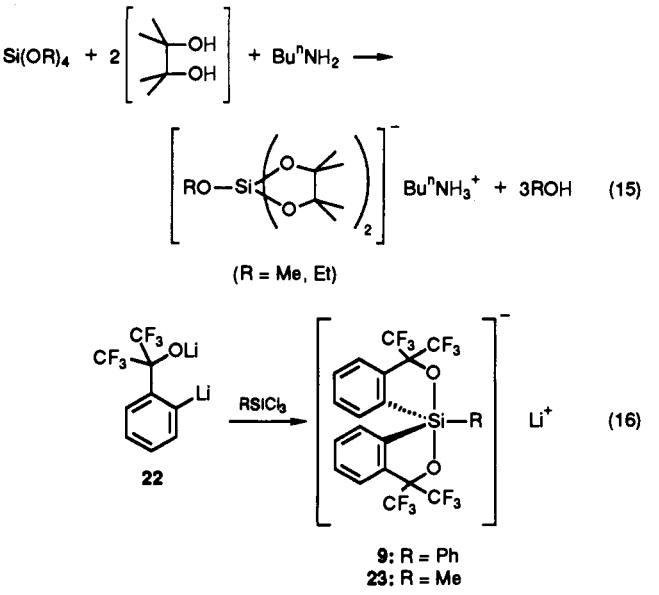


Allyl- and hydridobis(1,2-benzenediolato)silicates (refs 72 and 73, respectively) were synthesized as their lithium salts in this way, but they could not be isolated. However the potassium[71b] and tetramethyl ammonium salts[74] of the allyl silicate, prepared according to eqs 13c and 13b are stable and were isolated as crystalline solids.

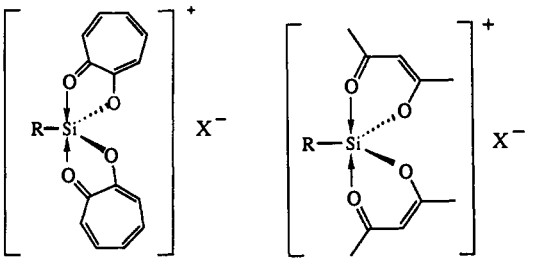
Aliphatic 1,2-diols also react easily with organotrialkoxysilanes or tetraalkoxysilanes[39,41] (eq 15) to give pentacoordinate anionic complexes.

The dilithium salt **22** is particularly effective in the synthesis of stable anionic pentacoordinate silicon species such as **9** and **23**[75] (eq 16).

Complexes derived from monoorganosilicon halides by their reaction with 2 mol of tropolone[76] or of 1,3-diketone[77] were assigned cationic pentacoordinate

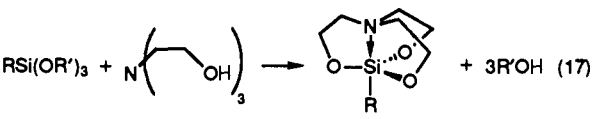


structures such as **24** and **25** on the basis of NMR, IR, UV, and chemical evidence.



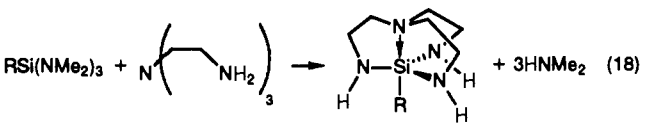
2. Substitution by Trialkanolamines and Tris(2-aminoethyl)amines

a. Preparation of Silatranes. In 1961, C. L. Frye et al.[78] reported the reaction of triethanolamine, and other trialkanolamines of suitable structure, with trifunctional silicon substrates to yield monomeric silanes **26** (eq 17) to which a pentacoordinate structure



was assigned from physical and chemical evidence. This fact was confirmed by the detailed X-ray crystallographic studies of Boer and co-workers.[79] Shortly after, C. L. Frye et al.[80] described the preparation and chemistry of novel silatranes bearing halo, acyloxy, siloxy, and hydroxy substituents at the apical silicon site, which exhibited some unusual properties. Since 1966, a series of more than 50 papers has been published by Voronkov and co-workers[81,82] who have extensively studied the structure, methods of preparation, and also the chemical and biological properties of this class of heterocyclic pentacoordinate compounds for which the term "silatrane" [83] has been widely accepted.

b. Preparation of Azasilatranes. Triazasilatranes (**27**) were synthesized more recently.[84] They are prepared[84,85] by heating tris(dimethylamino)silanes with tris(2-aminoethyl)amine (eq 18). A systematic multi-



27

nuclear NMR spectroscopic study of these compounds was published in 1987.[86] The results of a recent X-ray crystal-structure determination of the phenyl derivative 27 (R = Ph) have also been reported,[87] providing for the first time a set of molecular structure parameters for an azasilatrane. The data suggest that these derivatives are very similar to the silatranes, with an even stronger transannular interaction between silicon and the axial nitrogen atom.

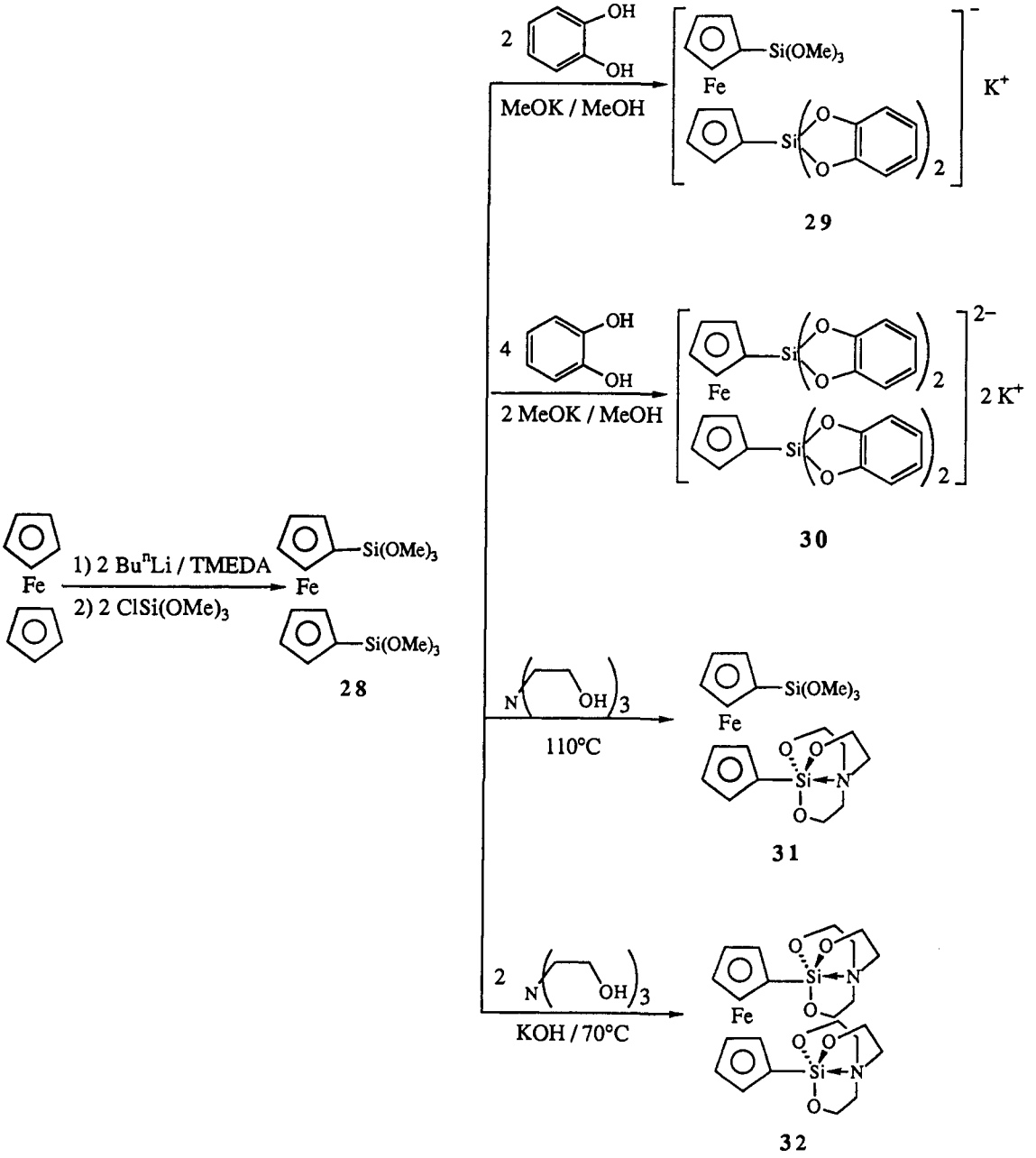
D. Synthesis of Compounds with Two Pentacoordinate Silicon Atoms

Complexes 29–32 have been obtained selectively and with good yields (Scheme 4) according to the methods previously described for the corresponding monopentacoordinate species and have been identified spectroscopically.[38]

An electrochemical study of these complexes[88] has shown a significant lowering of the redox potential corresponding to the reversible conversion Fe^{II}/Fe^{III} in contrast to the small increase in the potential in the case of 28 (Table 2). These results suggest that the pentacoordinate silicon groups behave as electron donors toward ferrocene.

Compounds 34–37 have been prepared from the dilithio derivative 33 according to the classical methods used for the corresponding singly pentacoordinate species (Scheme 5). All these compounds have been identified as doubly pentacoordinate species by spectroscopic data.[89] This study has shown that the two silicon atoms are independent and that their reactivity is identical to that of the monosilylated compounds.

Scheme 4



28

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30

31

32

Scheme 5

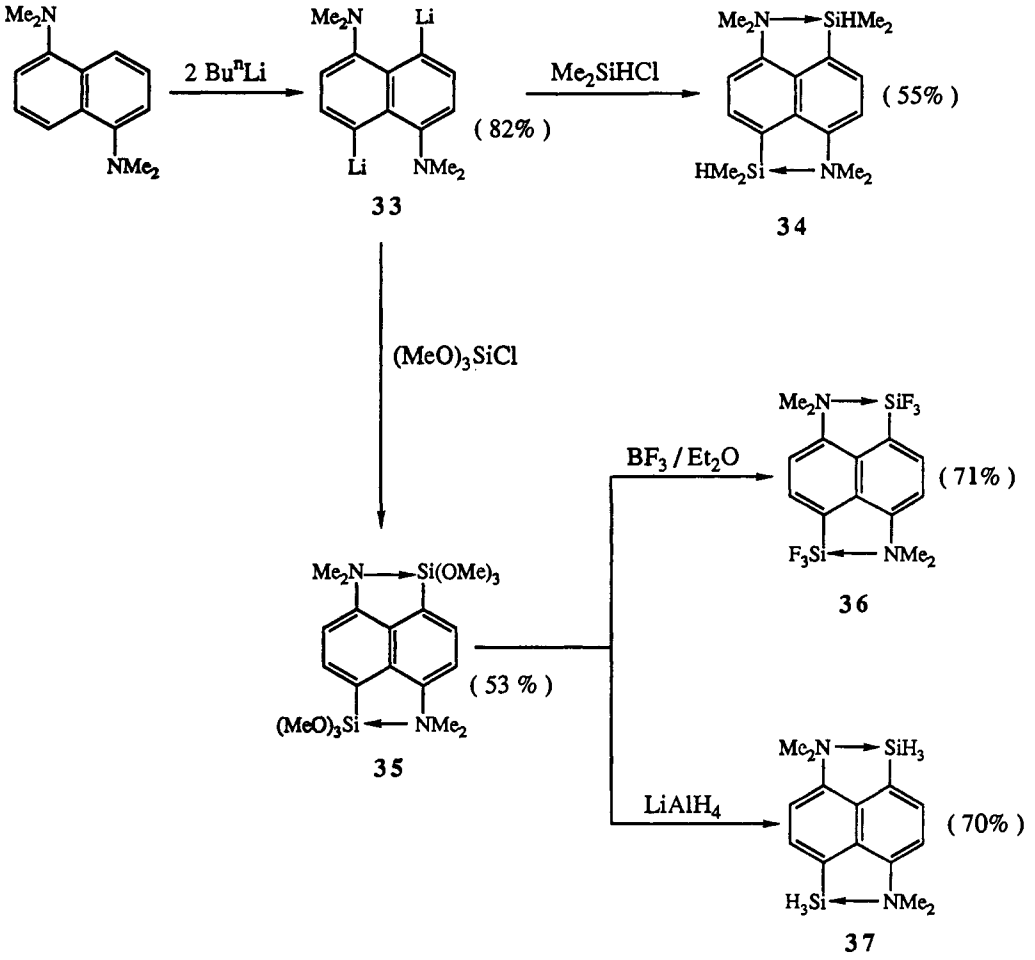


Table 2. Redox Potentials of Compounds 28–32

compound	$E_{1/2}$[a] (V)	$\Delta E_{1/2}$[b]	$\Delta E_{1/2}$[c]
ferrocene	+0.4		
28	+0.55	+0.15	
29	+0.31	−0.09	−0.24
30	+0.07	−0.33	−0.48
31	+0.21	−0.19	−0.34
32	−0.07	−0.47	−0.62

[a] Relative to SCE. [b] With respect to ferrocene. [c] With respect to 28.

III. Preparation of Hexacoordinate Silicon Compounds

Hexacoordinate silicon complexes are mainly prepared by methods which are analogous to those used for the preparation of pentacoordinate complexes:

(1) The addition reaction of nucleophilic anionic or neutral reagents with tetravalent silicon derivatives leading respectively to anionic or neutral complexes.

(2) The nucleophilic substitution of an organosilane, which is at least bifunctional, by bidentate ligands.

A. Coordination to a Tetracoordinate Silicon Compound

1. Fluoride Donation to a Halogenosilane

The hexafluorosilicate ion $[SiF_6]^{2-}$ is the parent of the ionic organopentafluorosilicate $[RSiF_5]^-$ compounds which were studied by Müller and co-workers.[17,18] These authors prepared $[RSiF_5]^-$ by coordination of fluoride anion to trifluorosilanes.[90] Organopentafluorosilicates can also be prepared by addition of fluoride ion to other trifunctional organosilanes $RSiX_3$ (X = Cl, Br, I, OR).[18] Subsequently Kumada et al.[91] developed a practical preparation of these organopentafluorosilicates by reaction of an excess of potassium fluoride in aqueous (or aqueous–alcoholic) solution with $RSiCl_3$ (eq 19).

$$RSiCl_3 \xrightarrow[H_2O,\,0\,^\circ C]{KF\ (excess)} [RSiF_5]^-K^+ \qquad (19)$$

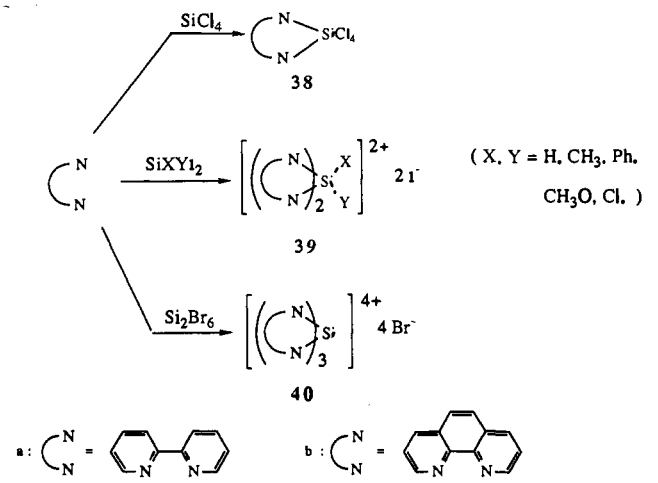
2. Intermolecular Coordination to an Organosilane

As indicated in section II.B.1 organosilanes with at least two electronegative groups on silicon may coordinate two nitrogen donors to give hexacoordinate complexes. In addition to $SiF_4 \cdot 2NH_3$ many complexes of analogous composition have been known for some time.[6] The series of hexacoordinate complexes[92] $Me_2SiX_2 \cdot 2py$, $MeSiX_3 \cdot 2py$, and $SiX_4 \cdot 2py$ (X = Cl, Br) provide an interesting contrast to the substitution of Me_3SiBr by pyridine to give $[Me_3Sipy]^+Br^-$ while Me_3SiCl and pyridine do not react at all.

Phosphines also may form adducts with tetrahalogenosilanes. In the latter case the stability of the adduct $SiX_4 \cdot 2PMe_3$ decreases in the order $SiF_4 \ll SiCl_4 \cong SiBr_4$, whereas the inverse order is observed for the stability of complexes of the type $SiX_4 \cdot 2NMe_3$.[93]

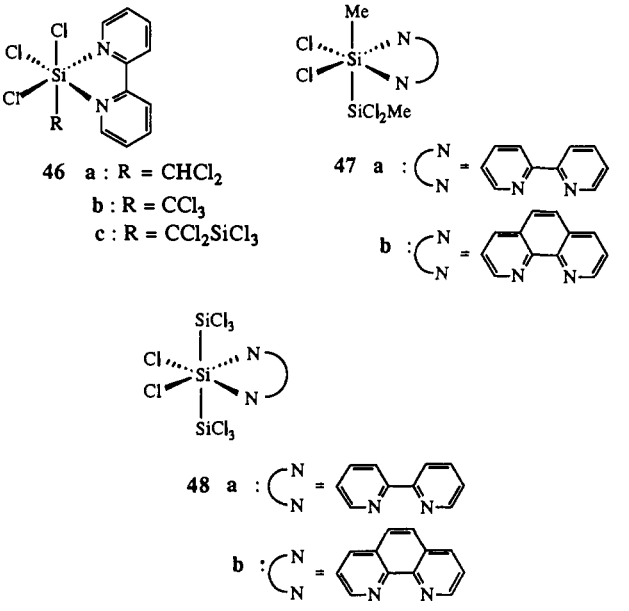
Diamines such as 2,2′-bipyridine and 1,10-phenanthroline coordinate easily to halogenosilanes to give neutral species **38**[94] or cationic ones **39**[95] and **40a**,[96] the

Scheme 6



nature of the complexes depending on the starting silane (Scheme 6). The hexacoordinate silicon complex **38a** can serve as starting material for the preparation of other hexacoordinate complexes. Substitution of chlorine by dilithiodipyridyl gives neutral complexes **41**[97] or **42**[98] (Scheme 7), formally Si^{II} and Si^{0}, respectively, depending on the stoichiometry of the reaction. Subsequently cationic complexes **43**[99] and **44**[100] may be obtained from **41** while reaction of **42** with iodine gives the +4 charged complex **45**[101] (Scheme 7).

Trichlorosilanes $RSiCl_3$ in which R is an electron-withdrawing group form 1:1 adducts with 2,2′-bipyridine (compounds **46**[102]). This amine, like 1,10-phenanthroline, can also add to 1,2-dimethyltetrachlorodisilane to produce compounds **47**[103] and to octachlorotrisilane to produce compounds **48**[103b,104] providing in all cases 1:1 adducts whatever the proportions of the components.

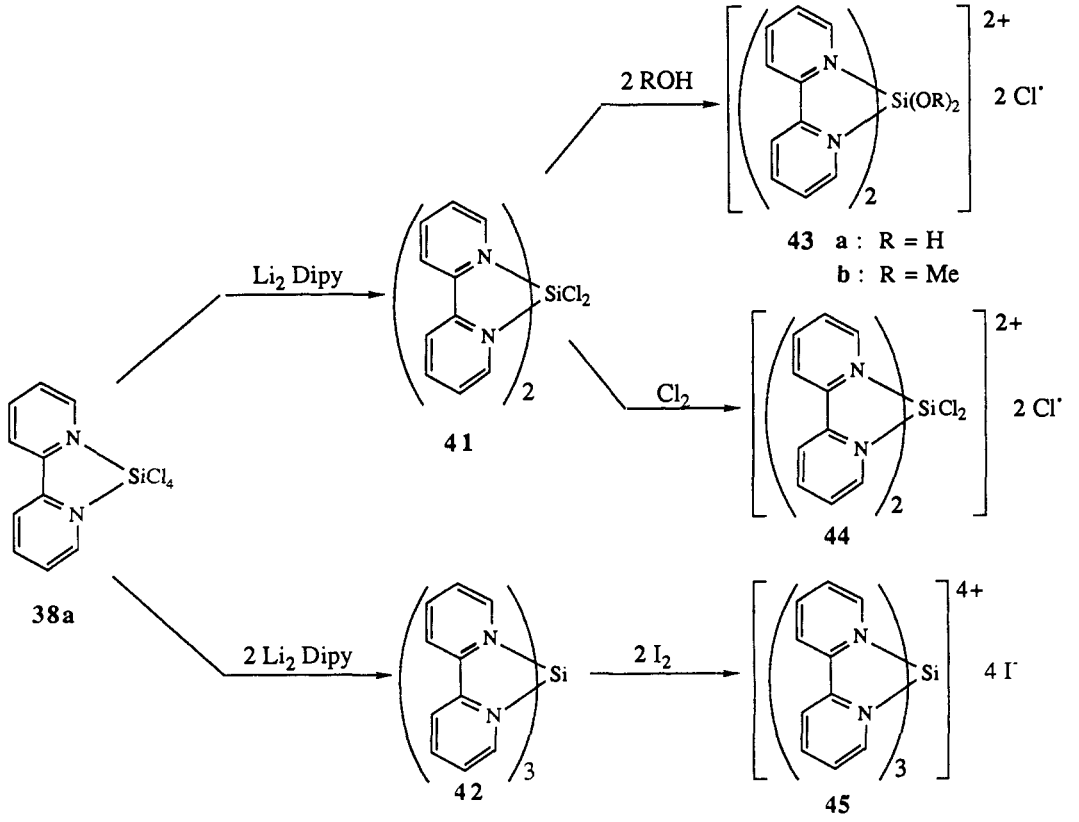


Interestingly, 1,10-phenanthroline coordinates with the spirosilane **8**[105] providing the sole example of a hexacoordinate complex, **49** derived from **8** (Scheme 8). By contrast the dilithio anion **22** affords exclusively complex **50**[106] which is pentacoordinated (Scheme 8).

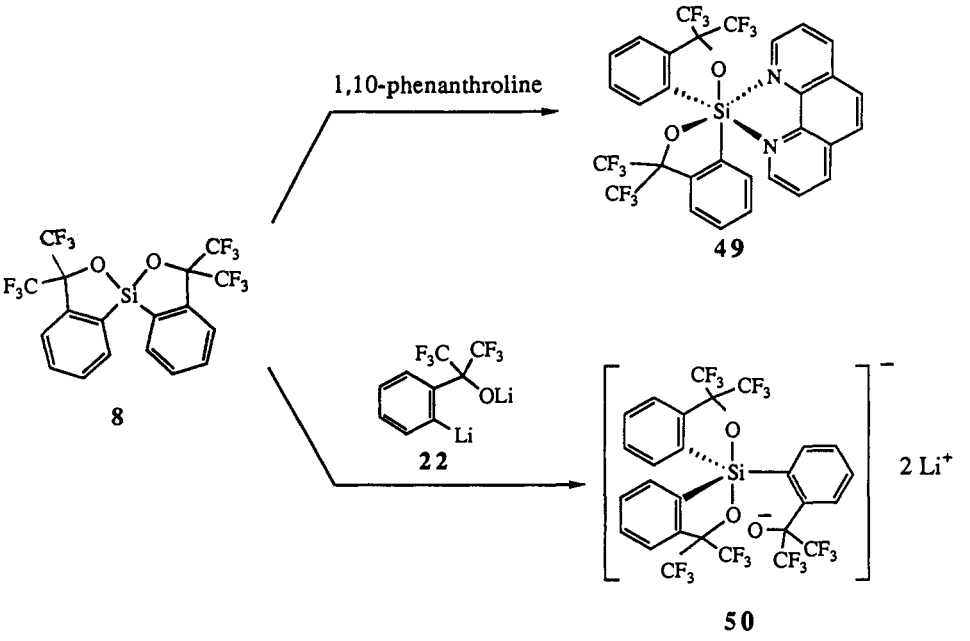
3. Intramolecular Coordination to an Organosilane

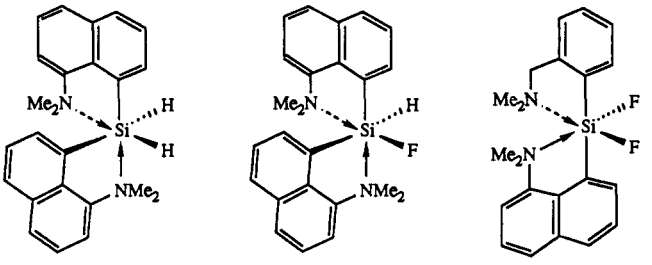
Neutral compounds bearing two donors such as **13** and **14** are also potentially hexacoordinated. Compounds **51–53** have been prepared.[107] Hexacoordination at silicon was inferred from variable-temperature NMR studies and X-ray data (the crystal structures will be discussed in section IV.B).

Scheme 7



Scheme 8

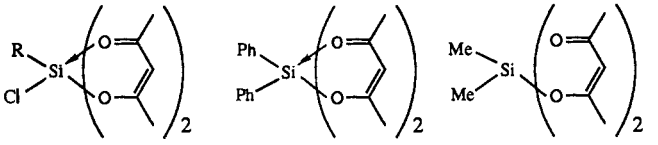




B. Substitution in a Tetrafunctional Silane by a Bidentate Ligand

The first hexacoordinate complex prepared following this strategy was the cationic complex **54** prepared by Dilthey in 1903[108] (Scheme 9). Further work on the preparation of complexes with β-diketones as ligands showed that the reaction product depends on the starting silane employed. From $Si(OAc)_4$ complex **55** is obtained[109] (Scheme 9) while from $SiCl_4$ the reaction product is the cationic complex **54**[108,110] (Scheme 9). Nevertheless the neutral complex **56** can be prepared from $SiCl_4$ but with a poor yield when the β-diketone is deficient[111] (Scheme 9).

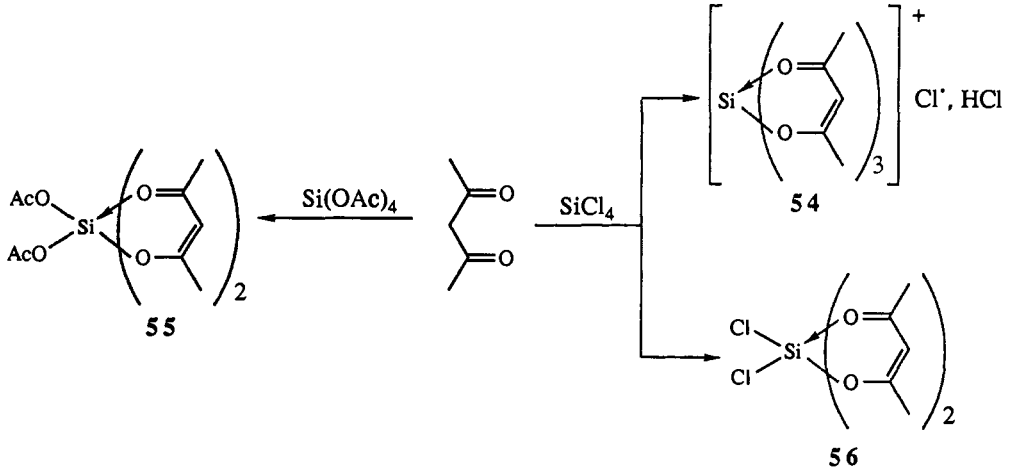
Neutral complexes **57**[110] and **58**[112] have been prepared from $RSiCl_3$ and Ph_2SiCl_2. However from Me_2SiCl_2 only the tetravalent silane **59** is formed,[110] indicating

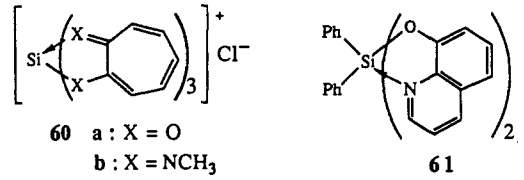


that the phenyl group is more favorable for hexacoordination than the methyl group in spite of the steric hindrance. Similarly, the cationic complexes **60**[113] are obtained with tropolone and *N,N'*-dimethylaminotroponimine, and the neutral complex **61**, with 8-hydroxyquinoline.[114]

The anionic complexes **62** are easily prepared by reaction of catechol with tetramethoxy (or tetraethoxy)-silane in basic conditions[69,115] (Scheme 10), but aliphatic 1,2-diols react with tetramethoxysilane under the same

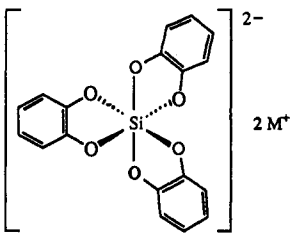
Scheme 9





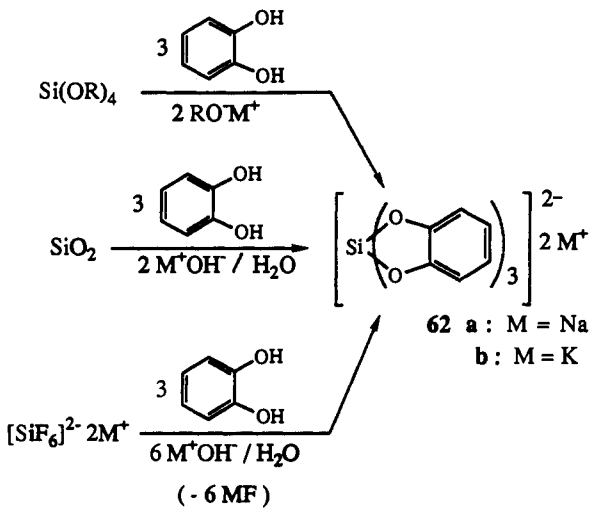
60 a : X = O
b : X = NCH_3

61

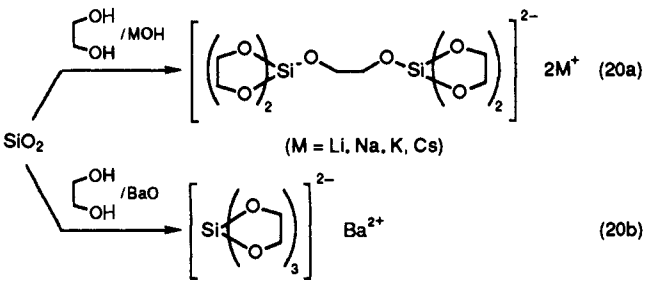


62 a : M = Na
b : M = K
c : M = Co
d : M = C_5H_5NH

Scheme 10



conditions to give exclusively pentacoordinate silicon complexes[39] (cf. eq 15). Catechol is such an effective ligand for the preparation of hypervalent silicon species that complexes **62** can be obtained not only directly from silica[116-118] but also from $[SiF_6]^{2-}2M^+$ [119] (M = Na, K) (Scheme 10), which is a byproduct of the fertilizer industry. These two preparations render complex **62** an attractive starting material for the preparation of organosilanes.[115,120] This aspect will be developed in section VII.C.2. It is worth noting that aliphatic 1,2-diols react with SiO_2 to give compounds with two pentacoordinate silicon atoms when the reaction is performed with MOH (M = Li, Na, K, or Cs)[121] (eq 20a) and the hexacoordinate complex when the reaction is performed with BaO[122] (eq 20b).

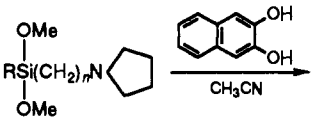


(20a)

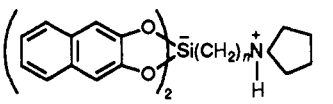
(M = Li, Na, K, Cs)

(20b)

Hexacoordinate silicon species with more than one carbon–silicon bond are less numerous than in the case of the pentacoordinate complexes. C. L. Frye[69] reported that the reaction of diphenyldimethoxysilane with catechol in the presence of triethylamine resulted in cleavage of one of the phenyl groups, affording phenylbis(1,2-benzenediolato)silicate (**21**) exclusively. In the same way pentacoordinate silicon complexes **64** are always obtained from silanes **63** with cleavage of phenyl, cyclohexyl, and even methyl groups (eq 21).[123]



63



(21)

64

(R = Ph, *n*-C_6H_{11}, Me, MeO) (*n* = 1, 2)

IV. Structures of Hypervalent Silicon Compounds

There is now a considerable body of structural data on hypervalent silicon derivatives. Several comprehensive reviews have been published on this aspect.[8,9] We will point out the most significant structural features of penta- and hexacoordinate silicon species which have been obtained from crystal data and solution NMR studies.

A. Structures of Pentacoordinate Silicon Compounds

1. Structures of Pentafluorosilicates

The results of the X-ray analysis of a series of fluorosilicates $[R_nSiF_{5-n}]^-$ (*n* = 0–3) with ligands of increasing steric bulk are now available.[22,28,32,124,125] These reveal that the geometry of the complex ions is close to trigonal bipyramidal with organic groups occupying the equatorial positions. Some observed Si–F bonds lengths are summarized in Table 3, from which

Table 3. Summary of Observed Si–F Bond Lengths (Å)

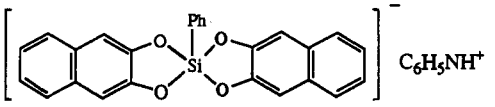
ion	axial	equatorial	ref
$[SiF_5]^-$	1.646	1.591 (av)	22
$[PhSiF_4]^-$	1.669 (av)	1.601 (av)	124
$[MesSiF_4]^-$	1.672 (av)	1.606 (av)	28
$[MePhSiF_3]^-$	1.692 (av)	1.621	32
$[(Mes)_2SiF_3]^-$	1.703 (av)	1.641	125
$[\alpha NpPh_2SiF_2]^-$	1.720		32
$[Me_3SiF_2]^-$	1.72-1.73		126

it may be seen that the lengths of axial Si–F bonds are always greater than the lengths of equatorial Si–F bonds. Moreover there is a tendency for both lengths to increase with increasing steric bulk of the organic groups as well as with the diminishing number of electronegative atoms.

2. Structures of Pentacoordinate Bicyclic Silicates

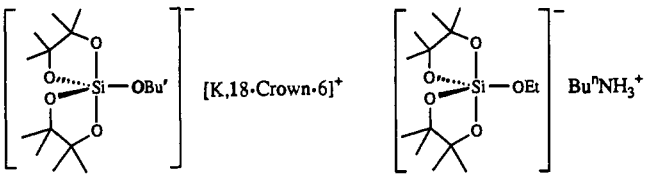
Much more structural variety is displayed by pentacoordinate bicyclic silicates. Holmes and coworkers[42,125,127-130] have explored the structures of the ions $RSi[(diolato)_2]^-$ as a function of both the group R

and the nature of the chelate and have shown that pentacoordinate bicyclic silicates, isoelectronic with phosphoranes, form a range of solid-state structures extending from the trigonal bipyramid (TBP) to the square or rectangular pyramid (RP) along the Berry pseudorotational coordinate.[131] It was observed that, as with phosphoranes,[132-133] the RP geometry is approached when two five-membered rings, containing like atoms in any one ring directly bonded to the central atom, are present. For example compound **7** is displaced by 68.7% from the trigonal bipyramid toward the square-pyramidal configuration, and **65** similarly by 97.6%.

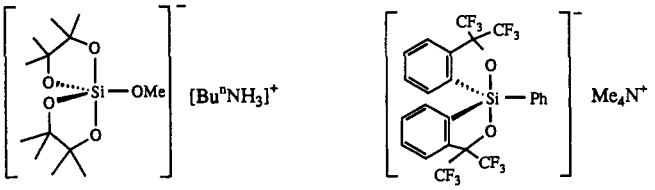


65

The spiro bispinacolate derivatives **66–68** provided[41] the first structural characterization of cyclic pentaoxysilicates. In terms of structural displacement from the TBP toward the RP, **66** is 24.1% displaced, **67** is 38.9% displaced, and **68**, 71.2%. Hydrogen bonding to the $[Bu^nNH_3]^+$ cation is certainly a factor in the greater structural displacements of **67** and **68**. The



66 **67**



68 **69**

series of compounds with two [α,α-bis(trifluoromethyl)-benzenemethanolato] ligands is also interesting. The structures of compounds **10**,[45] **11b**[48] (Scheme 2), and **69**[134] have been established and in all cases correspond to trigonal-bipyramidal geometry around the pentacoordinate silicon center, the R group occupying the equatorial position. Interestingly among the known spiro bicyclic silicates, **11b** has the highest TBP character (72.8%). The geometry of this series of compounds may derive from the substantial difference in the electronegativities of the ring carbon and oxygen atoms attached to the silicon center.

3. Structures of Pentacoordinate Silicon Compounds with Intramolecular Coordination

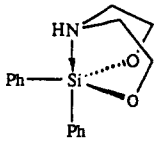
Silicon species in which pentacoordination at silicon is achieved by intramolecular ring closure of chelating groups are particularly interesting in relation to the stereochemistry of nucleophilic substitution at silicon. In these compounds, the donor atom may simulate a nucleophilic attack on silicon and these systems can serve as models for the geometry of intermediates in nucleophilic substitution at tetracoordinate silicon.

Table 4. Si–N Bond Distances (Å) in Some Silatranes (Ref 81)

X	Cl	$ClCH_2$	3-$NO_2C_6H_4$	C_6H_5 (γ)	C_6H_5 (β)	C_6H_5 (α)	CH_3
Si–N	2.02	2.12	2.12	2.13	2.15	2.19	2.17

Numerous crystal structure data concerning pentacoordinate silicon compounds with intramolecular coordination are now available.[63,65-67,79,81,82,87,135-150]

The silatranes **26** (eq 17) were one of the first intramolecular coordinated systems to be extensively studied. Structural data[79,81] show that the geometry at silicon corresponds to a distorted trigonal bipyramid with the nitrogen atom and the group X occupying axial positions. In almost all the silatranes which have been studied the Si–N distance lies between 2.0 and 2.2 Å. (Some Si–N bond distances are summarized in Table 4.) This is significantly shorter than the sum of the van der Waals radii for the silicon and nitrogen atoms (3.5 Å).[151] The presence of an electron-withdrawing substituent at the silicon atom (Cl, 3-$O_2NC_6H_4$, $ClCH_2$) shortens the interatomic Si–N distance. Insertion of a CH_2 group into the silatrane ring (3-homosilatranes) or replacement of the oxygen atom by this group (2-carbosilatranes) produces a more marked change in the geometry of the heterocycle and in the interatomic Si–N distance than does the nature of the substituent at the silicon atom.[8] It is worth noting that the X-ray analysis of compound **70** has shown it to have a bicyclic structure with nitrogen bonded to silicon. The ligands around the silicon atom form a trigonal bipyramid, as in silatrane **26** (eq 27), with a Si–N distance of 2.30 Å.[152]



70

The crystal structure of 1-phenyl-2,8,9-triazasilatrane (**27**, R = Ph) (eq 18) has been determined[87] by single-crystal X-ray diffraction. The silicon atom has a somewhat distorted trigonal-bipyramidal geometry with three N atoms in the equatorial positions and N and C(Ph) atoms in the axial positions, which are typical atrane features. The transannular N–Si bond length is 2.13 Å. Thus, replacement of equatorial oxygen atoms in the silatrane by nitrogen atoms in the triazasilatrane causes no significant change in the structure of the atrane framework and in particular in the trigonal-bipyramidal geometry of the silicon atom.

In other less constrained compounds with intramolecular dative bonds, the geometry around the silicon atom is always found to be a distorted trigonal bipyramid with the donor atom occupying an axial site. The rings formed in the chelated systems thus span axial and equatorial sites, a conformation which is favored for five-membered rings. Nevertheless examples of pentacoordinate silicon in a four-membered chelate ring are known despite ring strain.[148]

The second axial site trans to the donor atom is occupied by an electronegative atom (F, Cl, O, N) except

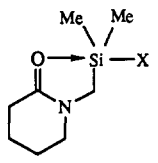
Table 5. Si–O and Si–X Bonds Lengths (Å) in Chelated Silicon Compounds 71 and 72

compd	Si–O	Si–X	ref
71a	1.954	2.307	141
71b	1.800	3.122	142
71c	1.749	3.734	143
72a	1.788	2.624	144
72b	1.879	2.432	145

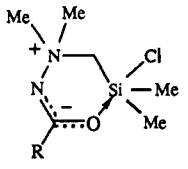
in the cases of organosilicon hydrides, discussed later. Crystal structure determinations have shown that the lengths of these coordinative bonds spread over the whole range between "normal" single bonds and "pure" van der Waals contacts, depending on the nature of the other substituents around the silicon atom. The crystal structure analysis of compound **16** for example has shown the Si–N bond length to be 1.97 Å[63] which is significantly shorter than the sum of the van der Waals radii[151] but longer than the mean covalent Si–N bond length (1.77 Å).

Bonds from silicon to other substituents are lengthened by comparison with the normal tetracoordinate distance. This is well illustrated by the molecular structure of compound **19**[67] in which the $Si_{(1)}$–$Cl_{(1)}$ bond length (2.35 Å) is 15% longer than that of the $Si_{(2)}$–$Cl_{(2)}$ bond at tetracoordinate silicon (2.05 Å).

The increase in length of the axial bond is always greater than that of the equatorial bonds (Table 3). The structures of (halodimethylsilyl)piperidones **71a–c** have been established[140,142,143] and have shown (Table 5) that the heavier the halogen, the longer is the Si–X bond and the shorter the intramolecular coordination, Si–O, so much so that in the iodo derivative **71c** it is within 10% of the typical Si–O covalent bond length. The silicon–iodine distance is not far short of that expected for an ion pair involving an iodide ion and a silicon cation, so in this case the constitution of the chelate is best represented in this way. In the same way the structures of compounds **72a**[145] and **72b**[145] show that the longer the Si–Cl bond, the closer is the approach of the oxygen atom to the silicon (Table 5).



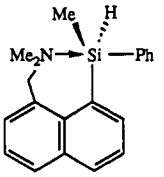
71 a : X = Cl
b : X = Br
c : X = I

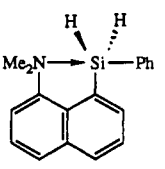


72 a : R = 4-$CH_3OC_6H_4$
b : R = CF_3

A particular case is that of the chlorosilatrane **26** (eq 17) (R = Cl) which is the only pentacoordinate chlorosilane with two short bonds in the two apical positions. The structure of **26** (R = Cl) established by X-ray diffraction[81] has shown that the Si–Cl bond is only 4% longer (2.12 Å) than the Si–Cl bond in tetracoordinate compounds (2.04 Å), while the Si–N bond (2.02 Å) is one of the shortest coordinative bonds observed in silatranes. The association of a short Si–Cl bond with a short Si–N bond in **26** (R = Cl) might be explained by the stereoelectronic overlap between the lone pairs at the oxygen atoms and the coordinative silicon–nitrogen bond. The unusual pattern of reactivity of the chlorosilatrane,[81,153] which will be reported in section VI.D.1, is most probably connected with the electronic structure and the geometry of the chlorosilatrane.

The occurrence of pentacoordination in the hydrogenosilanes is particularly interesting. The X-ray structures of **73a**,[65] **74**,[139] and **75**[139] have shown a



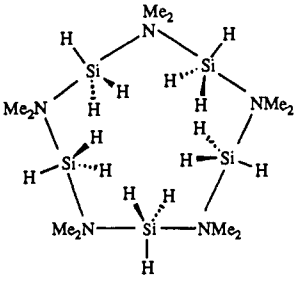


73 a : R = αNp
b : R = Ph

74

75

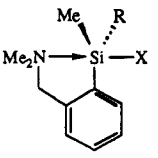
significant Si–N coordination, the geometry around the silicon center being a trigonal bipyramid. The donor nitrogen enters axially as it does in the case where the Si atom bears an electron-withdrawing group in the opposite axial site. Very interestingly, the hydrogen atoms were found to occupy equatorial sites in preference even to the aryl groups. The placement of hydrogen atoms in equatorial sites was also observed by Ebsworth et al. in compound **76**.[154]

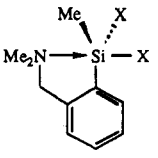


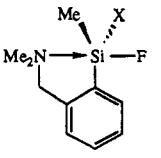
76

The observation of axial entry of the donor atom irrespective of the nature of the substituents at silicon (halogen, oxygen, or hydrogen) is supported by calculations[155] which show this geometry of attack to be preferred, even for the process corresponding to retention of configuration at silicon in nucleophilic substitution.

Variable-temperature ^1H NMR studies[64] of the monofunctional derivatives **77** and the bifunctional derivatives **78** (X ≠ H) revealed intramolecular coordination at low temperature by the presence of two signals from diastereotopic *N*-methyl groups. From







77 a : R = H
b : R = αNp

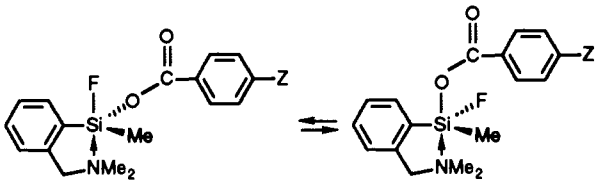
78

79

the coalescence of these signals derived free energies of activation for ring opening in the range 8–15 kcal mol^{-1} showed the stability of the chelated form to depend on X in order R < OR < H < F, SR < OAc, Cl, Br. In these systems therefore it may be concluded that the nitrogen

coordination is not a function of the electronegativity of X, as is the case of phosphorus compounds.[156] The aptitude for pentacoordination is determined by the polarizability of the Si–X bond under the influence of the donor atom.

NMR studies of bifunctional organosilanes **79**[157] containing fluorine and a range of other groups confirmed the preceding observations and established the apicophilicity of X relative to fluorine. In the ^{19}F NMR spectra of these various fluorosilanes, absorptions due to axial fluorine atoms are found at relatively low field, and an upfield shift correspondingly indicates occupation of an equatorial site. This correlation is the same as that for the phosphorus fluorides.[158] These experiments showed fluorine to be more apicophilic than hydrogen, alkoxy, or dialkylamino but less apicophilic than chlorine. In cases where X = benzoyloxy, a slow equilibrium was apparent at −95 °C in which both topomers could be distinguished (eq 22). Although that with F equatorial was always present in greater amount, the proportion was enhanced as electron-withdrawing substituents Z on the phenyl group increased the apicophilicity of the benzoyloxy moiety. The sequence of apicophilicities of X compared with apicophilicity of F increases in the order H < C(sp2) < OR, NR_2 < F < $OCOC_6H_4Z(p)$, Cl.



(22)

(Z = NO_2, H, MeO)

Interestingly this sequence parallels the tendency to inversion in nucleophilic substitution of X at a chiral silicon center and the susceptibility to racemization in nucleophilic solvents.[3a]

H, OR < F, SR < AcO, Cl, Br

increasing apicophilicity →

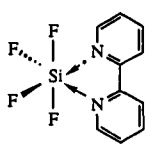
increasing rate of racemization →

shift of nucleophilic substitution mode

retention inversion →

B. Structures of Hexacoordinate Silicon Compounds

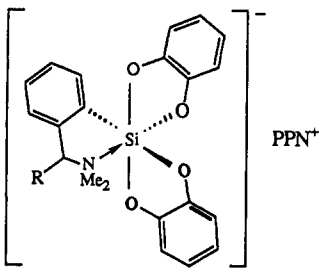
The structure of the dianion $[SiF_6]^{2-}$ was first established by X-ray diffraction in 1935,[159] and the expected octahedral geometry was found. The same geometry was found for the neutral adducts $SiF_4 \cdot 2py$[160] and $SiCl_4 \cdot 2PMe_3$[161] in which the donor ligands are in the trans arrangement and for complexes **49**[105] (Scheme 8), **62d**,[162] and **80**.[163]



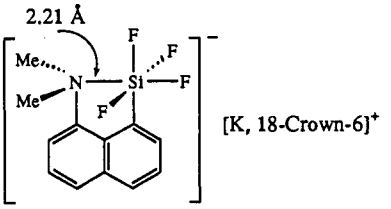
80

The structures of compounds **46**[102] and **47a**[164] have been determined. In these complexes there is addition of one bipyridine to one silicon atom which becomes octahedrally bonded. The hexacoordination of the silicon atom has also been established in compound **48b**.[104] In all cases the N–Si interactions are opposite to chlorine atoms. Moreover the N–Si distances are rather short since they are in the range 1.95 to 2.20 Å. In compounds **46c**, **47a**, and **48b**, the Si–Cl distances at the octahedral Si atom (2.15–2.40 Å) are lengthened compared with the Si–Cl distances at the tetrahedral Si atom (1.90–2.10 Å). In compound **47a** the two Si–CH_3 bond lengths were found to be 1.90 and 1.89 Å, corresponding to normal tetrahedral bond lengths.

Few examples of hexacoordinate silicon complexes with intramolecular coordination are known so far. The crystal structure of compound **81**[165] showed the Si atom to be hexacoordinated with an almost regular octahedral geometry. The angles at the silicon atom are 80° to 96°. The short Si–N distance (2.15 Å) is remarkable and is the shortest one found among such hexacoordinate silicon species known up to now. Such a strong interaction is entirely consistent with the high reactivity toward nucleophiles found for sodium phenylbis(1,2-benzenediolato)silicate[71a] (section VI.A.2).



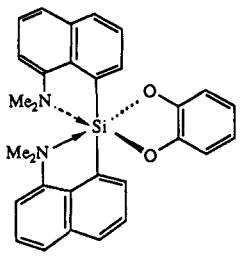
81 (R = H)
82 (R = Me)



83

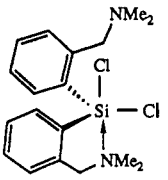
The single-crystal X-ray diffraction analysis of compound **83** reveals also that the anion adopts a slightly distorted octahedral geometry. The Si–N distance (2.21 Å)[166] is shorter than that in the pentacoordinate trifluorosilane **15** (2.32 Å).[147] This short Si–N bond could be explained by a better delocalization of negative charge onto the fluorine atoms.

The crystal structures of compounds **51–53**[107] and **84**[167] have also been determined and show that in each compound both nitrogen atoms are directed toward the silicon giving a formally hexacoordinate complex. The Si–N distances are in the range of 2.50 to 2.81 Å which is still shorter than the sum of van der Waals radii (3.5 Å).[151] The hydrogen and/or fluorine atoms are in each case cis to each other as are the two nitrogen atoms. The most striking feature of the structures of these compounds is that the silicon atom largely maintains



84

the basic tetrahedral geometry in spite of the two dative bonds with the nitrogen atoms, which leads to a structure similar to the bicapped tetrahedron. The structures can be considered as models for a tetrahedral silicon which undergoes two nucleophilic coordinations. Surprisingly compound 85 in which the silicon atom is bonded to two chlorine atoms is only pentacoordinated.[150]



85

V. Stereochemical Nonrigidity of Hypervalent Silicon Compounds

A. Pentacoordinate Silicon Compounds

Early studies by Klanberg and Muetterties[21] of the dynamic ^{19}F NMR spectra of pentacoordinate fluorosilicates suggested that these complexes, like their isoelectronic fluorophosphorane analogues,[158] were subject to more or less rapid intramolecular exchange of fluorine ligands between axial and equatorial sites in trigonal-bipyramidal structures. However, some doubt remained concerning the mechanism of site exchange, as impurity-catalyzed intermolecular fluorine exchange, comprehensively investigated by Janzen and co-workers,[23,168] was shown to be prevalent in the silicon systems. Only in 1986 did Damrauer and Danahey[27] show [K,18-crown-6]$^+$ salts of organofluorosilicates to be inert to intermolecular exchange and confirm the operation of an intramolecular process over the whole temperature range studied. More recent studies[28,29,169] in which ^{29}Si–^{19}F coupling was seen to persist in both the ^{29}Si and ^{19}F DNMR spectra throughout the temperature range covered (−100 to +30 °C) provide further proof of the intramolecular nature of the fluorine site exchange. This exchange is extremely fast for $[SiF_5]^-$ and the majority of $[RSiF_4]^-$ ions, resulting in a single ^{19}F resonance even at the lowest temperatures, but $[R_2SiF_3]^-$ ions provide limiting low-temperature spectra in which axial (low field) and equatorial (high field) fluorine atoms may be distinguished. Free energies of activation listed in Table 6 show that barriers to fluorine site exchange mostly lie in the range from about 9 to about 12 kcal mol^{-1}. The value of 12.8 kcal mol^{-1} for the activation energy for site exchange in the 2,4,6-tri-*tert*-butylphenyltetrafluorosilicate ion[28] is a uniquely elevated value for an $[RSiF_4]^-$ ion, which results from the severe steric hindrance provided by the two bulky ortho substituents on the phenyl group. A similar effect is seen for some of the $[R_2SiF_3]^-$ ions; energy barriers are by contrast lowered by electron-withdrawing groups in the para position, and a good linear relationship is obtained[31] with Hammett σ_p^+ for entries 4, 6, 8, and 11 (Table 6).

Table 6. Free Energies of Activation for Intramolecular Rearrangement of Acyclic Organofluorosilicates

entry	ion	$\Delta G^{\ddagger}$ (kcal mol^{-1})
1	$[2,4,6\text{-}Bu^t_3C_6H_2SiF_4]^-$	12.8[a,b]
2	$[4\text{-}NO_2C_6H_4)_2SiF_3]^-$	8.8[c]
3	$[(\alpha Np)_2SiF_3]^-$	9.3[c]
4	$[4\text{-}CF_3C_6H_4(Ph)SiF_3]^-$	9.7[d]
5	$[(2\text{-}MeC_6H_4)_2SiF_3]^-$	9.9[c]
6	$[4\text{-}ClC_6H_4(Ph)SiF_3]^-$	10.2[d]
7	$[Bu^t(Ph)SiF_3]^-$	10.4[c]
8	$[Ph_2SiF_3]^-$	10.4,[d] 10.6[c]
9	$[PhMeSiF_3]^-$	10.7[c]
10	$[(4\text{-}MeC_6H_4)_2SiF_3]^-$	10.7[c]
11	$[4\text{-}MeOC_6H_4(Ph)SiF_3]^-$	10.8[d]
12	$[2\text{-}MeC_6H_4(2,6\text{-}Me_2C_6H_3)SiF_3]^-$	11.3[c]
13	$[(2,6\text{-}Me_2C_6H_3)PhSiF_3]^-$	11.4,[c] 11.6[d]
14	$[(3,5\text{-}Me_2C_6H_3)(2,6\text{-}Me_2C_6H_3)SiF_3]^-$	12.3[d]
15	$[(2,6\text{-}Me_2C_6H_3)_2SiF_3]^-$	13–14[c]

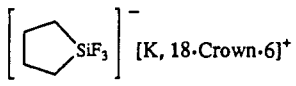
[a] E_a value. [b] Reference 28. [c] Reference 169. [d] Reference 31.

^1H DNMR studies of pentacoordinate acyclic silicates bearing ligands such as hydrogen and alkoxy have generally failed to distinguish between substituents in axial and equatorial sites, and rapid intramolecular exchange appears highly likely. An important exception to this generalization is provided[37b] by two salts $[H_2Si(OR)_3]^-K^+$ where R = Pr^i or Bu^s. NMR evidence for the occupancy of an equatorial site by one hydrogen atom, and of an axial site by another, under certain conditions, is found in both ^1H and ^{29}Si NMR spectra. Hydrogen normally occupies equatorial sites preferentially, and it is clear that the steric influence of the branched alkoxy groups is an important feature in determining the preferred conformation for these anions. It seems most likely too that coordination of the cation to the three alkoxy groups is necessary for the relative stability of this conformation, for in the presence of crown ether and in most donor solvents, only a singlet resonance is seen for the hydrogen ligands. The free energy of activation (16.3 kcal mol^{-1}) measured for the site exchange in the $[H_2Si(OPr^i)_3]^-$ ion is therefore not strictly comparable with the fluorine values. Calculations on the $[SiH_5]^-$ ion suggest a very low barrier to fluxional ligand exchange.[170]

Cyclic pentacoordinate trifluorosilicon compounds for which fluxionality has been investigated are of two types; those in which a silacarbocycle is present, and those in which ring closure is achieved by intramolecular donation from N → Si or O → Si. For the latter type of compound the dynamic behavior has been studied with many ligands other than fluorine also.

For the five-membered compounds 86,[29] 87,[30] and 88[43] fluorine site exchange occurs so readily that even at low temperatures a single ^{19}F NMR resonance only is seen, whereas for the six- and seven-membered silicates 89[29] and 90[43] the barrier for site exchange is comparable to that for the acyclic fluorosilicates (9.1 kcal mol^{-1} for 89 and 10.5 kcal mol^{-1} for 90).

In the chelated pentacoordinate silicon compounds, the values of the free energies of activation for the



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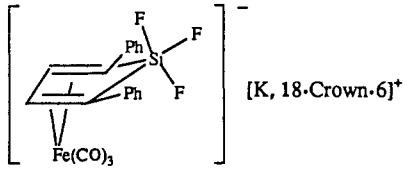

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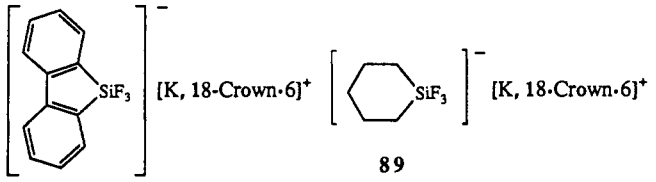
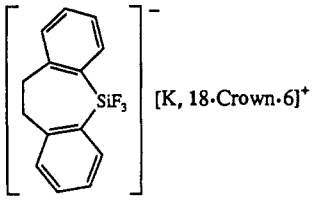


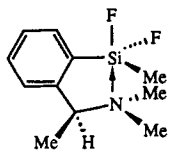
88 89



90

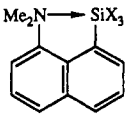
processes resulting in NMR equivalence of fluorine atoms range from 6.0 to 13.1 kcal mol^{-1}.[62,136,147,171-174] Since these values are similar to those determined for ring opening in such chelates (section IV.A.3) it is not certain that such equivalence is always due to a regular mechanism for site exchange in the pentacoordinate silane, i.e. a process in which the coordination number remains unchanged throughout, for an irregular mechanism in which the cycle is disrupted, allowing the silicon atom to become at least momentarily tetracoordinate, is also possible. This ambiguity was however eliminated in a number of instances by the incorporation of a chiral center in the α-position relative to the dimethylamino group, as an independent probe of the latter's decoordination and inversion.[147,174]

For example, in compound **91**, the limiting low-temperature ^{1}H spectrum displays[174] four separate methyl group resonances from the dimethylamino group, because of the chirality of both the benzylic



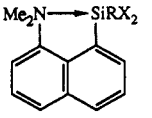
91

carbon atom and the pentacoordinate silicon atom. As the temperature is raised, a first coalescence of the four resonances to two occurs with a ΔG^* value of 9.4 kcal mol^{-1}. This arises from an intramolecular ligand exchange process, for there is a parallel coalescence of the axial and equatorial fluorine signals in the ^{19}F DNMR spectrum, characterized by a ΔG^* of 9.3 kcal mol^{-1}. In the ^{1}H spectrum the second coalescence to give a singlet for the NMe_2 signal takes place with a ΔG^* of 11.8 kcal mol^{-1} corresponding to Si–N bond opening accompanied by rotation and inversion at nitrogen. Furthermore, in peri-substituted naphthalene derivatives, where the rigid geometry of the ligand imposes close approach of the coordinating dimethylamino group to the silicon atom, the barrier to inversion of the Me_2N group is almost certainly at least 20 kcal mol^{-1}.[62,147] Values substantially lower than this for ligand or methyl group equivalence therefore reflect fluxional processes at silicon. Values for free energies of activation for site exchange processes at silicon are less than 7 kcal mol^{-1} for **92**,[175] **93**,[162] and **94**[62] but attain 12 kcal mol^{-1} for **15**.[62] They are slightly higher for **95**



92 : X = H
93 : X = OMe
94 : X = OEt
15 : X = F

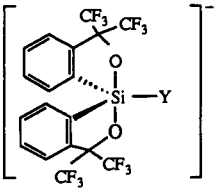
(11 kcal mol^{-1}),[62] **96** (12 kcal mol^{-1}),[62] and **98** (9 kcal mol^{-1}).[62] Compound **97** (ΔG^* = 9 kcal mol^{-1})[62] is the one example in which the occupancy of different sites by OMe ligands is directly apparent in the low-temperature ^{1}H NMR spectrum.[147]



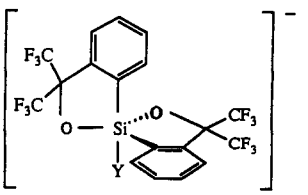
95 : R = Ph, X = Cl
96 : R = Ph, X = F
97 : R = Ph, X = OMe
98 : R = Me, X = Cl

The NMR experiments[174] show that although fluorine atoms permute between axial and equatorial sites, about the trigonal bipyramidal silicon atom in the pentacoordinate chelate, the fluorine atoms in compound **91** at all times retain their diastereotopic relationship with respect to the chiral benzylic center. For the diastereotopic distinction to be lost by permutation, it is necessary to have the five-membered ring in the diequatorial position.

The stereoisomerization of the bicyclic pentacoordinate silicates **99**,[134] and the related inversion of the



99



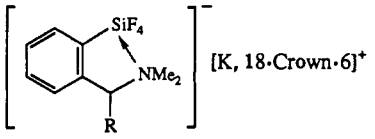
100

parent spirosilane **8** under the influence of weak nucleophiles,[176] have been extensively studied by Martin et al. Although an irregular mechanism for inversion of configuration cannot be completely excluded, it is

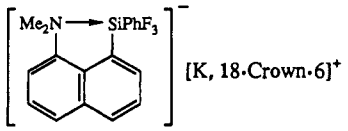
likely that the five-membered rings remain intact, even for the high energies measured for the isomerization with some of the equatorial ligands Y. The values of the free energy of activation for the inversion decrease, as the electron-withdrawing effect of the substituent increases, from 28.6 kcal mol^{-1} for Y = Bu^n to 17.5 kcal mol^{-1} for Y = F and 16.8 kcal mol^{-1} for Y = CN. An excellent linear correlation holds between the ΔG^* values and Taft σ^* inductive parameters. The highest energy structure along the pseudorotation pathway is probably **100**, in which the ligand Y occupies an apical site. The fact that this intermediate will be lower in energy the more electronegative is Y, in accord with the correlation established, is a strong argument in favor of the regular mechanism.

B. Hexacoordinate Silicon Compounds

Although the low-temperature ^{19}F NMR spectrum of the ion $[PhSiF_5]^{2-}$ shows[177] one apical and four basal fluorine atoms, with coupling of the latter to ^{29}Si, fluorine site exchange which is apparent at ambient temperature proceeds by intermolecular exchange, since coupling is lost as the fluorine resonances coalesce. Regular stereomutation has however been established[166] in a number of chelate complexes formed with ligands **13** and **14**. Free energies of activation for fluorine site exchange in fluorosilicate complexes were found to be 11 kcal mol^{-1} for **101a** and **101b** and 15 kcal mol^{-1} for **83** and **102**. Evidence for a regular mechanism is analogous to that obtained in the similar studies of their pentacoordinate precursors.



101 a : R = H
b : R = Me



102

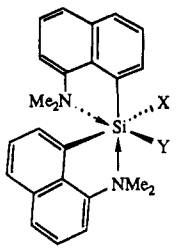
The bis(1,2-benzenediolato) chelates with benzylamine ligands, **81** and **82**, display[165] no diastereotopy of the NMe_2 groups with respect to the chirality of the hexacoordinate center, even at the lowest temperature attainable. The free energy of activation for the equivalence of the NMe_2 groups in **82** was found to be 10.5 kcal mol^{-1}. Since nitrogen inversion has been estimated to have an energy lower than 6 kcal mol^{-1},[178] this equivalence corresponds to breaking of the Si–N coordinate bond. A very rapid nondissociative stereoisomerization about silicon is therefore indicated, with a free energy of activation lower than 7 kcal mol^{-1}.

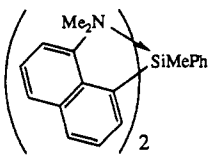
The bis-chelate complexes **52** and **103–105** are also fluxional.[179] DNMR studies have shown unambiguously that a nondissociative mechanism operates. Free energies of activation for stereomutation are given in Table 7. They are similar for all four compounds (<15 kcal mol^{-1}) and differ little with ligand electronegativity,

Table 7. Free Energies of Activation, at 300 K, for Stereoisomerization of Neutral Hexacoordinate Silicon Complexes

compd (substituents)	ΔG^* (kcal mol^{-1})
52 (H,F)	14.7
103 (H,OMe)	15.2
104 (H,Me)	9.3
105 (Me,Ph)	12.7

thus showing that hexacoordination occurs even when the silicon atom is bound only to carbon atoms, apart from the coordinated nitrogen atoms.





105

52 : X = H, Y = F
103 : X = H, Y = OMe
104 : X = H, Y = Me

VI. Reactivity of Pentacoordinate Silicon Compounds

One reason for the great interest in the chemistry of hypervalent silicon species originates in mechanistic studies performed on the racemization, hydrolysis, and alcoholysis[180,181] of tetracoordinate chlorosilanes. These reactions have been shown to be activated by nucleophiles, and kinetic data have established that the rate laws in both cases are very similar and involve two molecules of nucleophilic reagent (Scheme 11).

Scheme 11

$$v_{rac} = k_{rac}\,[R_1R_2R_3Si\text{-}Cl]\,[Nu]^2$$

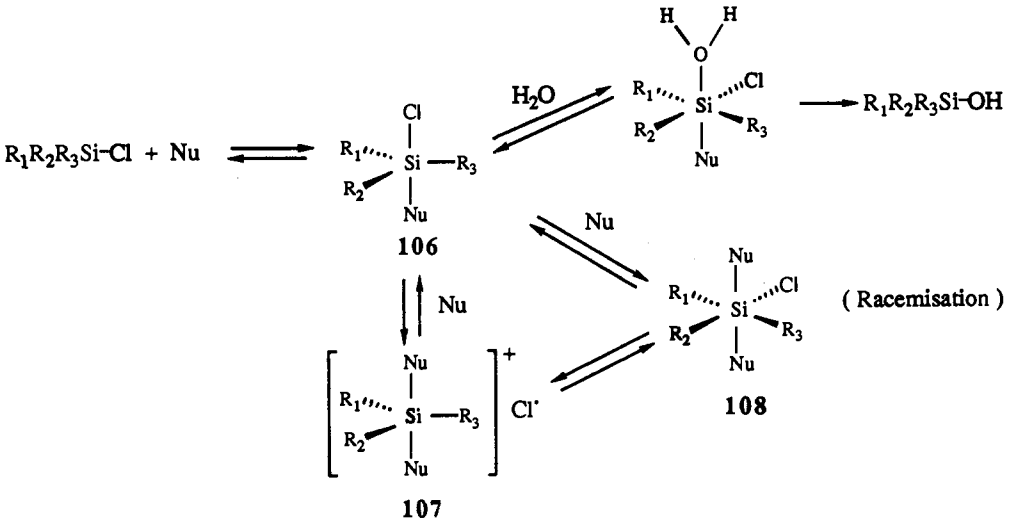
$$v_{H_2O} = k'_{H_2O}\,[R_1R_2R_3Si\text{-}Cl]\,[H_2O]\,[Nu]$$

Nu = Nucleophilic catalyst

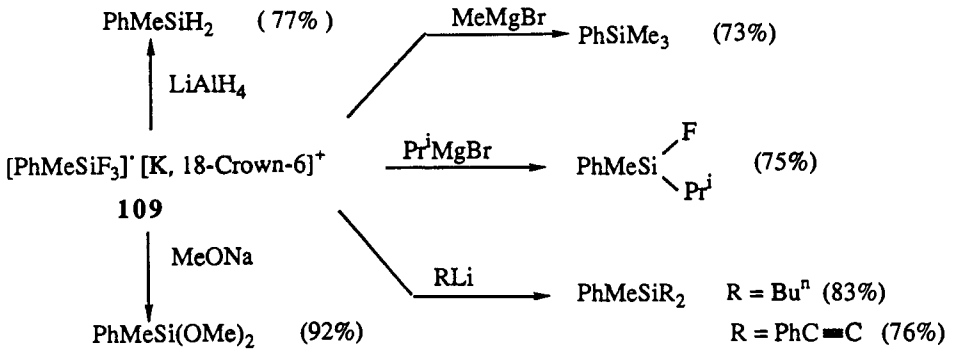
Entropies of activation were evaluated as $\Delta S^* = -40$ to -60 e.u. and enthalpies of activation as small as $\Delta H^* < 3$ kcal mol^{-1}. These features point to a mechanism controlled by the entropy of activation. The mechanism proposed (Scheme 12) involves an initial and reversible attack of the activating nucleophilic catalyst on the substrate to give a pentacoordinate silicon intermediate **106**. This is followed in the rate-determining step by reaction with a second molecule of the same nucleophile in the case of racemization and by reaction with a molecule of the incoming nucleophile which substitutes the Si–X bond in the case of "nucleophile-assisted" nucleophilic substitution at silicon. The large negative values of the entropy of activation are consistent with highly organized transition states. In the case of racemization a symmetrical species **107** or **108** is formed in the second step; the pathway for substitution is identical except for the nature of the nucleophile which is then the substituting reagent.

The mechanistic implications of this process are the following:

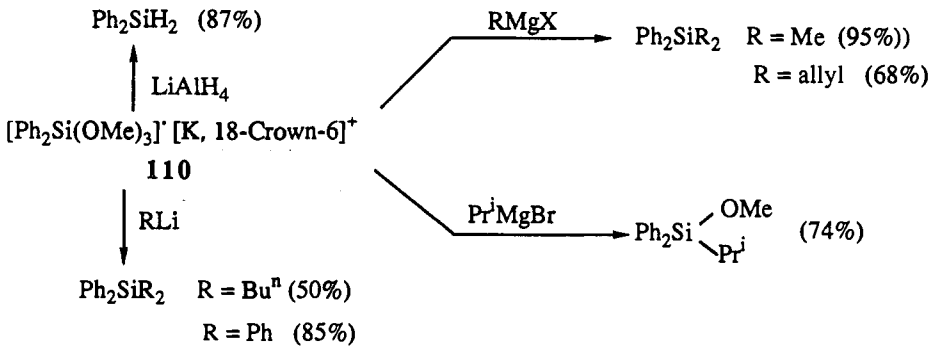
Scheme 12



Scheme 13



Scheme 14



(1) The pentacoordinate silicon species **106** must react faster with nucleophiles than the starting tetracoordinate silane, since there is acceleration of the racemization and of the hydrolysis of chlorosilanes in the presence of a nucleophilic catalyst even if the silicon species **106** is negatively charged (in the case of nucleophilic activation by F^- or RCO_2^- for instance).

(2) The rate-determining step involves nucleophilic attack on a pentacoordinate silicon atom via a hexacoordinate intermediate (or transition state).

It is in this context and in order to elucidate the mechanistic implications of this process that the study of the reactivity of pentacoordinate silicon species toward nucleophiles has been developed. The features favoring the transformation of a pentacoordinate silicon species to a hexacoordinate one have been investigated.

A. Pentacoordinate Alkyl- and Arylsilicates

1. Pentacoordinate Fluoro- and Methoxyorganosilicates

a. Reaction with Organometallic Compounds. The pentacoordinate silicates **109–112** react[33,182] with nucleophiles such as $LiAlH_4$, RMgX, RLi, and MeONa to give the tetravalent silicon derivatives in good yields (Schemes 13–15).

Interestingly these pentacoordinate silicates are much more reactive than the corresponding tetracoordinate silanes with hindered Grignard reagents such as Pr^iMgBr or Bu^tMgBr. Semiquantitative comparisons of the relative reactivity are shown in Scheme 16. These experimental results are supported by calculations which show that the positive charge on the central silicon atom is at least maintained[183] and may well be in-

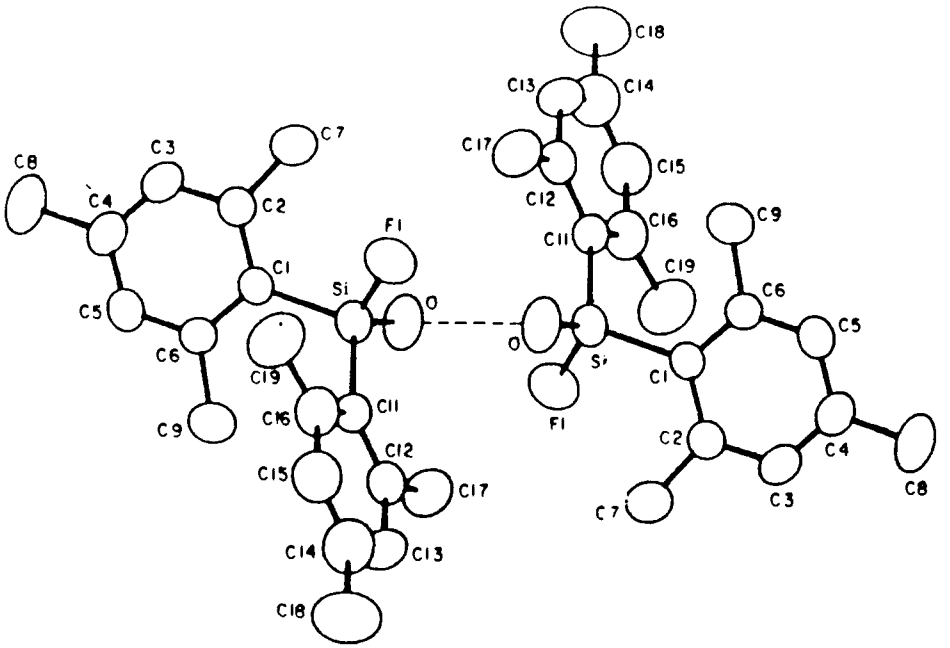
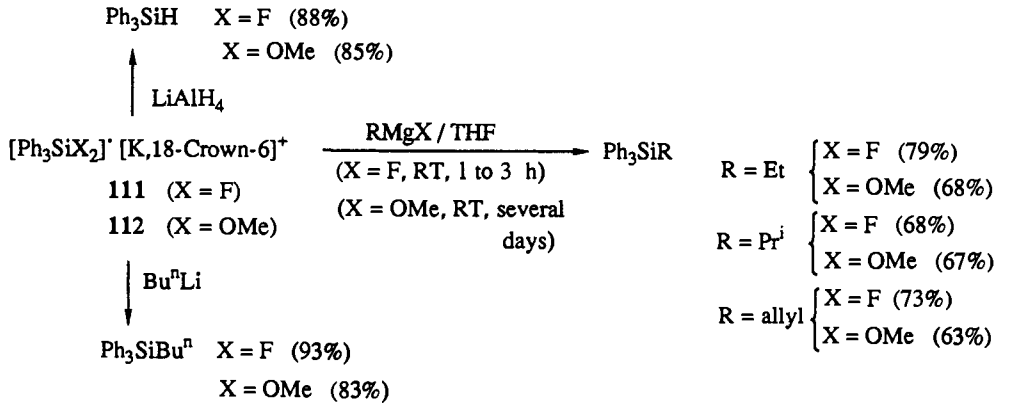
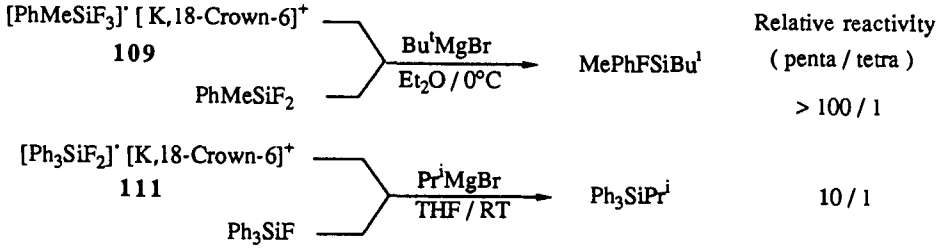


Figure 1. ORTEP plot of the anion in $\{[Me_2Si(F)O]_2[H]\}^-[Et_4N]^+$. The interaction of the oxygen atoms with the protons is indicated by a dashed line.

Scheme 15



Scheme 16



creased[184] by coordination of an additional ligand, even when the lignd is anionic (fluoride or hydride ion). The residual positive charge on silicon together with the lengthening of the silicon–ligand bonds, particularly in the apical position of the five-coordinate intermediate, as reproduced by the calculations, account for the higher reactivity of the pentacoordinate silicon species. The high reactivity of pentacoordinate organofluorosilicates toward nucleophiles was also evident in the study of the hydrolysis of dimesityldifluorosilane Mes_2SiF_2.[125] This compound does not react with water in refluxing acetonitrile. However rapid reaction occurs when tetraethylammonium fluoride hydrate is introduced. To confirm that $[Mes_2SiF_3]^-$, which was presumed to be formed in this process, is indeed very sensitive to hydrolysis, $[Mes_2SiF_3]^-[K, 18\text{-crown-6}]^+$ was prepared. This preformed complex was found to be extensively hydrolyzed after 5 min in aqueous acetone. In the two hydrolytic procedures the same silicon-containing products were found, viz. the hydrogen bisilonate $\{[Mes_2Si(F)O]_2[H]\}^-Et_4N^+$ and the disiloxane $(Mes_2SiF)_2O$. The hydrogen bisilonate, the structure of which was established by X-ray analysis (Figure 1), was postulated to be an intermediate in the hydrolysis pathway from $[Mes_2SiF_3]^-$ to $(Mes_2SiF)_2O$.

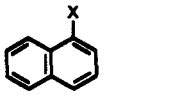
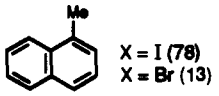
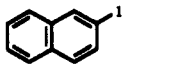
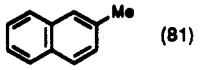
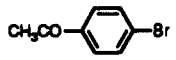
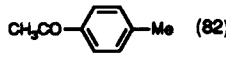
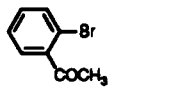
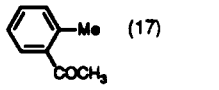
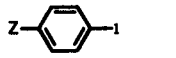
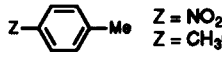
b. Cross-Coupling Reaction of Pentacoordinate Fluoroorganosilicates with Aryl Halides. Tris-(diethylamido)sulfonium difluorotrimethylsilicate (TAS

$TMSF_2$) was found to deliver a methyl group to an aryl halide[185] chemoselectively, in the presence of a catalytic amount of allylpalladium chloride dimer (eq 23, Table 8).

$$Ar\text{–}X + [(CH_3)_3SiF_2]^- \xrightarrow{(\eta^3\text{-}C_3H_5PdCl)_2} Ar\text{–}CH_3 \quad (23)$$

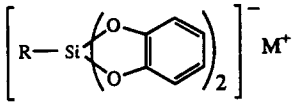
This reaction constitutes a simple preparation of methylated aromatic compounds through pentacoordinate organosilicates.

Table 8. Methylation of Aromatic Halides with TAS $TMSF_2$ Catalyzed by Allylpalladium Chloride Dimer

halide	product (yield)
	 X = I (78) X = Br (13)
	 (81)
	 (82)
	 (17)
	 Z = NO_2 (86) Z = CH_3OCO (84)

2. Pentacoordinate Bis(1,2-benzenediolato)organosilicates

a. **Reaction with Nucleophilic Reagents.** The bis(1,2-benzenediolato)organosilicates **113–115** were also found[71a,186] to be very reactive toward nucleophilic reagents such as RMgX, RLi and metallic hydrides.



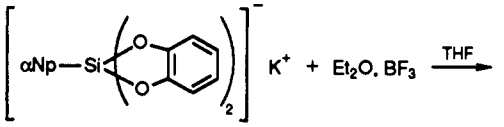
113 : R = Me
114 : R = Ph
115 : R = αNp

{ a : M = Na
b : M = K

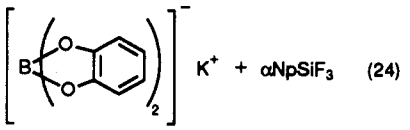
Treatment with 3 molar equiv of an organolithium or organomagnesium reagent led to the tetrasubstituted silanes $RSiR'_3$ (Scheme 17). Addition of only 2 molar equiv of organometallic reagent (R'MgX or R'Li) apparently gave the intermediate **116**, which, without being isolated, could subsequently be reduced by lithium aluminum hydride to give organosilanes of type RR'_2SiH, or by reaction with other nucleophilic reagents to give further organosilicon compounds (Scheme 18). However in some cases (for purification purposes) it is better to hydrolyze the intermediate and isolate and purify **117** before adding the second nucleophile (Scheme 19).

A study of the reactivity of complexes **113a–115a** toward Grignard reagents containing a hydrogen atom in the β position, activated by Cp_2TiCl_2, has been made.[187] These Grignard reagents in the presence of certain transition metal compounds have been found to be as powerful reducing agents as $LiAlH_4$ toward Si–X bonds.[188] The use of this method permits the preparation of hydrosilanes in one step from complexes **113a–115a** (Scheme 20). The reaction product depends on the nature of the Grignard reagent. Primary alkyl Grignard reagents give monohydrosilanes whereas secondary and tertiary alkyl Grignard reagents yield dihydrosilanes. As will be shown in section VII.C.2, in the case of the reaction of primary Grignard reagents, the initial reaction with the Grignard reagent gives intermediate **116**, which is then reduced "in situ". In the case of tertiary Grignard reagents it has been suggested that reduction of the complex to $RSiH_3$ first occurs, followed by reaction of Grignard reagent in the presence of Cp_2TiCl_2 to give the dihydrosilane. This is supported by the fact that complex **115a** reacts with Bu^tMgBr (3 molar equiv) in the presence of Cp_2TiCl_2 (1.5 molar equiv) to give $\alpha NpSiH_3$, and that $\alpha NpSiH_3$ in its turn reacts with Bu^tMgBr in the presence of Cp_2TiCl_2 to give $\alpha NpBu^tSiH_2$.

Lewis acids such as BF_3 induce ligand exchange in complex **115b** to give the borate **118** in good yield[119] (eq 24).

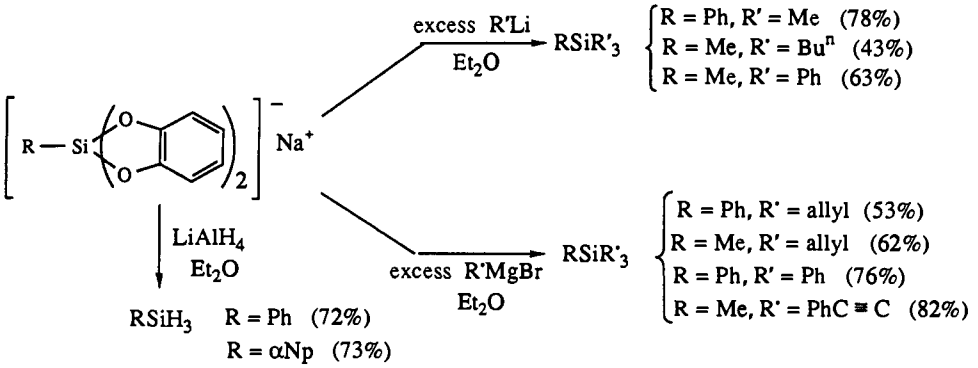


115b

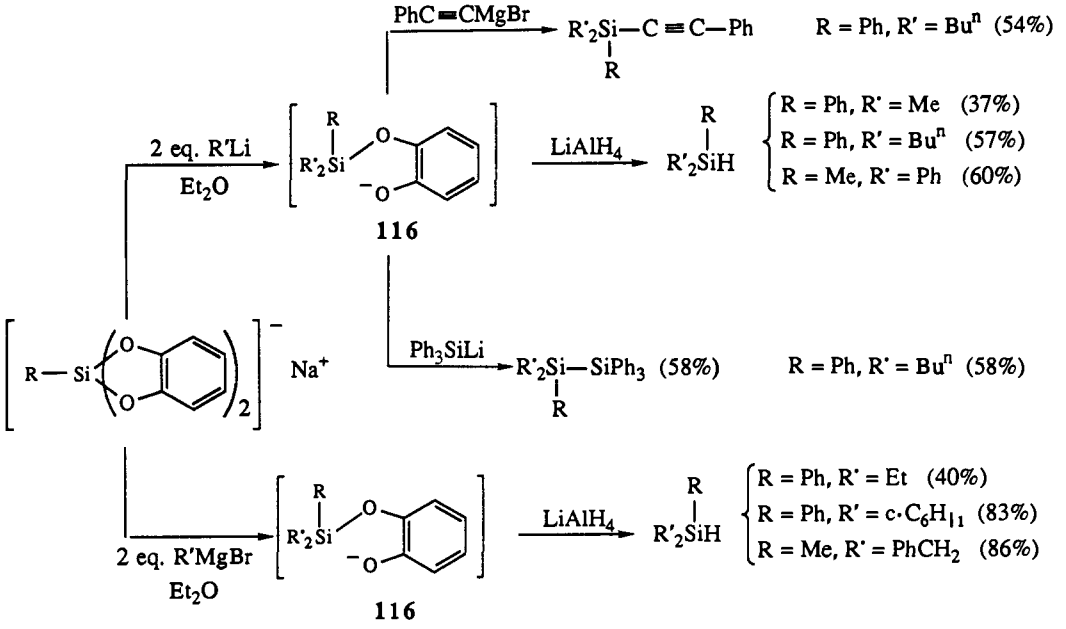


118 (24)

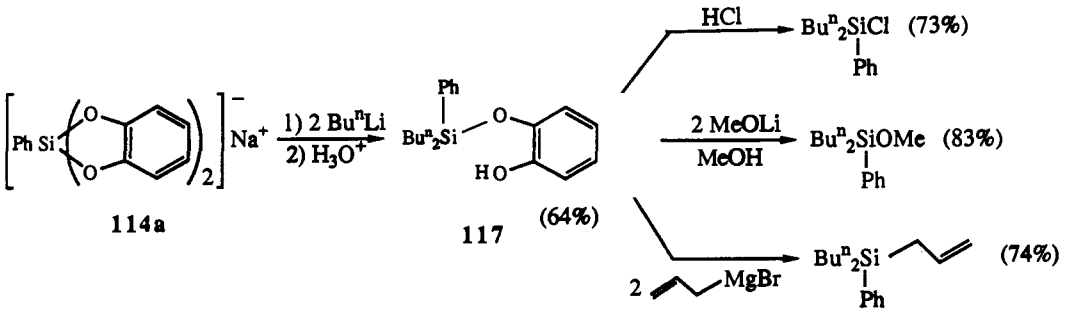
Scheme 17



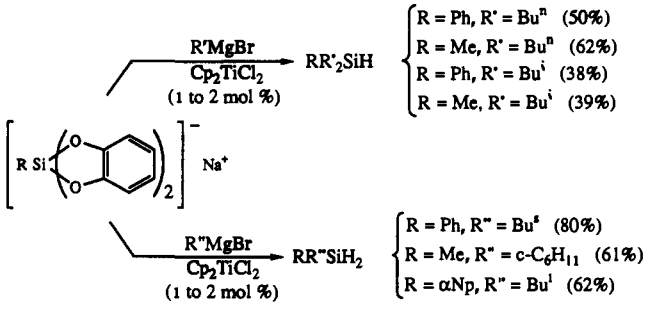
Scheme 18



Scheme 19



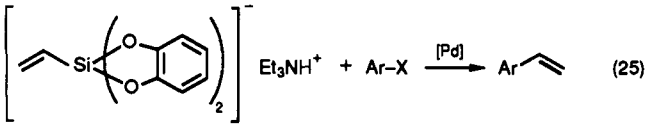
Scheme 20



R' : primary Grignard reagent

R" : secondary or tertiary Grignard reagent

b. Cross-Coupling Reaction of Vinylsilicate with Organic Iodides and Triflates. The pentacoordinate vinylsilicate **119** reacts with aryl and vinyl iodides and aryl triflates in the presence of a palladium complex to give the corresponding cross-coupled products stereospecifically[189] (eq 25 and Table 9). This cross-

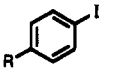
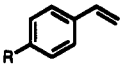
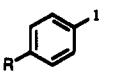
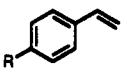
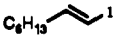
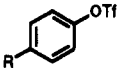
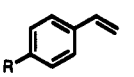
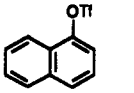
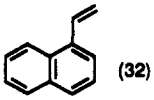


(25)

119

coupling reaction can be achieved directly from vinyltrimethoxysilane and catechol without isolation of **119**.

Table 9. Pd-Catalyzed Cross-Coupling of Complex 119 with Organic Halides and Triflates in Dioxane at Reflux During 60 h

organic halide	catalyst	product (yield %)
	$[PdCl(C_3H_5)]_2$	 R = H (30) R = NO_2 (76)
	$PdCl_2(PhCN)_2$	 R = Me (38) R = OMe (35) R = NO_2 (84)
	$PdCl_2(PhCN)_2$	 (29)
	$Pd(PPh_3)_4$	 R = CH_3CO (52) R = NO_2 (57)[a] R = CHO (41)
	$Pd(PPh_3)_4$	 (32)

[a] Refluxing for 12 h.

B. Pentacoordinate Hydridosilicates

1. Pentacoordinate Alkoxyhydridosilicates

Pentacoordinate hydridosilicates have been postulated as the reactive species in the reduction of carbonyl compounds with hydrosilanes in the presence of fluoride or alkoxide ion.[16,73,190,191] The isolated species $[HSi(OEt)_4]^-K^+$ (**120**) and $[H_2Si(OPr^i)_3]^-K^+$ (**121b**) were studied in detail.[35,36,37,192] They show much more variety

in their reactions than $HSi(OR)_3$ since they can behave as electrophile reagents, basic reagents, reducing reagents, and SET reagents.

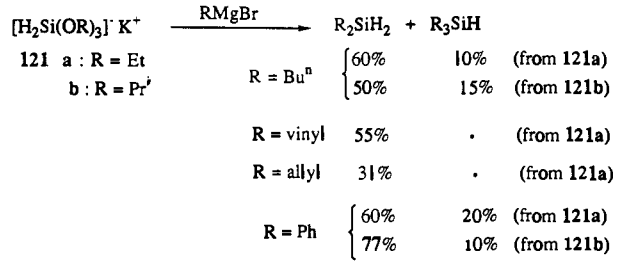
a. Reaction with Grignard Reagents. The electrophilic character of the silicon atom in hydridosilicates was demonstrated in reactions with Grignard reagents. **120** reacted readily with a slight excess of Grignard reagent at low temperature to give trialkylsilanes R_3SiH in good yield[36] (eq 26). Similarly dihydrosilicates

$$[HSi(OEt)_4]^-K^+ + \underset{\textbf{120}}{} \quad 3RMgBr \xrightarrow[-78\ ^\circ C\ \text{to}\ 0\ ^\circ C/2\ h]{THF} R_3SiH$$

$$R = Ph\ (66\%),\ R = Bu^n\ (62\%),\ R = PhCH_2\ (70\%) \qquad (26)$$

121a and **121b** underwent nucleophilic displacement at silicon with Grignard reagents to give a mixture of diorganosilanes R_2SiH_2 and triorganosilanes R_3SiH[37] (Scheme 21). The reaction took place readily under

Scheme 21



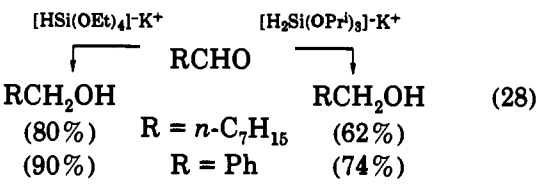
mild conditions with **121a**. Higher temperatures were required in the case of **121b**. This reaction constitutes a convenient way to prepare divinyl- and diallylsilanes, compounds of these types not being easily accessible by conventional methods. Moreover the formation of R_2SiH_2 provides good chemical evidence for the structure of **121a** which has not been isolated because of fast redistribution reactions.[37b]

b. Basic Reactions. **120** and **121b** exhibit basic properties. Reaction with phenylacetylene in THF gave potassium acetylide which was trapped with Me_3SiCl[36,37b] (eq 27). In a similar manner the metalation of Ph_3CH was effected by **120**, as shown by the recovery of Ph_3CD in 35% yield after deuterolysis.

$$PhC{\equiv}CH \xrightarrow[THF/-20\ ^\circ C]{\textbf{120 or 121b}} PhC{\equiv}C^-K^+ \xrightarrow{Me_3SiCl} PhC{\equiv}CSiMe_3 \qquad (27)$$

87% from **120**
82% from **121b**

c. Reduction of Carbonyl Compounds. Hydridosilicates **120** and **121b** were found to reduce aldehydes and ketones in the absence of a catalyst and under very mild conditions[36,37] (eqs 28 and 29). Yields of primary and secondary alcohols were generally high. Lower yields were obtained in the case of $PhCOCH_3$ with both reducing agents because of partial enolization of the ketone. It is important to note also that the reduction of benzophenone gave only benzhydrol. No trace of the blue ketyl radical anion was detected, and no benzopinacol was isolated. Furthermore a dilute mixture of **120** or **121b** and benzophenone gave no ESR



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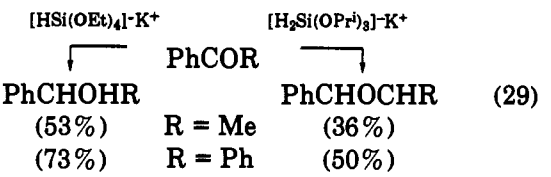
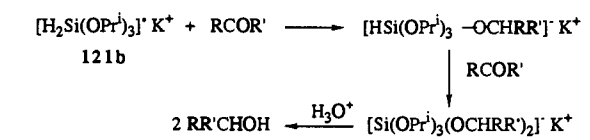


(29)

signal. It is thus clear that the reduction proceeds by a heterolytic pathway.

In the case of the dihydrosilicate **121b** both hydrogen atoms are utilized in the reduction of carbonyl compounds, probably in two successive steps (Scheme 22).

Scheme 22



120 reduces esters to alcohols with good yields[36] (eq 30) and even amides to aldehydes[193] (eq 31). Under similar

$$RCO_2Et + 2[HSi(OEt)_4]^-K^+ \xrightarrow{THF\ H_3O^+} RCH_2OH \qquad (30)$$

$$R = Ph\ (86\%);\ R = n\text{-}C_{11}H_{23}\ (65\%)$$

$$RCONMe_2 + [HSi(OEt)_4]^-K^+ \xrightarrow{THF\ H_3O^+} RCHO \qquad (31)$$

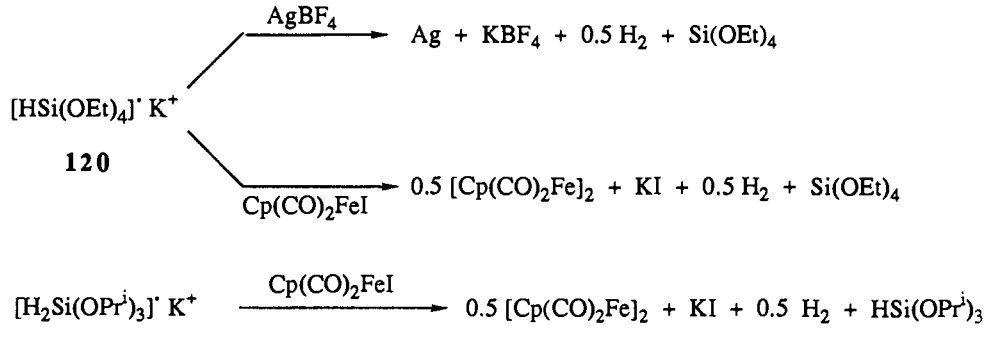
$$R = Ph\ (69\%);\ R = p\text{-}ClC_6H_4\ (60\%);\ R = p\text{-}MeOC_6H_4\ (86\%)$$

conditions, triethoxysilane and triisopropylsilane were found to be completely unreactive. The high reactivity of $[HSi(OEt)_4]^-K^+$ and $[H_2Si(OPr^i)_3]^-K^+$ toward carbonyl compounds thus strongly supports the involvement of pentacoordinate silicates as reactive species in the case of the reduction of carbonyl compounds by $HSi(OEt)_3$ in the presence of alkoxide or fluoride ions[16] (section VIII.A.2).

d. Hydridosilicates as Single Electron-Transfer Reagents. The ability of **120** to react by single-electron transfer was displayed in its reaction with oxidizing reagents such as $AgBF_4$.[36] Evolution of dihydrogen was observed and $Si(OEt)_4$ was recovered in good yield. Moreover **120** and **121b** both reacted with $Cp(CO)_2FeI$ to give quantitatively the dimer $[Cp(CO)_2Fe]_2$[36,37b] (Scheme 23).

Furthermore the ESR spectra of solutions of **120** and **121b** in *p*-dinitrobenzene (DNB) or 2,6-di-*tert*-butylbenzoquinone (DTBQ) correspond to those of the radical anion of DNB or DTBQ. These results indicate that the hydridosilicates studied can behave as SET reagents. In constrast, neither solutions of neutral penta- or hexacoordinate hydrogenosilanes such as **73** or **51** nor the fluorosilicate **111** (Scheme 15) give an ESR signal with 2,6-di-*tert*-butylbenzoquinone under

Scheme 23



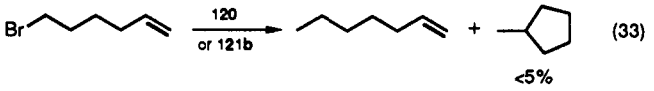
similar conditions. $HSi(OEt)_3$ itself did not produce the radical anion when mixed with *p*-dinitrobenzene.

e. Reaction with Organic Halides. Pentacoordinate hydridosilicates **120** and **121b** are also able to reduce alkyl halides to the corresponding alkane[36,37b] (eq 32) under conditions where $HSi(OEt)_3$ is unreactive.

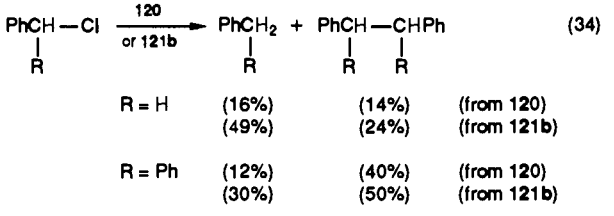
$$n\text{-}C_{12}H_{25}\text{-}X \xrightarrow[\text{or 121b}]{120} n\text{-}C_{12}H_{26} \quad (32)$$

X = Cl (33% from **120**)
X = Cl (25% from **121b**)
X = Br (47% from **120**)
X = Br (81% from **121b**)

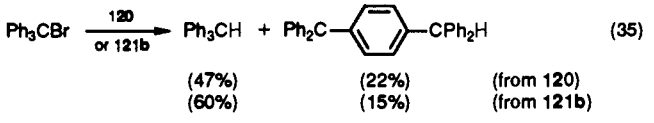
In order to get information about the mechanism of the reduction, the reduction of 6-bromo-1-hexene was investigated. In both cases, 1-hexene (eq 33) was the



major product and less than 5% of methyl cyclopentane was obtained. These results suggest that a hydride transfer process is operating in the reduction of primary alkyl halides, rather than a SET mechanism. In the base of benzyl halides or diphenylmethyl chloride the corresponding dimers were obtained in addition to toluene or diphenylmethane (eq 34). The reaction of



Ph_3CBr with **120** or **121b** gave a mixture of Ph_3CH and of (4-tritylphenyl)diphenylmethane (eq 35) after hydrolysis. Moreover in both cases the reaction mixtures gave ESR spectra consistent with the resonance of the trityl radical, which would be generated by one electron transfer from the hydridosilicate to Ph_3CBr. Thus two distinct mechanisms appear to be possible in these reactions: a mechanism of direct nucleophilic substitution for the reduction of primary alkyl halides and a SET mechanism for the reduction of benzylic or trityl halides.



f. Alcoholysis of Hydridosilicates. The course of the alcoholysis of $[HSi(OR)_4]^-K^+$ and $[H_2Si(OR)_3]^-K^+$ was studied[194] and compared with the alcoholysis of $HSi(OR)_3$. In the presence of 18-crown-6 ether the hydridosilicates $[HSi(OR)_4]^-K^+$ (R = Me, Et, Bu^n, Ph) reacted with alcohols with rapid evolution of dihydrogen and formation of pentaalkoxysilicates (eq 36). When the reaction was performed in the absence of crown ether (eq 37), the tetraalkoxysilane was the product,

$$[HSi(OR)_4]^-K^+ + ROH + 18\text{-crown-}6 \rightarrow [Si(OR)_5]^-[K,18\text{-crown-}6]^+ + H_2 \quad (36)$$
R = Me, Et, Bu^n, Ph

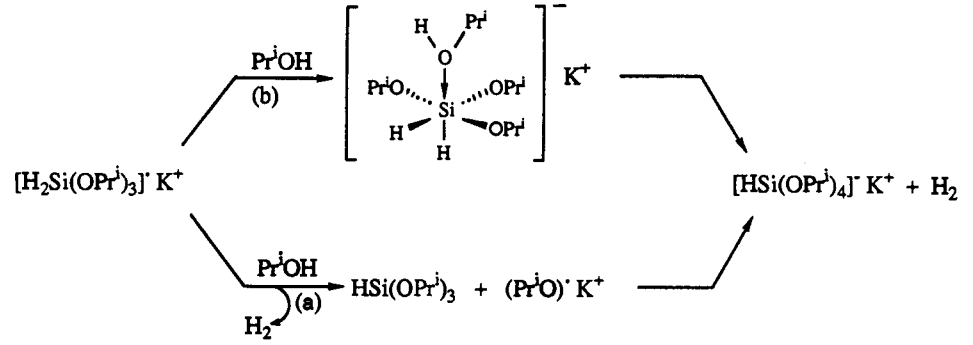
$$[HSi(OR)_4]^-K^+ + ROH \rightarrow Si(OR)_4 + H_2 + RO^-K^+ \quad (37)$$

not the pentaalkoxysilicate. In this case dihydrogen was evolved very quickly and $Si(OR)_4$ no doubt resulted from the decomposition of the transient pentacoordinate species $[Si(OR)_5]^-K^+$ which is very unstable in the absence of crown ether. Consequently in the presence of ROH, $[HSi(OR)_4]K^+$ undergoes nucleophilic substitution to give a new pentacoordinate silicon derivative $[Si(OR)_5]^-K^+$, which can be isolated only in the presence of crown ether. It is important to note that $HSi(OR)_3$ does not react with alcohols in the absence of a catalyst.

The dihydrosilicate $[H_2Si(OPr^i)_3]^-K^+$ reacted with 1 equiv of 2-propanol to give quantitatively the pentacoordinate silicon derivative $[HSi(OPr^i)_4]^-K^+$. The formation of $[HSi(OPr^i)_4]^-K^+$ can be observed in this case since it is a stable compound even in the absence of crown ether. This reaction can be rationalized in two different ways, either as an acid–base reaction (Scheme 24, reaction a), followed by the formation of the pentacoordinate hydridosilicate, or as a nucleophilic substitution reaction at silicon via a hexacoordinate intermediate (or transition state) (Scheme 24, reaction b).

The mechanism involving an acid–base reaction has been ruled out.[36] So it can be concluded that the reaction proceeds through direct nucleophilic substitution at silicon involving a hexacoordinate silicon intermediate. It is worth noting that the alcoholysis of hydridosilicates constitutes the first example of nucleophilic substitution at a pentacoordinate silicon

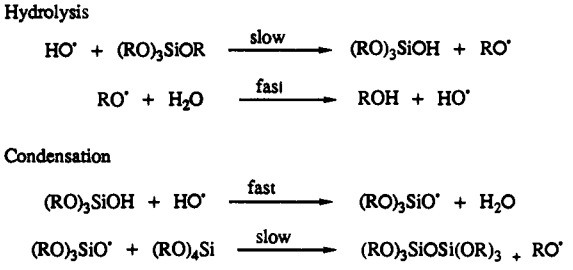
Scheme 24



species leading to another pentacoordinate silicon species.

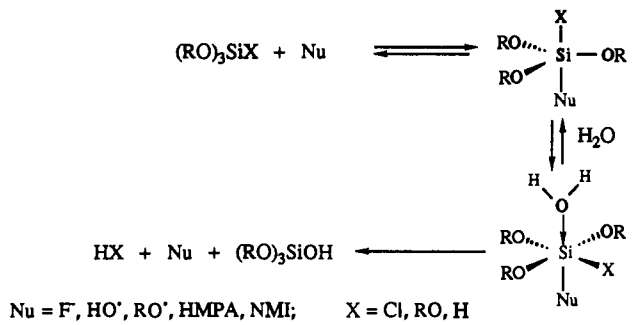
g. Role of Pentacoordinate Intermediates in the Hydrolysis Reactions of Organic Silicates. During the past decade there has been enormous growth in interest in the sol–gel process.[195,196] This process can provide practical routes for a new generation of advanced materials for structural, electrical, optical, and optoelectronic applications. The key reaction in the sol–gel process for the preparation of silica is the hydrolysis of an organic silicate, usually $Si(OMe)_4$ or $Si(OEt)_4$. In basic conditions two mechanisms may be proposed.[197] The first is an SN_2 reaction induced by OH^- (Scheme 25), and the second, a nucleophilic

Scheme 25



substitution reaction assisted by a nucleophile, with formation of a pentacoordinate silicate (Scheme 26).

Scheme 26



With a view to determining the possible role of pentacoordinate anionic silicon species in the process, the hydrolysis and gel times of the isolated pentaalkoxysilicates $[Si(OR)_5]^-[K,18\text{-crown-}6]^+$ (R = Me, Et, Ph) were studied[194] and compared to the hydrolysis and gel times of $Si(OR)_4$ and $Si(OR)_4$ in the presence of 10% ROK (R = Me, Et, Ph). The tetravalent silicon derivatives $Si(OR)_4$ (R = Me, Et, Ph) were found to hydrolyze with difficulty under neutral conditions. When a catalytic amount of ROK was added, the rate of the hydrolysis reaction increased; even more rapid hydrolysis was observed with silicates $[Si(OR)_5]^-[K,18\text{-crown-}6]^+$. For example the hydrolysis of $Si(OPh)_4$ gave a gel only after 5 days. When 10% of PhOK was added a monolithic gel was obtained after 40 min. Finally a gel appeared immediately on hydrolysis of $[Si(OPh)_5]^-[K,18\text{-crown-}6]^+$ (Table 10).

Table 10. Hydrolysis of $Si(OR)_4$ and $[Si(OR)_5]^-$ in THF at Room Temperature

entry	silicate	reaction time	aspect
1	$Si(OMe)_4$	5 days	viscous liquid
2	$Si(OMe)_4$ + 10% MeOK	7 h	liquid + solid
3	$[Si(OMe)_5]^-[K,18\text{-crown-}6]^+$	<1 min	white precipitate
4	$Si(OEt)_4$	7 days	liquid
5	$Si(OEt)_4$ + 10% EtOK	4 h	liquid
6	$[Si(OEt)_5]^-[K,18\text{-crown-}6]^+$	2–3 h	early stage of gelification
7	$Si(OPh)_4$	5 days	early stage of gelification
8	$Si(OPh)_4$ + 10% PhOK	40 min	white precipitate
9	$[Si(OPh)_5]^-[K,18\text{-crown-}6]^+$	<1 min	gel

These results cannot all be interpreted by a base-catalyzed reaction (Scheme 25). Indeed PhO^- is less basic than EtO^- but reacts faster (Table 10, compare entries 4 and 5 with entries 7 and 8). These results, which are in agreement with the greater susceptibility to hydrolysis of isolated pentacoordinate silicates, suggest that RO^- acts as a coordinating nucleophilic agent in these reactions; the mechanism of basic catalysis could be in fact a nucleophilic assistance. However during the hydrolysis of $Si(OR)_4$ and $[Si(OR)_5]^-[K,18\text{-crown-}6]^+$ it did not prove possible to isolate any intermediate, therefore no real proof of the proposed mechanism (cf. Scheme 24, route b) was obtained. In order to shed some light on this mechanism, the hydrolysis of $HSi(OR)_3$ (R = Me, Et, Bu^n, Pr^i, Ph) in neutral and basic conditions was compared to that of the preformed pentacoordinate silicon derivatives $[HSi(OR)_4]^-K^+$. The presence of the Si–H bond helps in following the course of the reaction by virtue of its prominent band in the IR spectrum and the possibility of observing the evolution of dihydrogen. The hydrolysis reactions were studied in dilute solutions in THF. The results are reported in Table 11, from which the following conclusions may be drawn.

The hydrolysis of $HSi(OR)_3$ (R = Me, Et, Bu^n, Pr^i, Ph) is slow (several days) in neutral or acidic conditions. The IR spectra of the hydrolysis products showed that the Si–H bond was still present except in the case of $HSi(OPh)_3$. This means that hydrolysis of Si–OR bonds

Table 11. Hydrolysis of $HSi(OR)_3$ and $[HSi(OR)_4]^-K^+$ in THF at Room Temperature

entry	starting material	reaction time	aspect	Si-H bond: ν (cm^{-1})
1	$HSi(OMe)_3$	5 days	liquid + gel	2254
2	$[HSi(OMe)_4]^-K^+$	<1 min	powder	no Si-H
3	$HSi(OEt)_3$	5 days	viscous liquid	2252
4	$HSi(OEt)_3$ + EtOK (10%)	1 h	gel	no Si-H
5	$[HSi(OEt)_4]^-K^+$	13 min	gel	no Si-H
6	$HSi(OBu^n)_3$	5 days	liquid	2245
7	$HSi(OBu^n)_3$ + Bu^nOK (10%)	15 h	gel	no Si-H
8	$[HSi(OBu^n)_4]^-K^+$	2 h	gel	no Si-H
9	$HSi(OPr^i)_3$	5 days	liquid	2238
10	$HSi(OPr^i)_3$ + Pr^iOK (10%)	7 days	viscous liquid	no Si-H
11	$[HSi(OPr^i)_4]^-K^+$	30 h	gel	no Si-H
12	$HSi(OPh)_3$	7 days	gel	2243 (very weak)
13	$HSi(OPh)_3$ + PhOK (10%)	20 min	gel	no Si-H
14	$[HSi(OPh)_4]^-K^+$	3 min	gel	no Si-H

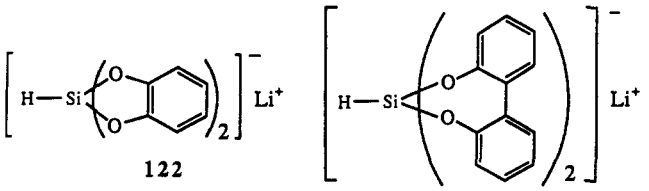
occurs before hydrolysis of the Si-H bond. Hydrolysis of trialkoxysilanes (R = Et, Bu^n, Ph) was greatly favored by the addition of 10% of the corresponding potassium alkoxide (aryloxide) (Table 11). With all these compounds evolution of dihydrogen occurred with formation of a gel in which no Si-H bond remained. The hydrolysis of $HSi(OPr^i)_3$ in the presence of Pr^iOK was somewhat different, since there was immediate evolution of dihydrogen and a monolithic gel was formed after 7 days only.

Hydrolysis of pentacoordinate hydridosilicates was very fast except when the R group was isopropyl. The formation of a gel was always observed, whatever the nature of the R group. In all cases immediate evolution of dihydrogen occurred, and the IR spectra of the gels indicated the absence of Si-H bonds, as for the hydrolysis of tetracoordinate compounds $HSi(OR)_3$ in basic conditions.

These experimental results show that the hydrolysis reaction proceeds by a nucleophilic rather than a base-catalyzed process. The nucleophilic displacement takes place on a pentacoordinate silicon species and results in the formation of a hexacoordinate intermediate (or transition state) by coordination of a molecule of H_2O.

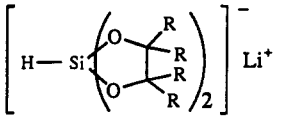
2. Bis(diolato)hydridosilicates

Trichlorosilane reacts at low temperature (−78 °C) with the dilithio derivatives of catechol (eq 14), 2,2′-dihydroxybiphenyl, or aliphatic diols such as 1,2-ethanediol and pinacol to give solutions presumably containing complexes **122**, **123**, or **124**.[73] However these complexes are unstable at room temperature since all attempts to isolate them have failed. Nevertheless these solutions are able to reduce aldehydes and ketones, but not esters, in the absence of catalyst and in good yield (eqs 38 and 39). The catechol and 2,2′-dihydroxybi-



122

123



124 a : R = H
b : R = Me

$$PhCHO \xrightarrow{122} PhCH_2OH\ (96\%) \qquad (38)$$

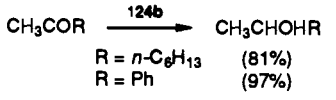
$$RCOCH_3 \xrightarrow{122,\ 123,\ or\ 124} RCHOHCH_3 \qquad (39)$$

R = Ph 98% (from **122**); 97% (from **123**); 50% (from **124a** and **124b**)

R = n-C_5H_{11} 90% (from **123**)

phenyl preparations led to good reducing agents. In contrast the reducing agents produced from aliphatic diols were much less effective and the solutions formed from monoalcohols were totally ineffective in reducing ketones. All excellent linear Hammett plot for the reduction of substituted benzaldehydes with **122** was obtained, which indicates that hydride transfer is involved in the rate-determining step.

Solutions of complex **124b** have also been obtained from trialkoxysilanes and lithium pinacolate.[191] These solutions reduce aldehydes and ketones chemo- and stereoselectively (eqs 40 and 41). The reduction of



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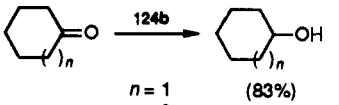


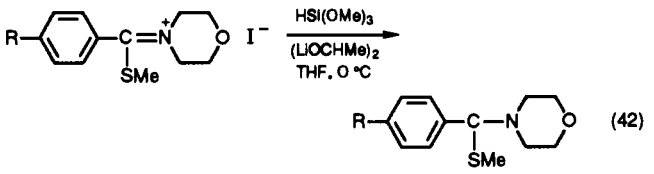
(41)

2-methylcyclohexanone, for example, gave *cis*-2-methylcyclohexanol with 85% stereoselectivity.

A solution of trimethoxysilane and dilithium 2,3-butanediolate also reduced (alkylthio)methyleniminium salts (eq 42) to the corresponding *S,N*-acetals in high yield.[198]

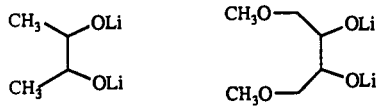
Enantioselective hydrosilylation of ketones was achieved[199] by using a mixture of trialkoxysilane and the dilithium salt of a chiral diol or amino alcohol **125**, **126**, **127**, or **128** (eq 43).

The reducing properties of the hydridosilicate **129** were also studied. This complex was originally pre-

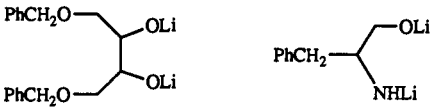


(42)

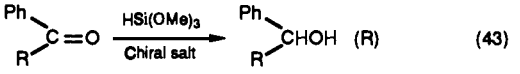
R = H (88%); MeO (98%); Cl (76%); NO_2 (79%); CN (74%); Me_2N (74%)



125 (R,R) 126 (S,S)



127 (S,S) 128 (S)



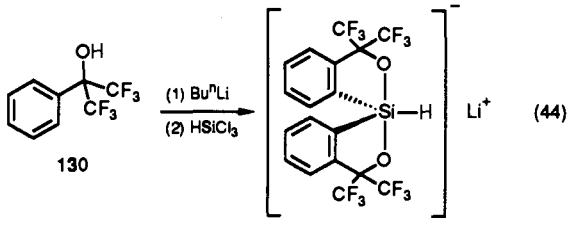
(43)

chiral salt 125 { R = Me, 41% (22% ee); R = Et, 52% (36% ee); R = Pr^i, 48% (44% ee)

chiral salt 126 { R = Me, 66% (40% ee); R = Et, 70% (53% ee); R = Pr^i, 63% (69% ee)

chiral salt 127 { R = Me, 78% (44% ee); R = Et, 66% (54% ee); R = Pr^i, 55% (69% ee)

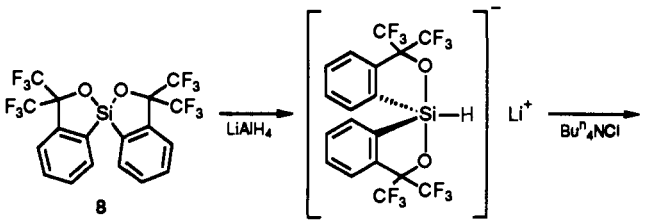
pared[200] by reaction of $HSiCl_3$ with the dilithio derivative of hexafluorocumyl alcohol **130** in THF in the presence of TMEDA at −78 °C (eq **44**). Such solutions



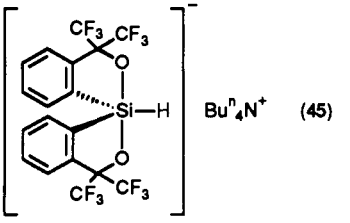
130 129

(44)

were found to reduce ketones and aldehydes at 0 °C, but the complex itself appeared to be rather unstable and purification proved difficult, even after isolation as the bis(phosphoranyl)iminium salt. It was subsequently shown[46] that reaction of the spirosilane **8** with lithium aluminium hydride gave a more stable product that could be isolated and purified as the lithium salt **129** or as the tetrabutyl ammonium salt **131** (eq **45**). Solutions of these pure salts reduced aldehydes and ketones only very slowly, but in the presence of the spirosilane **8** as a catalyst, the process is much more efficient and more selective. Under these conditions, reduction of aldehydes, ketones, and ketals occurs readily; α,β-unsaturated esters, aldehydes, ketones, and nitriles are also reduced, with predominant 1,4-addition of the hydride. The notable acceptor properties of silane **8**, resulting in coordination of the carbonyl oxygen atom,[47,176] are most probably responsible for this catalytic effect. It is possible that the reducing properties of the solutions obtained according to eq **44** result from the presence of a small amount of **8**.



8 129



(45)

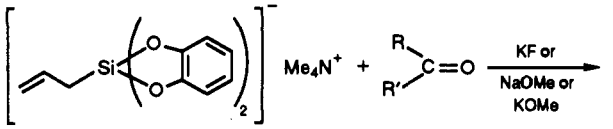
131

C. Pentacoordinate Allylsilicates

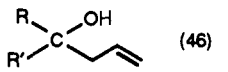
The reactivity of allylsilanes, with catalysis by electrophiles as well as nucleophiles has been extensively studied and used in organic synthesis.[13,14,201-203] The stereoselectivity observed on nucleophilic activation led the authors to propose pentacoordinate allylsilicates as intermediates (section VIII.D.2) and to synthesize a number of examples of such species.

1. *Bis(1,2-benzenediolato)allylsilicates*

Complex **132** which was the first pentacoordinate allylsilicate to be prepared[74] reacts readily with aldehydes under nucleophilic conditions (KF, NaOMe or Bu^n_4NF) to give the corresponding homoallyl alcohols **133** (eq **46** and Table 12). Allyl transfer to ketones is



132



(46)

133

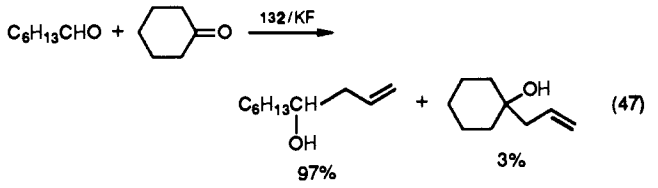
more difficult and requires NaOMe or KOMe as catalyst (Table 12), so it is possible to obtain selective transfer

Table 12. Reaction of Allylsilicate 132 with Carbonyl Compounds under Nucleophilic Conditions in DMSO

carbonyl compound	catalyst	reaction conditions	alcohol 133, yield (%)
PhCHO	KF (1 equiv)	75 °C, 3 h	71
	MeONa (1 equiv)	20 °C, 0.25 h	49
$PhCH_2CH_2CHO$	KF (1 equiv)	60 °C, 3 h	52
	Bu^n_4NF (0.2 equiv)[a]	40 °C, 8 h	68
$C_6H_{13}CHO$	MeONa (1 equiv)	20 °C, 2 h	84
$PhCOCH_3$	MeONa (1 equiv)	85 °C, 23 h	47
	MeOK (1 equiv)	85 °C, 10 h	48

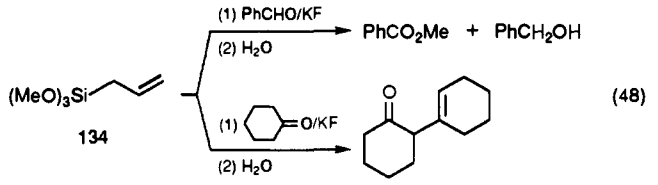
[a] In CH_2Cl_2.

to an aldehyde even in the presence of a ketone (eq 47).



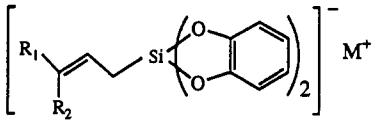
(47)

The reactivity of allyltrimethoxysilane (**134**) is quite different from that of **132** since in the presence of KF cleavage of the Si–O bond occurs. The generation of methoxide subsequently induces crotonization or a Cannizzaro reaction (eq 48).



(48)

Conversely, the unstable lithium salts of bis(1,2-benzenediolato)allylsilicates **135a–138a**, as well as the isolated PPN salts **135c–138c** react slowly with aromatic aldehydes without any catalyst[72,204] (Table 13). The

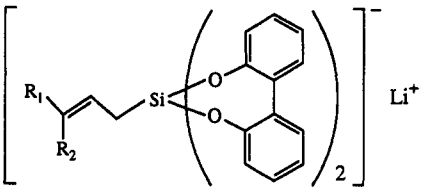


135 : $R_1 = R_2 = H$
136 : $R_1 = R_2 = Me$
137 : R_1 = Me; R_2 = H
138 : R_1 = H; R_2 = Me

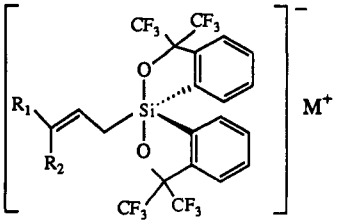
a : M = Li
b : M = Et_3NH
c : M = PPN

bis(2,2′-biphenolato)allylsilicates **139a** and **139b** are also reactive[72,204] toward aromatic aldehydes, whereas complexes **140a** and **140b** bearing Martin's ligand do not react[204] at all with benzaldehyde whether formed in situ as lithium salts (M = Li) or isolated as PPN salts (M = PPN).

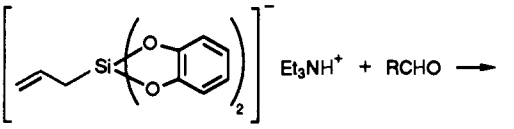
The triethylammonium salts **135b–138b** are slightly more reactive since they react with aromatic (Table 13) and aliphatic aldehydes (eq 49) without any catalyst.[205] The reaction of allylic complexes **136–138** is regiospecific, C–C bond formation occurring exclusively at the γ-carbon of the allylic silicates (eq 50). All these reactions are also stereospecific, giving anti and syn homoallyl alcohols from (*E*)- and (*Z*)-2-butenylsilicates, respectively (Table 13). The influence of the solvent on the allylation of benzaldehyde by **135b** was

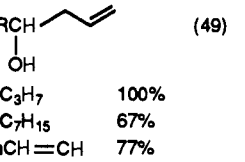


139 a : $R_1 = R_2 = H$
b : $R_1 = R_2 = Me$

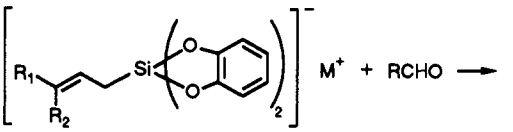


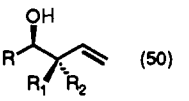
140 a : $R_1 = R_2 = H$
b : $R_1 = R_2 = Me$





(49)





(50)

141

examined.[205] It was shown that the neat reaction gives the best yields and that nonpolar and noncomplexing solvents also work well, whereas solvents with high dielectric constants do not give satisfactory results.

Aldehydes can also be allylated directly by reaction with allyltrimethoxysilane in the presence of stoichiometric quantities of catechol and triethylamine. However only a low yield of homoallyl alcohol is obtained with a catalytic amount of catechol or triethylamine, which indicates that the reaction proceeds

Table 13. Reaction of Allylsilicates 135–138 with PhCHO.

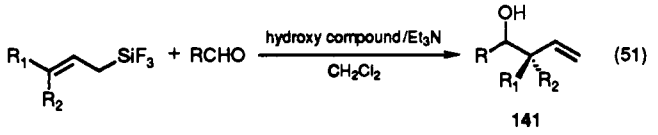
complexes	reaction conditions	alcohol 141 (R = Ph) yield (%)
135a	reflux, THF, 90 h	91[a]
135c	reflux, THF, 90 h	90[a]
135b	reflux, CH_2Cl_2, 10 h	86[b]
136a	reflux, THF, 90 h	87[a]
136c	reflux, THF, 90 h	80[a]
136b	reflux, $CHCl_3$, 12 h	72[b]
137a (*E*/*Z* = 88/12)	reflux, THF, 90 h	82[a] (erythro/threo = 12/88)
137b (*E*/*Z* = 90/10)	reflux, $CHCl_3$, 12 h	88[b] (erythro/threo = 10/90)
138a (*E*/*Z* = 21/79)	reflux, THF, 90 h	91[a] (erythro/threo = 78/22)

[a] Reference 72. [b] Reference 205.

via the bis(1,2-benzenediolato)allylsilicate generated in situ.[205]

2. Pentacoordinate Fluoroallylsilicates

It was found that aldehydes could be allylated with 2-alkenyltrifluorosilanes in the presence of a wide variety of hydroxy compounds and triethylamine under mild conditions[206] (eq 51, Table 14). Monohydroxy



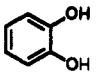
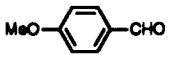
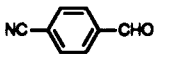
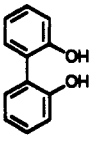
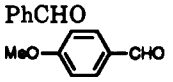
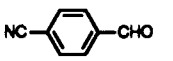
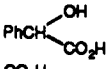
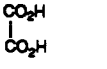
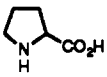
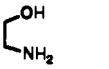
(51)

141

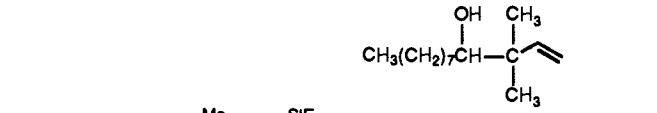
compounds such as methanol can also be used but they are less efficient than diols like catechol or 2,2′-dihydroxybiphenyl. This allylation can be carried out even in the presence of water.

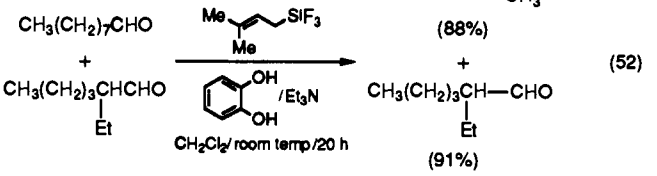
The system allyltrifluorosilane/diol/triethylamine does not display the same reactivity as the bis(1,2-benzenediolato)allylsilicate, since it reacts selectively with linear aliphatic aldehydes in the presence of α-branched alkanals[206] (eq 52). Moreover the stereochemistry observed[204] is the same as that obtained from complexes **136–138**:[72,205] threo and erythro homoallyl alcohols result respectively from (*E*)- and (*Z*)-2-butenyltrifluorosilanes (eqs 53 and 54). This suggests the formation in situ of the dialkoxydifluoroallylsilicate **142** (eq 55).

Table 14. Allylation of Aldehydes by Prenyltrifluorosilane in the Presence of Hydroxy Compounds and Et_3N at Room Temperature[a]

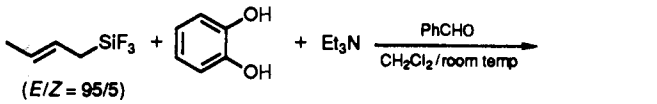
hydroxy compound	aldehyde	reaction time (h)	alcohol **141** yield (%)
	PhCHO	20	93
		20	82
		20	84
	$PhCH_2CH_2CHO$	20	86
	$CH_3(CH_2)_7CHO$	20	87
	PhCHO	48	88
		46	84
		60	70
	PhCHO	24	83
	PhCHO	24	90
	PhCHO	15	72
	PhCHO	30	45
$MeOH^b$	PhCHO	48	83

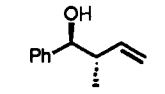
[a] Ratio of aldehyde/prenyltrifluorosilane/diol/Et_3N = 1/1.5/1.5/3. [b] Ratio of aldehyde/prenyltrifluorosilane/MeOH/Et_3N = 1/2/4/4.





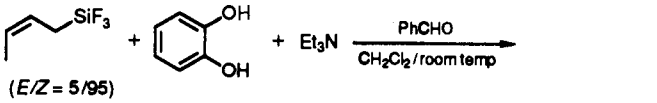
(52)

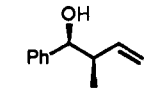




(53)

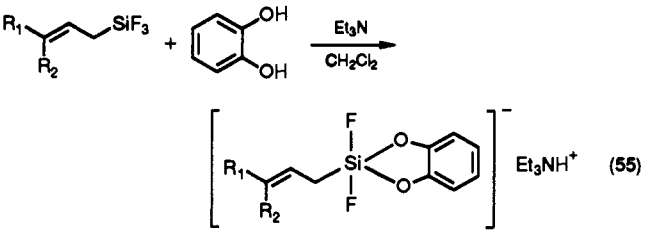
93% (anti/syn = 94/6)





(54)

89% (anti/syn = 5/95)

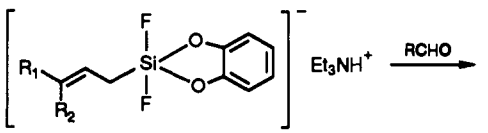


(55)

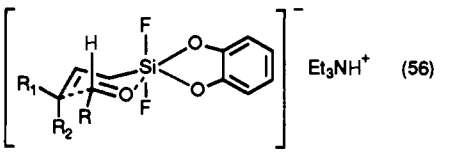
142

3. Mechanism

The high regio- and stereoselectivity observed with pentacoordinate allylsilicates was explained by a six-membered cyclic transition state having a chair conformation[204] (eq 56). A stereochemical study of the

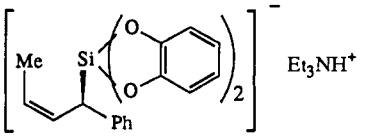


142

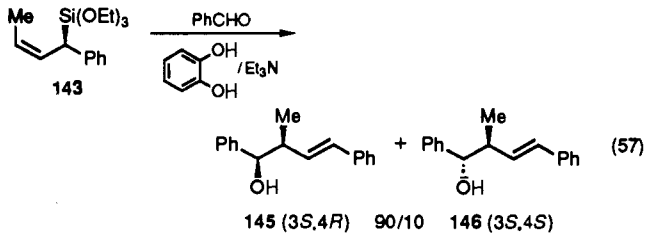


(56)

allylation of aldehydes with the optically active allylsilicate **143** supported this hypothesis.[207] Complex **144** generated in situ reacted with benzaldehyde to give the isomeric allylic alcohols **145** and **146** in the ratio 90/10 (eq 57). The 3*S* configuration of **145** and **146** clearly demonstrates that the γ-carbon of the allysilicate attacks the aldehyde on the same side as the silyl group. This stereochemical result is also consistent with a mechanism involving a six-membered cyclic transition

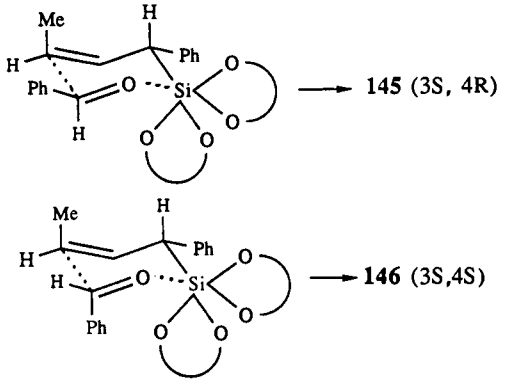


144 (R)



state (Scheme 27). This cyclic transition state leads to the formation of a hexacoordinate silicon center as has

Scheme 27



frequently been proposed to occur in the course of a number of reactions at silicon.[3,11,208-210] Moreover the involvement of a hexacoordinate silicon intermediate (or transition state) in these reactions is corroborated by the difference in the reactivity of pentacoordinate allylsilicates as a function of the substituents. The triethylammonium salt of bis(1,2-benzenediolato)-allylsilicate reacts with both aromatic and aliphatic aldehydes.[205] Difluoro(1,2-benzediolato)allylsilicate (142) reacts with aromatic aldehydes and with linear aliphatic aldehydes but does not react with secondary and tertiary aldehydes.[206] In contrast both linear and α-branched aldehydes are allylated smoothly with allylic tetrafluorosilicates derived from the allylic trifluorosilane/CsF system[204,211] (section VIII.D.2). The reactivity of pentacoordinate allylsilicates clearly depends on the ligands around the silicon atom, increasing in line with the electronegativity of these ligands.

D. Silatranes and Azasilatranes

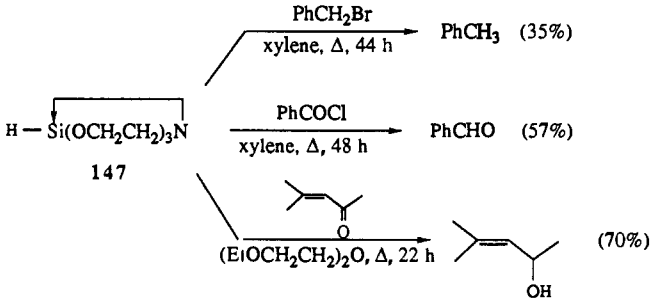
1. Silatranes

Whereas the physicochemical properties of silatranes and their derivatives have been studied in detail,[81,212-214] their reactivity has not been so extensively explored because of their generally unreactive nature. Thus C. L. Frye reported early in 1971 the completely unexpected stability toward solvolysis of 1-chlorosilatrane, which can be successfully recrystallized from alcoholic solution.[80]

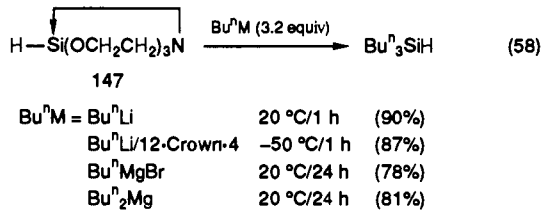
The reaction most studied is the cleavage of the apical bond opposite to the transannular Si–N bond, which was reviewed by Voronkov et al. in 1982.[81] The electrophilic reactions of 1-iodosilatrane have been studied recently[82] and are summarized in Scheme 28.

Silatrane **147** was shown[215] to reduce some carbonyl compounds, azoxybenzene, benzoyl chloride, and benzyl bromide (Scheme 29). However its reactivity toward

Scheme 29

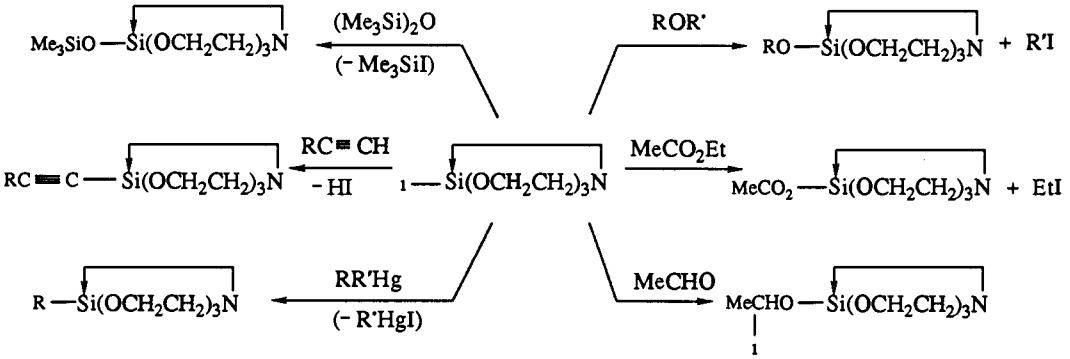


these compounds is low compared with that of the bis(1,2-benzenediolato)hydridosilicate **122**.[73] Indeed long reaction times and high temperatures are necessary. The reactivity of silatranes toward nucleophilic reagents was investigated.[153] Silatrane **147** reacts with *n*-butyllithium to give tri-*n*-butylsilane (eq 58), even

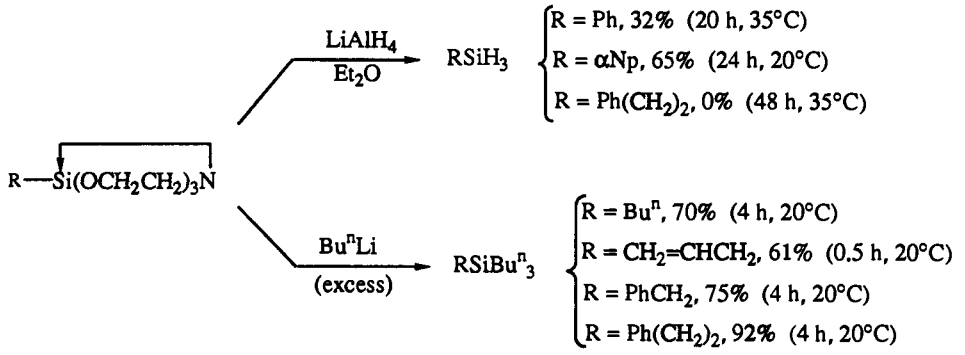


with a deficiency of the organometallic reagent. The initial attack is thus the rate-determining step and

Scheme 28



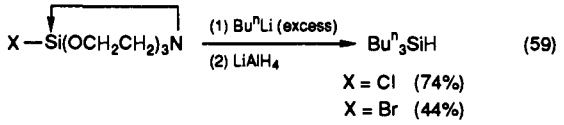
Scheme 30



involves the cleavage of a silicon–oxygen bond. In the presence of 12-crown-4 ether the reaction proceeds much more rapidly. This means that cleavage of the silicon–oxygen bond results from direct nucleophilic attack on silicon and that coordination of the silatrane nitrogen atom to the lithium cation is not implicated in this reaction. Silatrane reacts also with Grignard reagents but more slowly (eq 58).

Arylsilatranes but not alkylsilatranes are reduced by lithium aluminium hydride to the corresponding arylsilane (Scheme 30), and Bu^nLi coverts both aryl- and alkylsilatranes to the corresponding tetraorganosilanes (Scheme 30).

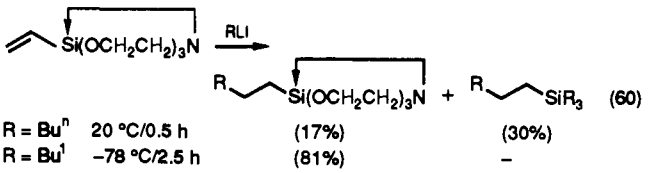
Chloro- and bromosilatranes were found to react with Bu^nLi to give, after reduction with $LiAlH_4$, tri-*n*-butylsilane as the major product, even when an excess of Bu^nLi was used (eq 59). It was confirmed that the



(59)

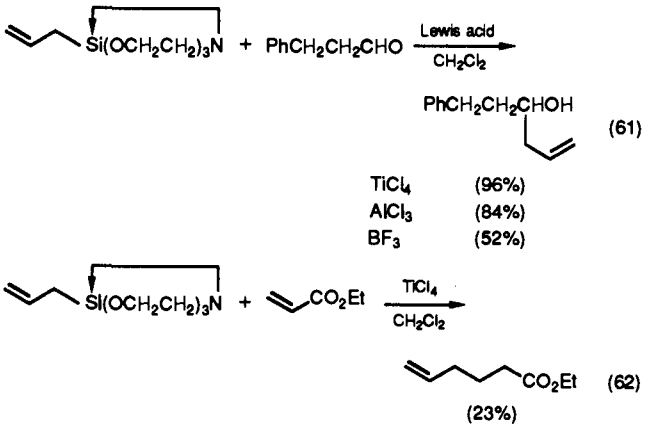
reaction of chlorosilatrane with Bu^nLi did not give any Bu^n_3SiCl before reduction. Moreover since only a poor yield of Bu^n_4Si was obtained from an excess of Bu^nLi with chlorosilatrane after prolonged reaction, it can be concluded that the initial substitution involves cleavage of an Si–O bond instead of the Si–Cl bond as is usually observed with chloroalkoxysilanes. The low reactivity of chlorosilatrane is connected with its unusual geometry,[81] since backside attack is excluded because of steric hindrance and flank attack is not favorable because of the low s character of the Si–Cl bond.[216]

Vinylsilatranes display the same reactivity toward organolithium reagents[153] as the corresponding tetracoordinate silicon compounds,[217] as illustrated in equation 60. Allylsilatrane reacts with carbonyl compounds



(60)

in the presence of a catalytic amount of a Lewis acid[74] (eqs 61 and 62) as do allylsilanes,[218] but does not react with carbonyl compounds by nucleophilic activation (KF or NaOMe) in contrast with the bis(1,2-benzenediolato)allylsilicate **132**[74] (eq 46).



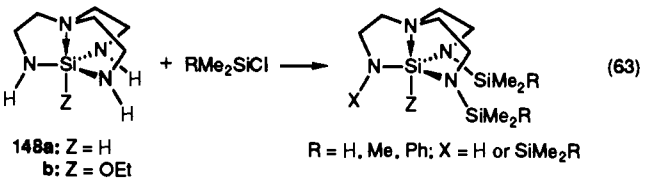
(61)

(62)

2. Azasilatranes

1-Hydroazasilatrane (**148a**) reacts slowly with CCl_4 to give 1-chloroazasilatrane.[85] The reaction rate was found to be considerably increased by the addition of a catalytic amount of a bis(phosphine)platinum or -palladium dichloride.

Silylation of the NH functional groups of azasilatranes is effected by chlorosilanes.[85] The degree of substitution depends on the nature of the azasilatrane and the chlorosilane. 1-Hydroazasilatrane **148a** reacts with an excess of a chlorosilane of the type $ClSiMe_2R$ (R = H, Me, or Ph) to give silylation of the equatorial NH functional groups (eq 63). With 1-ethoxyazasilatrane

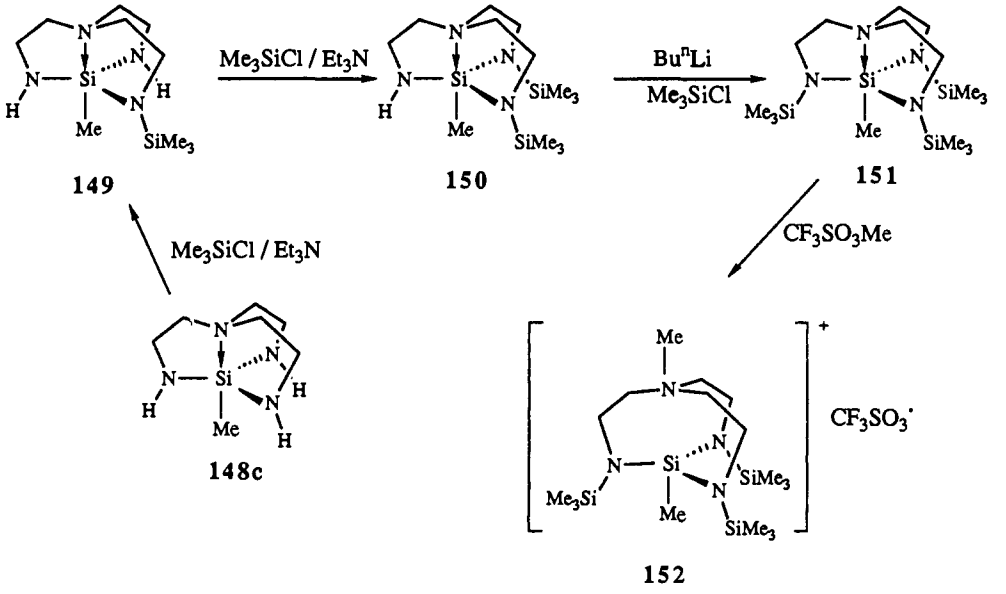


(63)

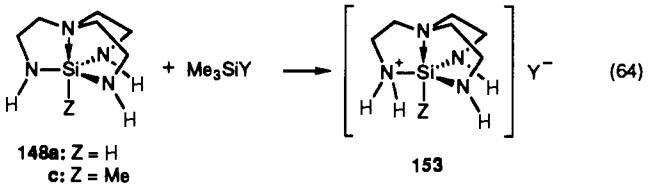
(**148b**) there is substitution of all three amino groups with $ClSiMe_2H$, disubstitution with $ClSiMe_3$ and $ClSiMe_2Ph$, and no substitution with $ClSiMe_2Bu^t$. In all cases there is retention of the atrane structure.

Trimethylsilylation of 1-methylazasilatrane (**148c**) proceeds stepwise to give **149** and **150**. Further silylation occurs on reaction of Bu^nLi followed by Me_3SiCl (Scheme 31). This third substitution renders N_{ax} sufficiently basic to react with CF_3SO_3Me and gives **152** in which the silicon atom is tetracoordinated.[219] 1-Methyl- and 1-hydroazasilatranes react also with the weakly electrophilic Me_3SiN_3 or Me_3SiNCS to give

Scheme 31

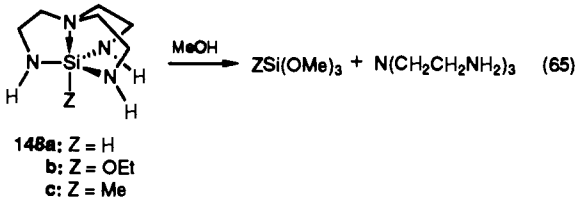


(among other products) salts **153**, containing equatorially protonated cations[220] (eq 64).



(64)

Azasilatranes **148a–c** solvolyze in methanol at room temperature to give the corresponding trimethoxysilanes (eq 65); no intermediate was detected in these reactions.[221]

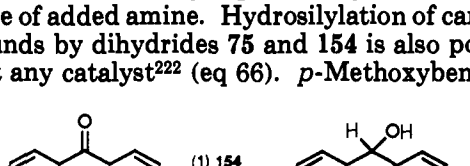


(65)

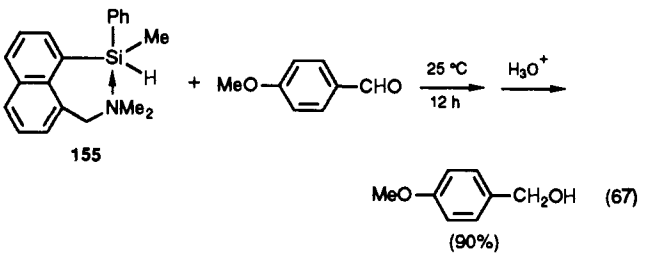
E. Neutral Pentacoordinate Silicon Derivatives

1. Pentacoordinate Silicon Hydrides

Pentacoordinate silicon hydrides **73a**, **75**, and **154** react, without added catalyst, with alcohols and carboxylic acids[222] to give alkoxy- or acyloxysilanes with evolution of dihydrogen (Scheme 32). The reaction occurs even with bulky alcohols such as 2-propanol and 1-menthol. Under the same conditions αNpPhSiH$_2$ does not react with CH_3CO_2H or CH_3OH even in the presence of added amine. Hydrosilylation of carbonyl compounds by dihydrides **75** and **154** is also possible without any catalyst[222] (eq 66). *p*-Methoxybenzaldehyde is reduced by the pentacoordinate monohydrogenosilane **155** (eq 67), whereas hydrosilylation of carboxyl compounds does not occur with the tetracoordinate dihydrogenosilane αNpPhSiH$_2$.

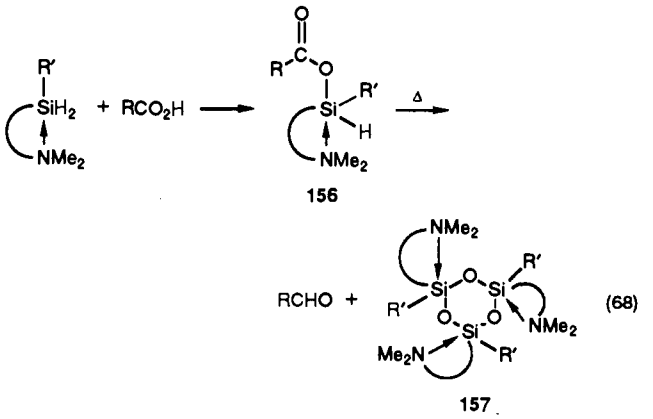


(66)



(67)

a. **Reduction of Acids to Aldehydes.** It was shown[223] that simply heating the silyl carboxylates **156** obtained by reaction of a carboxylic acid with the pentacoordinate dihydrogenosilanes **73b**, **75**, or **154** (eq 68) afforded aldehydes in 50–95% yields (Table 15).



(68)

The residual silicon moiety was identified as the cyclosiloxane trimer **157**. Carbon dioxide and formic acid also reacted with pentacoordinate hydrogenosilanes to give formaldehyde. These reactions will be detailed later on. The preparation of aldehydes in this way is selective since fluoro, nitro, cyano, methoxy, and heteroaryl groups do not react with the silane. Aliphatic acids can be successfully reduced in fair to good yields.

Scheme 32

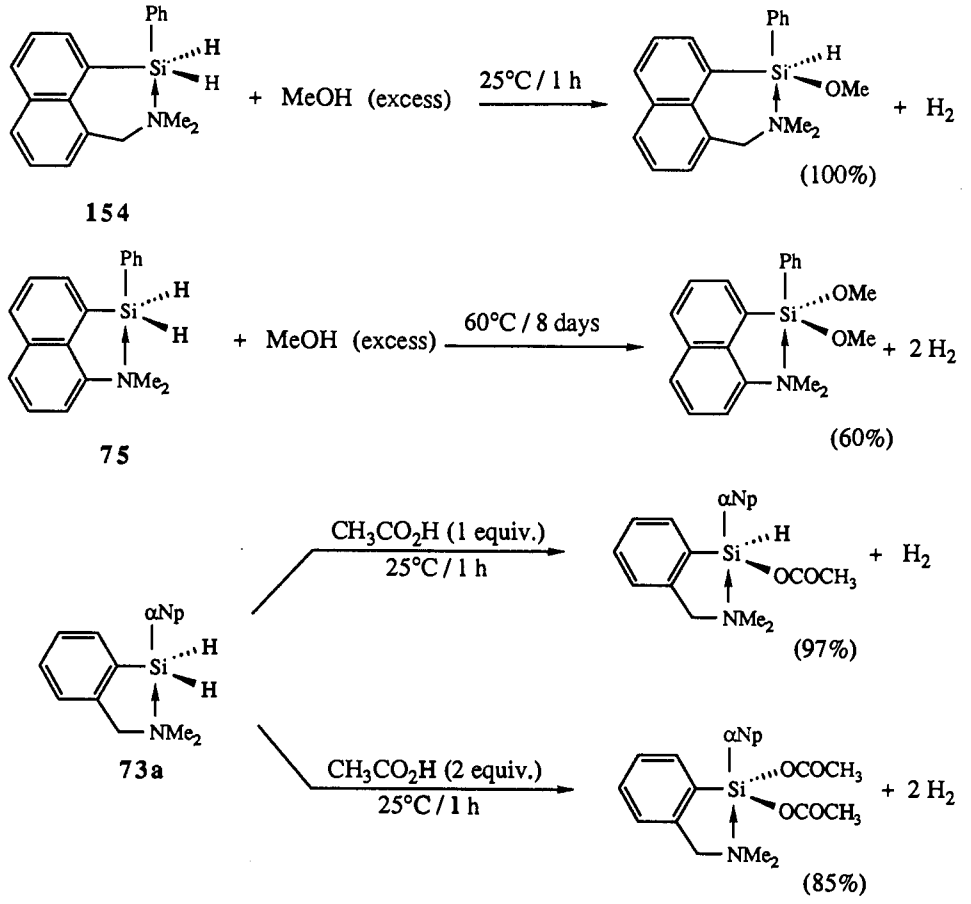
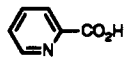
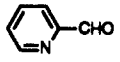
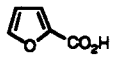
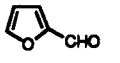
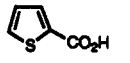
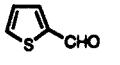
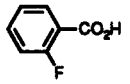
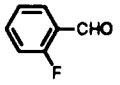
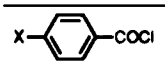
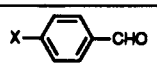
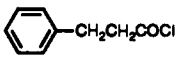
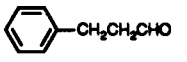
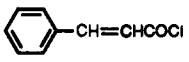
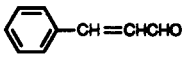
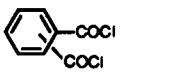
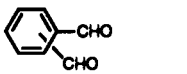
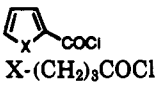
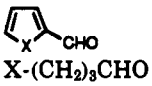


Table 15. Reduction of Carboxylic Acids to Aldehydes Using the Pentacoordinate Silicon Hydride 154

acids	aldehydes	yield (%)
$CH_3CH_2CO_2H$	CH_3CH_2CHO	85
$(CH_3)_3CCO_2H$	$(CH_3)_3CCHO$	50
$PhCH{=}CHCO_2H$	$PhCH{=}CHCHO$	71[a]
$p\text{-}NO_2C_6H_4CO_2H$	$p\text{-}NO_2C_6H_4CHO$	60
		90
		76
		88
		72[b]

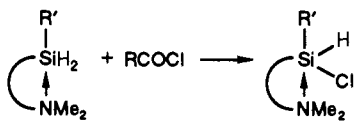
[a] Yield of 50% with **75** as reducing agent and yield of 65% with **73b**. [b] **75** is used as reducing agent.

Table 16. Reduction of Acid Chlorides to Aldehydes Using the Pentacoordinate Silicon Hydride 73b

acid chloride	aldehyde	yield (%)
		X = H, 90 X = NO_2, 90 X = MeO, 91
		87
		86
		meta, 89 para, 85
		X = O, 87 X = S, 86
$X\text{-}(CH_2)_3COCl$	$X\text{-}(CH_2)_3CHO$	X = Br, 90 X = Cl, 82
$EtOCO(CH_2)_8COCl$	$EtOCO(CH_2)_8CHO$	80

The reduction of α,β-unsaturated acids also provides the corresponding α,β-unsaturated aldehydes. It is worth noting that the six-membered cyclic pentacoordinate dihydride **154** is a more efficient reducing agent than the five-membered ring derivatives **75** and **73b**. Under similar conditions the tetracoordinate silyl ester αNpPhSi(H)OCOPh gives less than 3% of benzaldehyde after 48 h at 200 °C. This sequence constitutes a direct transformation of carboxylic acids into aldehydes through the thermal decomposition of pentacoordinate silicon species.

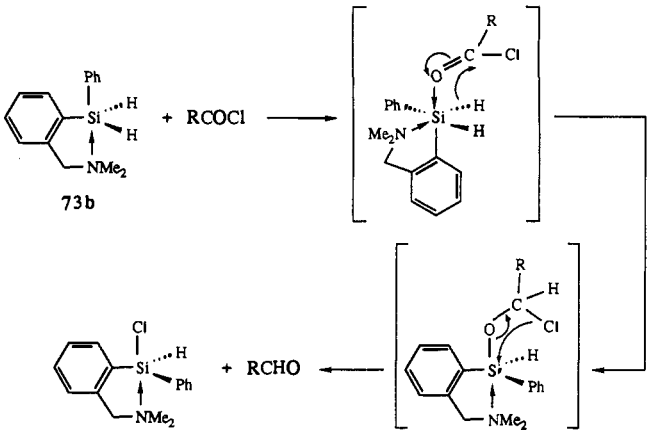
b. Reduction of Acid Chlorides to Aldehydes. Aldehydes are also obtained by reaction of **73b**, **75**, and **154** with acyl chlorides[224] (eq 69 and Table 16). This



(69)

very clean Rosenmund-type reaction is also another unexpected reaction of pentacoordinate hydrogenosilanes. The reaction is selective, since halogeno, methoxy, and nitroaryl groups, as well as heteroaryl groups and C=C double bonds remain unchanged. This method is effective also for the conversion of dicarboxylic acid chlorides into dialdehydes. The best results

Scheme 33

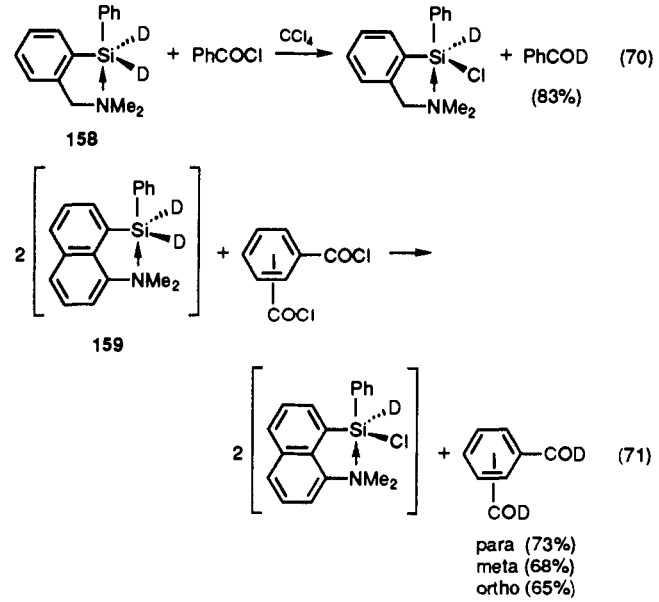


were obtained with silane **73b**, except for the reduction of ethyl chlorothioformate which requires the more efficient silane **154**, and in the case of the conversion of benzoyl bromide into benzaldehyde, which requires the less active silane **75**. Selected results are reported in Table 16. This reaction constitutes a useful alternative method for the direct conversion of acid chlorides into aldehydes.

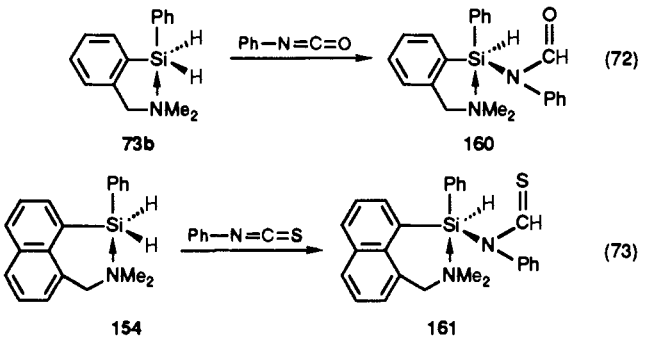
The following mechanism has been proposed for this reaction[225] (Scheme 33): (1) coordination of the carbonyl group to the silicon atom to give a hexacoordinate silicon intermediate; (2) transfer of hydride from silicon to carbon; (3) migration of the chlorine atom to silicon, giving the chlorosilane and the aldehyde.

It was verified that the reduction of acid chlorides by pentacoordinate hydrosilanes did not proceed by a free-radical process.

In addition to the formation of functional aldehydes, the reduction of acid chlorides by pentacoordinate dihydrosilanes has been used for the synthesis of deuterioaldehydes of very high isotopic purity from dideuteriosilanes[225] (eqs 70 and 71). The reactivity of the dideuteriosilanes **158** and **159** was found to be comparable to that of the corresponding dihydrosilanes ($k_H/k_D < 2$).



c. Hydrosilylation of Isocyanates and Isothiocyanates. The high reactivity of pentacoordinate silicon hydrides was also used to synthesize N-functionalized formamido and thioformamido compounds. Hydrosilylation of isocyanates and isothiocyanates by pentacoordinate dihydrosilanes is easily achieved without any added catalyst[226] (eqs 72 and 73).



Both the formamide **160** and the thioformamide **161** react with acid chlorides to afford highly functionalized formamides, *N*-acylthioformamides (Scheme 34 and Table 17) and chlorosilane. The method is selective

Scheme 34

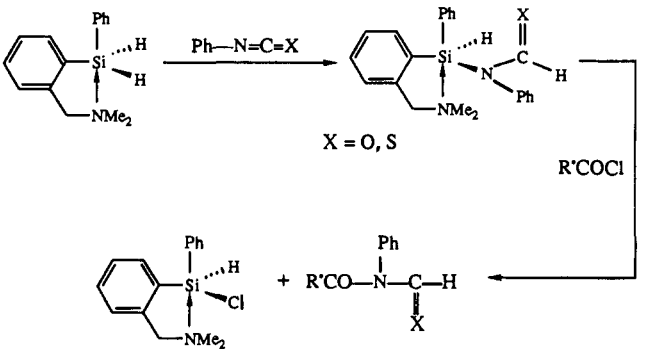
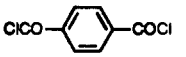
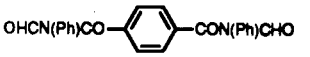
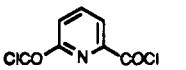
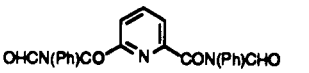
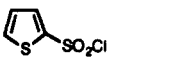
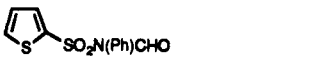
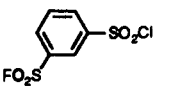
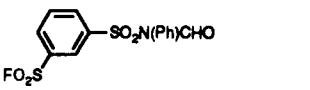
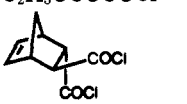
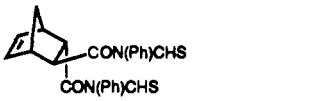
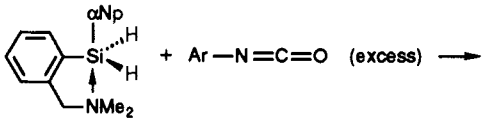


Table 17. Reaction of Compounds 160 and 161 with Electrophiles

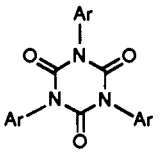
silane	acid chloride	product	yield (%)
160	CH_2=CHCOCl	CH_2=CHCON(Ph)CHO	72
	$C_2H_5OCOCOCl$	$C_2H_5OCOCON(Ph)CHO$	85
	C_2H_5SCOCl	$C_2H_5SCON(Ph)CHO$	80
	PhOCSCl	PhOCSN(Ph)CHO	69
			85
			80
			74
			79
161			70
	$ClCO(CH_2)_8COCl$	$SHCN(Ph)CO(CH_2)_8CON$-(Ph)CHS	72
	$C_2H_5OCOCOCl$	$C_2H_5OCOCON(Ph)CHS$	70
			81

since esters, alkoxy or thioalkoxy substituents, heteroaryl groups, and C=C double bonds remain unchanged. It is also suitable for the conversion of dicarboxylic acid chlorides to the corresponding diformamides and has been successfully extended to the preparation of other N-substituted formamides using sulfonyl chlorides as electrophiles (Table 17).

Attempts to promote insertion of PhN=C=O into the second Si—H bond of the dihydrosilane **73b** failed and instead the formation of the trimer **162** of phenyl isocyanate resulted.[227] The trimer could be obtained from **73b** or from the addition product **160** but better yields were obtained by direct reaction of a large excess of PhN=C=O with **73b** (eq 74). The trimerization of



73b



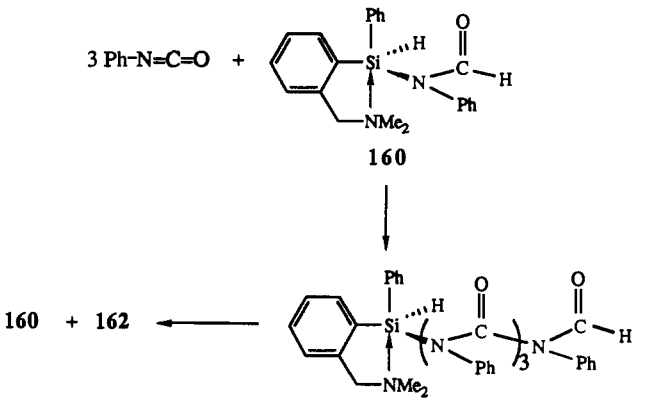
(74)

162

Ar = Ph (85%)
Ar = 4-MeC_6H_4 (73%)

arylisocyanates can most obviously be explained by repeated insertion of ArN=C=O into the Si—N bond of the Si—N(R)(C=O) group. After three insertions, elimination of trimer with reformation of the intermediate silylamide **160** apparently occurs (Scheme 35).

Scheme 35



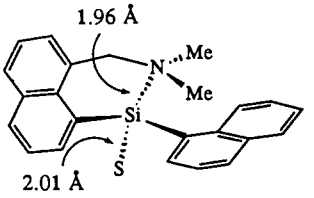
The enhanced reactivity of pentacoordinate silicon hydrides has been exploited for the hydrosilylation of aryl- and alkylcarbodiimides[228] (Scheme 36). The silane **154** reacts with a stoichiometric amount of *p*-tolylcarbodiimide to give in almost quantitative yield the corresponding N^1-silylformamidine **163** whereas the reaction of silane **154** with N^1,N^2-dialkylformamidines resulted in N^1,N^2-dialkyl-*C*-acyl amidines **164** also in nearly quantitative yield. This difference in regioselectivity has not yet been explained. Formic acid cleaved the Si–N bond of **163** and **164** to give formamidine **165**, whereas electrophilic cleavage of **163** and **164** by acid chlorides gave respectively N^1-acylformamides **166** and *C*-acyl amidines **167** (Scheme 36).

This mild approach to *N*-acylformamidines and *C*-acyl amidines by hydrosilylation of carbodiimides with pentacoordinate silicon hydrides is of synthetic interest, since there is no other method available for obtaining *C*-acyl amidines. *N*-Acylformamidines can be obtained[229] under much more drastic conditions (high temperatures 140–200 °C) by reaction of alkylcarbodiimides with silicon hydrides, catalyzed by $PdCl_2$ or $(PPh_3)_3RhCl$, giving N^1-silylformamidines, followed by the cleavage of the Si–N bond with acid chlorides. The regioselectivity of the hydrosilylation of alkylcarbodiimides with pentacoordinate silicon hydrides is different from that observed by Ojima and Inaba.[229] At present, no reason for this difference can be given.

d. Preparation of Donor-Stabilized Low-Coordinate Silicon Compounds. Carbon dioxide reacts quantitatively even at low temperatures with the highly reactive hydride **154** to give the silyl formate **168**[230] which may also be obtained by reaction of **154** with formic acid (Scheme 37). **168** decomposes on heating with evolution of formaldehyde and formation of a residue, identified as the trimer **170** of the silanone **169** (Scheme 37). Further evidence for the formation of the transient silanone was obtained by performing the thermolysis in the presence of an excess of $(Me_2SiO)_3$, an efficient trapping agent for low coordinate silicon species.[231] The major product was then the eight-membered ring compound **171** resulting from the insertion of the silanone **169** into hexamethylcyclotrisiloxane (Scheme 37). This reaction provides a mild method of converting CO_2 into formaldehyde through the pentacoordinate silyl ester of formic acid.

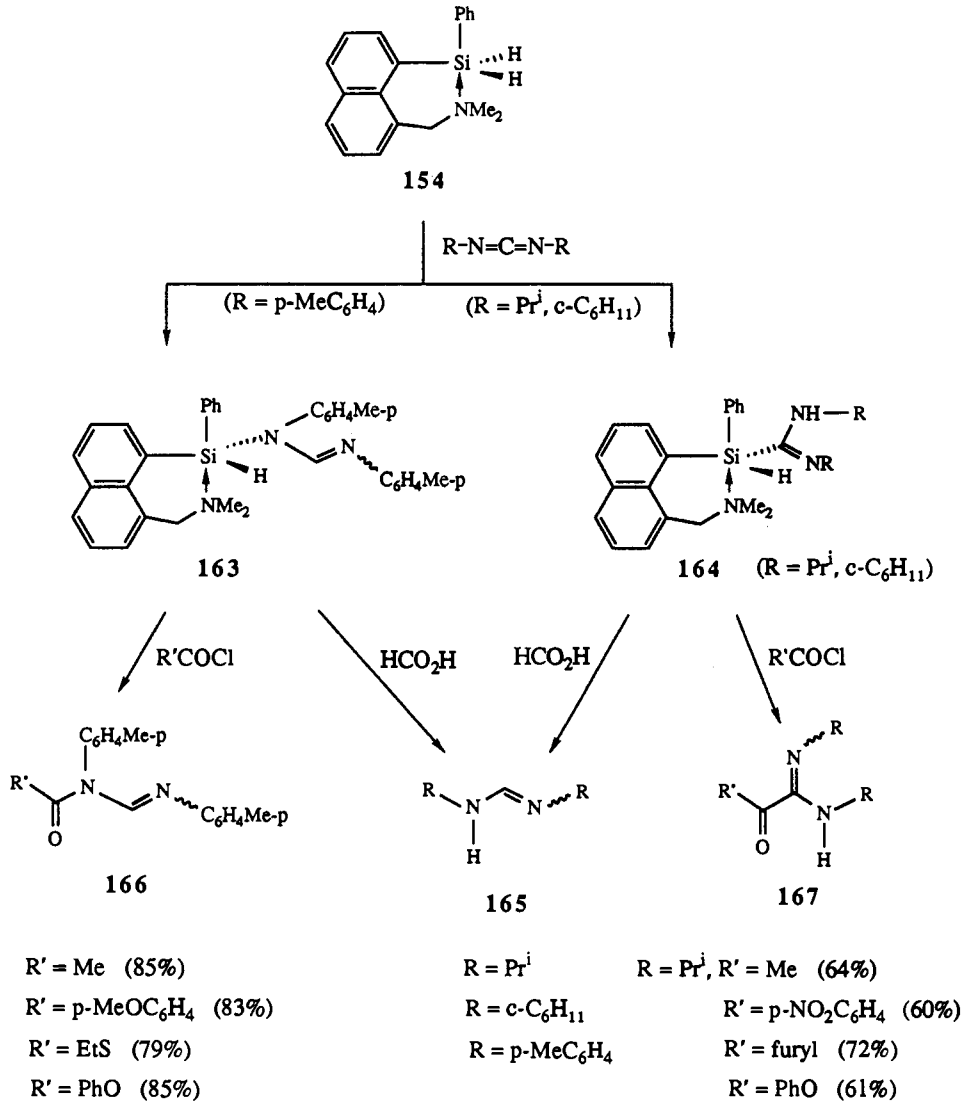
CS_2 also reacts with **154** in an analogous manner to give the silyl ester **172** of dithioformic acid.[232] This bifunctional pentacoordinate hydrosilyl ester decomposes very easily at room temperature, giving the first isolable silanethione **173a** (Scheme 38). The silanethione oxidizes very easily to give the same trimeric siloxane **170** as that obtained from the silanone **169** (Scheme 37). Furthermore, when the oxidation of **173a** is performed in the presence of $(Me_2SiO)_3$, the cyclotetrasiloxane **171** is also obtained. In contrast, when the formation of the silanethione is performed in the presence of $(Me_2SiO)_3$, the insertion product of **173a** into $(Me_2SiO)_3$ is not formed. These results suggest that the oxidation product of the silanethione **173a** is the silanone **169** (Scheme 38). Addition of sulfur to **154** readily provides **173a**. The addition of Se affords similarly the monomeric silaneselone **174**; the transient formation of one other silaneselone (Et_2Si=Se) had been previously reported.[233] Compound **174** is also extremely sensitive to air.

The reactivity of the silanethione **173a** was found to be unexpectedly low toward electrophiles as well as nucleophiles. This could be explained in part by the participation of the resonance betaine structure in the electronic distribution of **173a** (Scheme 38). As de-

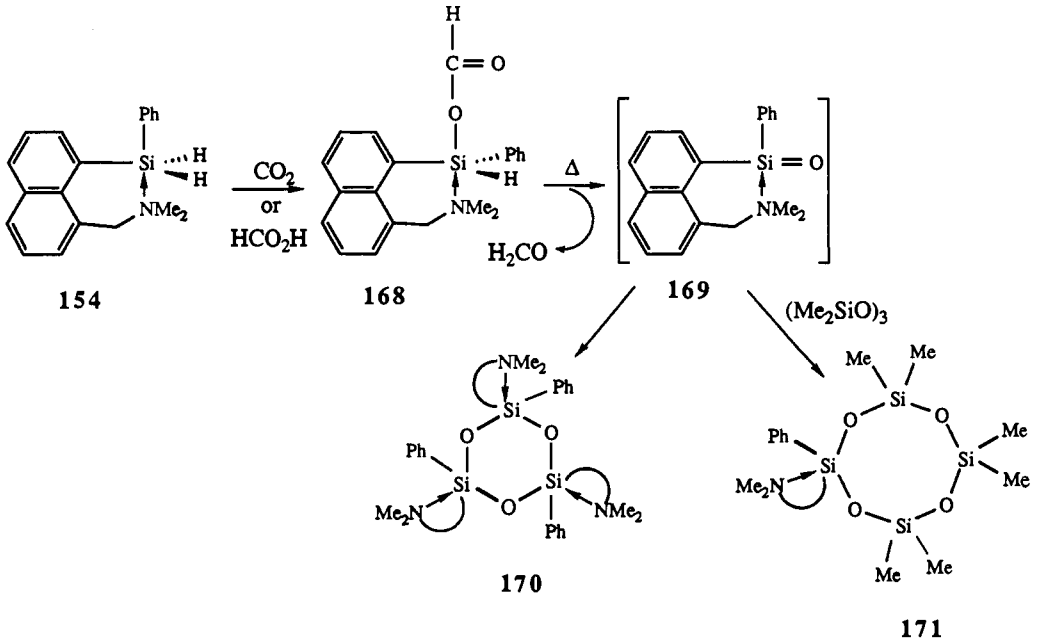


173b

Scheme 36

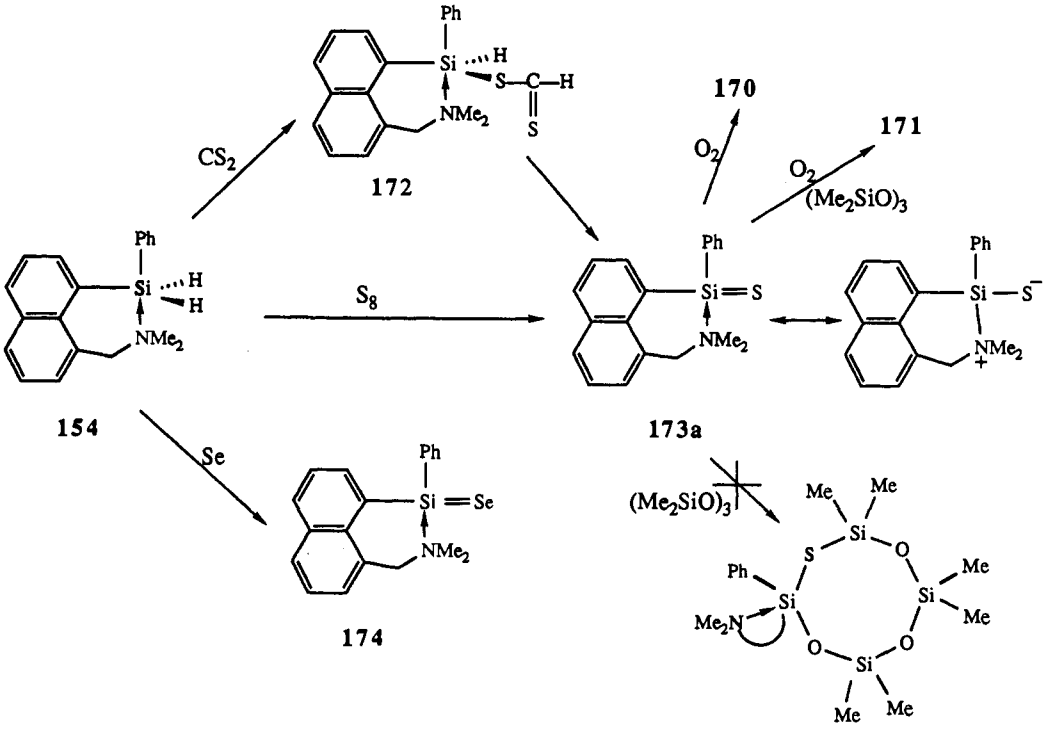


Scheme 37

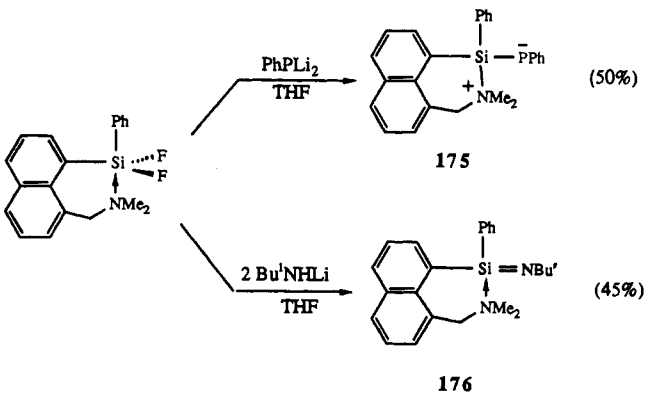


finitive proof of the formation of the silanethione **173a**, the more bulky silanethione **173b** was synthesized and its structure established by X-ray analysis.[232] The Si–S bond (2.013 Å) is shorter than a Si–S single bond (2.16

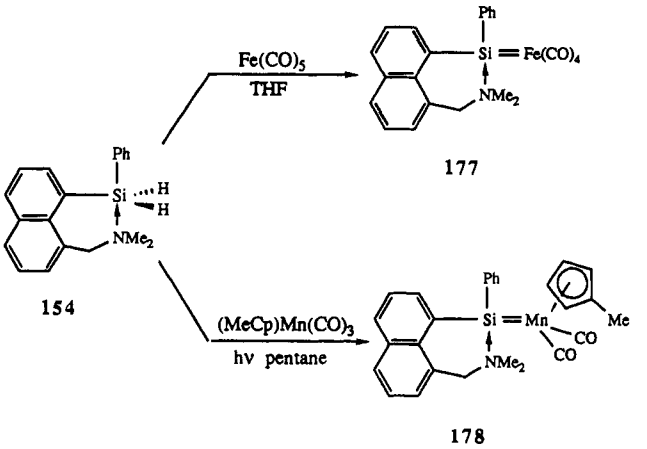
Scheme 38



Scheme 39



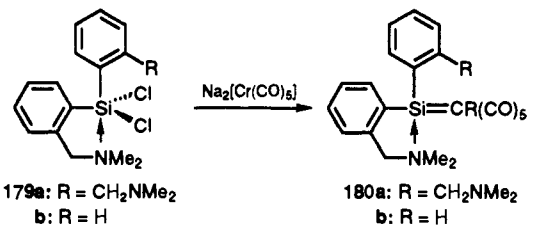
Scheme 40



Å). The Si–N distance (1.96 Å) is slightly longer than an Si–N σ-bond (1.79 Å) supporting a very strong association of the arylamino substituent with silicon. The silicon center displays a distorted tetrahedral environment.

It was found[234] that the same arylamino group stabilizes the silaphosphene **175** and the silanimine **176** by intramolecular coordination (Scheme 39). The structures of **175** and **176** were established by NMR spectroscopy. These compounds are inert toward nucleophiles and electrophiles but are highly sensitive to oxygen and moisture.

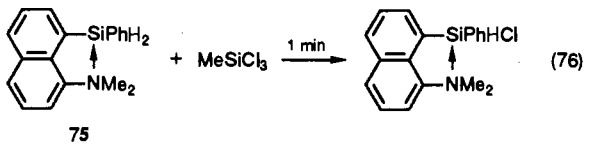
Other donor-stabilized (silylene) complexes have been prepared from pentacoordinate silicon compounds. The silanediyl transition-metal complexes **177** and **178** were readily formed[234] by the dehydrogenative coupling reaction of pentacoordinate silane **154** with the appropriate metal carbonyls (Scheme 40). A preliminary study of the reactivity of complex **177** has shown it to be unreactive toward alcohols and unsaturated hydrocarbons but highly oxidizable and hydrolyzable. Coupling of the pentacoordinate dichlorosilanes **179a** and **179b** with $Na_2[Cr(CO)_5]$ resulted exclusively in the formation of the complexes **180a** and **180b**[150] (eq 75).

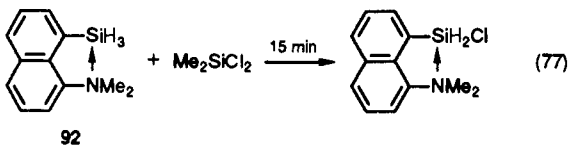


(75)

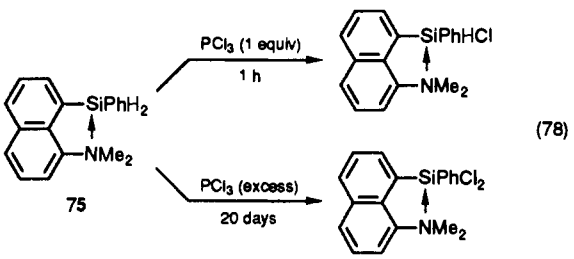
On the basis of spectroscopic data the silanediyl structure could be unequivocally assigned to **180a** and **180b**. These conclusions were confirmed and supplemented by single-crystal X-ray structure analysis of **180a**, which showed the Cr–Si bond length (2.41 Å) to be noticeably short.[235,236] One Si–N distance is 3.31 Å, which may be regarded as a van der Waals contact. The other one (2.04 Å) is shorter than the Si–N distance of the coordinate dimethylamino substituent in the dichlorosilane **179a**. This underlines the high electrophilicity of the silicon atom in **180a**.

e. Hydrogen–Halogen Exchange Reactions. Hydrogen–halogen exchange with pentacoordinate hydrogenosilanes has been found to be very easy and very selective, using chlorosilanes or halogenophosphorus compounds[237] as sources of chlorine. Monochlorination only of **75** and of **92** was effected quantitatively with $MeSiCl_3$ or Me_2SiCl_2, even in the presence of an excess of chlorosilane (eqs 76 and 77). The monochlorination



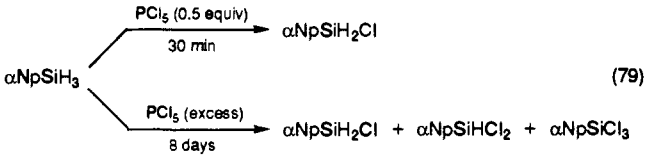


of **75** is also possible with 1 molar equiv of PCl_3, whereas an excess of PCl_3 leads to formation of dichlorinated product after a long reaction time (eq 78). It is



important to note that, under the same conditions, hydrogen–halogen exchange is not observed with $PhSiH_3$, nor with $\alpha NpSiH_3$.

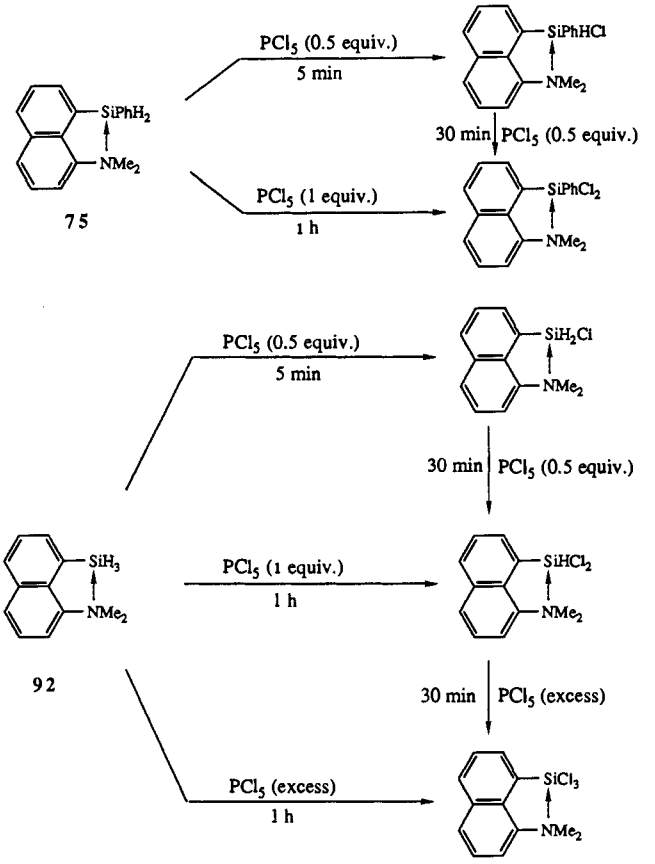
PCl_5 is a more efficient reagent for hydrogen–halogen exchange in pentacoordinate hydrosilanes.[237] The reaction is selective and according to the quantity of reagent, the mono-, di-, or trisubstituted product (Scheme 41) can be obtained quantitatively. The halogenation of $\alpha NpSiH_3$ with PCl_5 is possible, but the reaction is not selective, and the exchange is slower than for a pentacoordinate hydrogenosilane (eq 79).



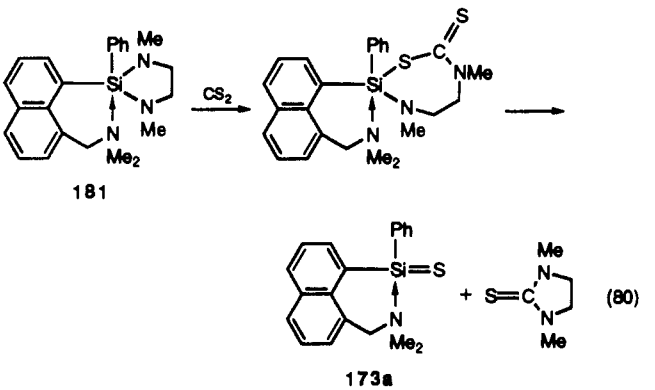
2. Pentacoordinate Diaminosilanes

Facile aminosilylation of heterocumulenes was observed by Lappert and co-workers[238,239] some years ago; reaction of heterocumulenes with pentacoordinate diaminosilanes was studied to determine whether subsequent formation of low-coordinate silicon species from these adducts was possible.[240] The insertion of 1 mol only of CS_2 into the Si–N bond was observed with pentacoordinate cyclic diaminosilanes **181** (eq 80), regardless of the quantity of the reagent. The insertion compound decomposed easily to give the corresponding silanethione **173a** together with the substituted

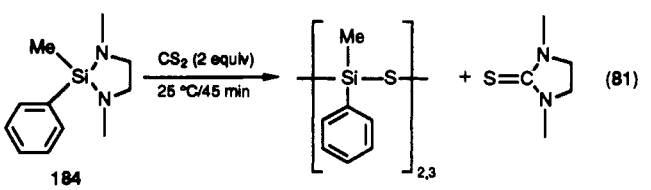
Scheme 41



thiourea (eq 80). The reaction of CS_2 with the pentacoordinate acyclic diaminosilane **183** is more specific,

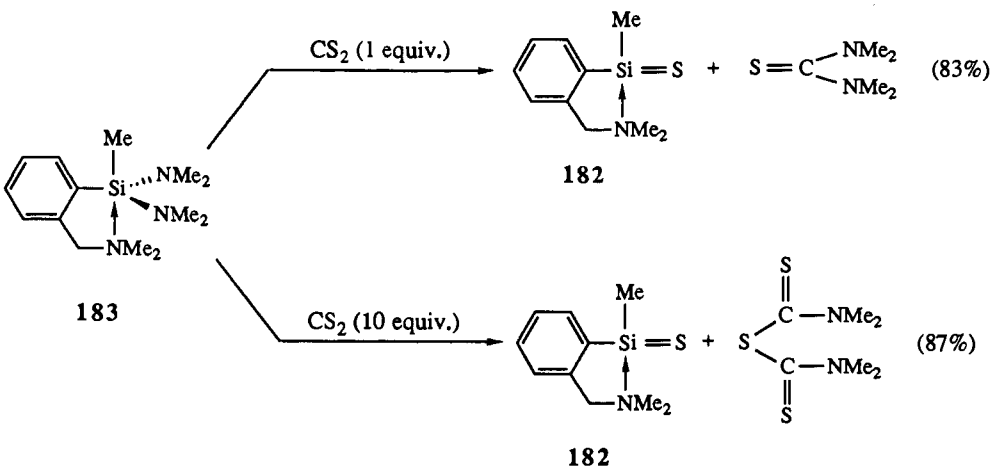


but in any case the thermal decomposition of the insertion product gave the silanethione **182** (Scheme 42). The tetracoordinate diaminosilane **184** reacts similarly under mild conditions with 2 molar equiv of CS_2 in the absence of added catalyst to give dimeric and trimeric methylphenylsilathianes (eq 81).

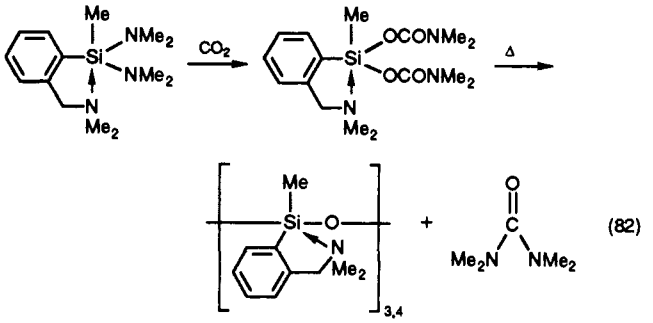


Insertion of CO_2 into the Si–N bonds of pentacoordinate diaminosilanes occurs under very mild condi-

Scheme 42



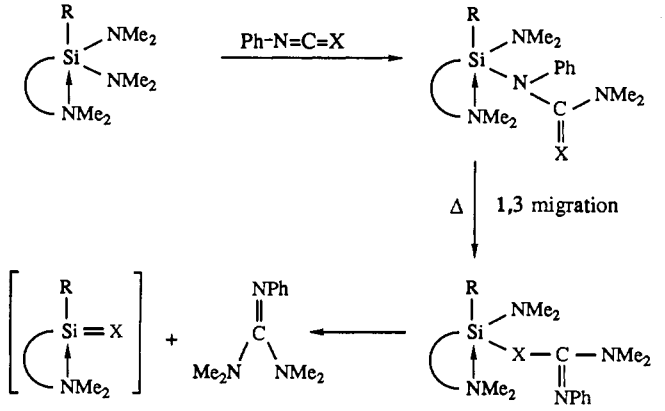
tions. The adducts decompose only when the mixtures are warmed (eq 82). In contrast, decomposition of the



adducts obtained from tetracoordinate diaminosilanes occurs even at room temperature with slow formation of a complicated mixture of siloxanes.

PhNCO and PhNCS react also with pentacoordinate diaminosilanes to give the mono- or diinsertion product according to the ratio of the reactants. Spectroscopic data indicate clearly the initial regioselective formation of ureido(thio)silanes (N-silylation). Rearrangement (1,3-migration) possibly occurs before the thermal decomposition step which leads to the transient silanone from PhNCO and to the silanethione from PhNCS (Scheme 43). 1,3-Migration in amidosilanes is a well-

Scheme 43



known process.[241] Such a rearrangement has previously been suggested to take place during the decomposition of a pentacoordinate thioamidosilane.[225] The products of insertion of PhNCO and PhNCS into tetracoordinate diaminosilanes are stable in refluxing CCl_4 for 12 h. Heating at 120–130 °C results in their thermal decomposition.[240]

F. Aptitude of Pentacoordinate Silicon Compounds To Become Hexacoordinate: Structure–Reactivity Relationships

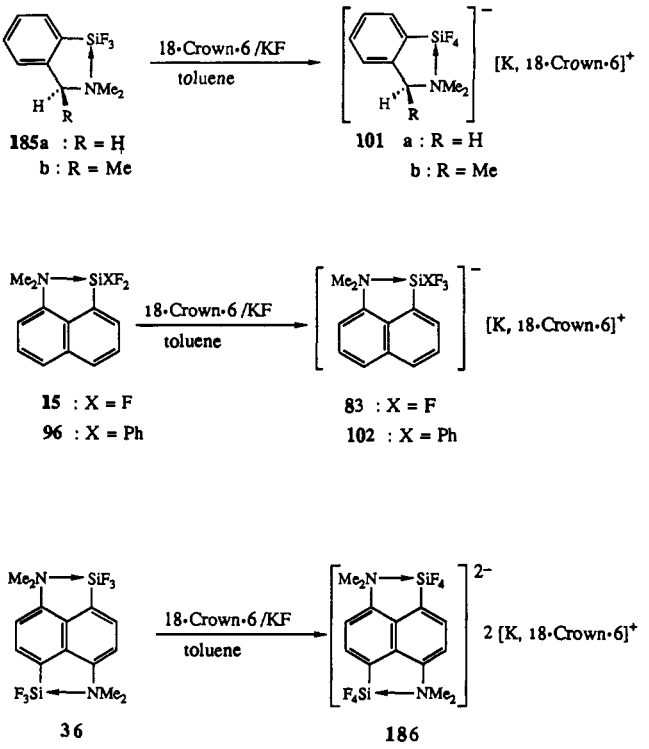
Pentacoordinate anionic and neutral silicon species have been shown (in this section) to be able to undergo facile nucleophilic substitution at silicon by strong nucleophiles. Hexacoordinate silicon species have frequently been proposed as intermediates or transition states in these reactions.[3,11,180,208–210] In order to obtain information on the involvement of such species in the reactivity of pentacoordinate silicon compounds, a range of pentacoordinate models have been prepared in which hexacoordination may be achieved by intramolecular coordination. Following the proposal developed by Dunitz and Britton,[242] these models should provide an indication of the possible pathway for nucleophilic attack at the silicon atom and give a picture of the geometry of the intermediate formed during these reactions.

Hexacoordinate fluorosilicates **83**, **101a**, **101b**, **102**, and **186**, have been synthesized from the corresponding pentacoordinate fluorosilanes by reaction with 1 equiv of 18-crown-6/KF in high yields.[166] Interestingly **15** reacts with KF, even in the absence of crown ether, to give a stable salt with spectroscopic characteristics identical to those of the crown salt **83** (Scheme 44).

It was also observed that whereas F^- coordination takes place with pentacoordinate di- and trifluorosilanes to give the corresponding hexacoordinate tri- and tetrafluorosilicates, the pentacoordinate monofluorosilicates do not react.

The hexacoordination of compounds **83**, **101**, **102**, and **186** in solution was demonstrated unambiguously by ^{29}Si and ^{19}F NMR data.[166] The X-ray crystal structure of **83** was determined. The complex was found to exhibit slightly distorted octahedral geometry in which the four Si–F bonds are approximately equivalent (1.65–1.68 Å), the shortest being the Si–F bond opposite to the Si–N coordinate bond. Si–F bond lengths lie in the same range as those for $[SiF_6]^{2-}$ complexes.[8,159] The Si–N distance in **83** (2.21 Å) is short compared with the previously reported values (2.59–2.81 Å) for the neutral hexacoordinate difluorosilane **53**.[107] It is shorter than

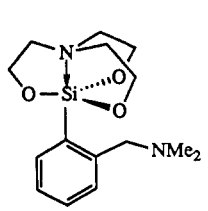
Scheme 44



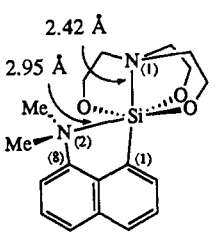
that in the neutral pentacoordinate starting material **15** (Scheme 44) (2.31 Å).[147]

The molecular structure[165] of the bis(1,2-benzenediolato)silicate **81** shows that the anion adopts an octahedral geometry very similar to that of complex **83**. **81** more closely resembles a hexacoordinate species than a pentacoordinate species since the lengths of the six Si–O bonds in the anionic hexacoordinate silicon complex **62d**[162] are very close to those of **81** (between 1.765 and 1.813 Å, average value 1.784 Å). The short Si–N distance (2.15 Å) illustrates the electrophilic character of the silicon atom, which is in agreement with the high reactivity of bis(1,2-benzenediolato)silicates **113a–115a**[71a] toward nucleophiles.

These results show the highly electrophilic character of the pentacoordinate silicon atom when surrounded by electron-withdrawing fluoro or catecholato substituents. To obtain additional information about the ability of pentacoordinate silicon species to become hexacoordinated, the structures of other pentacoordinate silicon derivatives have been examined. The molecular structures of silatranes **187** and **188** which might also become hexacoordinated by intramolecular coordination have been determined.[243] The single-



187

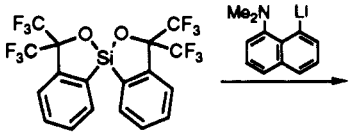


188

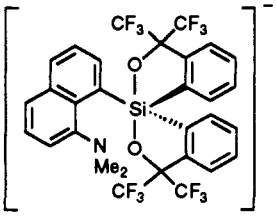
crystal X-ray diffraction analysis of **187** has shown that the NMe_2 group is not coordinated to the silicon atom, in contrast to the situation for the anionic pentacoordinate silicate **81**. The structure of **187** displays the same geometry (trigonal bipyramidal) about the silicon atom as that usually observed with silatranes.[81]

The case of the silatrane **188** is more arguable. In solution, the ^1H NMR spectrum exhibits a sharp singlet at room temperature for the NMe_2 group. The ^{29}Si chemical shift of **188** in solution appears at $\delta = -70.56$ ppm downfield from that of (1-naphthyl)silatrane ($\delta = -80.49$ ppm). These results indicate that the silicon atom remains pentacoordinated in solution. Nevertheless, the X-ray structure of **188** reveals that the geometry about the silicon atom is hexacoordinated with a highly distorted octahedral geometry. The length of the Si–N(2) bond (2.95 Å) indicates a weak interaction between the silicon and nitrogen atoms, imposed by the rigid geometry of the 8-(dimethylamino)-1-naphthyl group. The Si–N(1) bond distance (2.42 Å) is about 10% longer than the Si–N bond in phenylsilatrane (2.19 Å). Moreover the naphthyl group is no longer planar. A measure of this out-of-plane deformation is given by the dihedral angle N(2)–C(8)–C(1)–Si the value of which is as large as 27°. In conclusion the overall result illustrate the difficulty for silatranes to become hexacoordinated. The rigidity of the silatrane cage is certainly not favorable for hexacoordination because of the narrowing of the O–Si–O bond angles required for conversion into a near-octahedral structure. Moreover the electrophilic character of the silicon atom which is a function of the nature of the surrounding ligands is inherently rather weak.

The case of compounds of Martin's ligand has also been studied.[106] The compound **189** has been prepared by reaction of the corresponding lithio derivative with the spirosilane **8** (eq 83). The X-ray structure analysis



8



(83)

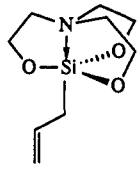
189

of **189** has not yet been completed. However in solution the ^{29}Si NMR chemical shift of **189** ($\delta = -74.3$ ppm) corresponds to a pentacoordinate silicon atom. The absence of observable diastereotopy in the ^1H NMR spectrum of the NMe_2 group indicates the lack of coordination of this group to the silicon atom, as in the case of compound **188**. It is significant that, whereas silane **8** coordinates a further ligand easily to give pentacoordinate complexes[45,46,48] or a 1:1 adduct,[47] no case is known where **8** forms a hexacoordinate compound by addition of two nucleophiles.[47]

A parallel exists between the aptitude of pentacoordinate silicon species to become hexacoordinated and the reactivity of these species. For instance, there is a dramatic difference in reactivity between the pen-

tacoordinate hydridosilanes **122**, **147** (Scheme 29), and **129** (eq 44) toward carbonyl compounds. Bis(1,2-benzendiolato)hydridosilicate (**122**)[73] reduces aldehydes and ketones easily without any catalyst (eqs 38 and 39). Hydridosilatrane **147** reduces carbonyl compounds[215] but reaction conditions are more severe; heating and long reaction times are necessary (Scheme 29). Pure lithium hydridosilicate **129**, as well as the corresponding tetrabutylammonium salt **131** (eq 45), have been found to reduce aldehydes only very slowly.[46] The reactivity of **122** toward carbonyl compounds can be explained by the formation of a hexacoordinate intermediate by coordination of the oxygen of the carbonyl to the silicon, facilitating the transfer of the hydride anion to the carbonyl group. This hypothesis is supported by the hexacoordination of compound **81**. In contrast, the formation of a hexacoordinate intermediate by coordination of the oxygen of the carbonyl group to the silicon atom in **147** and **129** is much less likely, as the structural study of silatranes **187** and **188** and the NMR study of **189** have shown.

The difference in reactivity between allylsilicates **135b**, **190**, and **140a** can be explained similarly. Com-



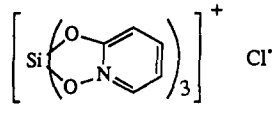
190

plex **135b** reacts easily with aldehydes without a catalyst.[205] The stereoselectivity of this reaction is nicely rationalized by the formation of a six-membered cyclic transition state[204] (Scheme 27) in which the silicon atom is hexacoordinated. This interpretation agrees with the ease with which compounds of this series become hexacoordinated (cf. structure of **81**). In contrast compounds **190**[74] and **140a**[204] do not react with carbonyl compounds under the same conditions. This inertness again can be explained by the difficulty for the silicon atom to become hexacoordinated in these structures.

VII. Reactivity of Hexacoordinate Silicon Compounds

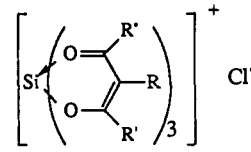
A. Cationic Complexes

The chemical reactivity of hexacoordinate cationic complexes depends on the nature of the ligands and varies widely from one complex to another. Thus compound **191** is so stable to hydrolysis that it can be recovered unchanged from evaporation of an aqueous solution.[244] However the chelate **60b** from (*N,N'*-dimethylamino)troponimine is susceptible to acid-catalyzed hydrolysis,[113] whereas the hydrolysis of the tris(tropolonate) **60a** is catalyzed by hydroxide ion.[245]



191

Complexes of 1,3-diketonates have been investigated several times. **192** (R = H, R' = Me or Ph) hydrolyzes slowly in weak aqueous acid and rapidly in alkaline medium.[246,247] Substituents at position 3 of 2,4-pentanedionates **192** (R' = Me, R = benzyl, allyl, Me, Et, Pr^i, OAc, or Cl) also increase the rate of hydrolysis.[248]



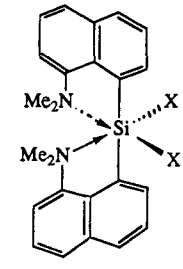
192

Studies of the racemization of some of these chiral chelates have also been carried out. The rates of racemization are the same as those of hydrolysis.[246,249]

The tris(2,2'-bipyridine) complex **45** (Scheme 7) is stable in aqueous solution, as are the bis(2,2'-bipyridine) complexes **43a** and **43b**,[96,99,101] (Scheme 7). Complexes **39a**,[95] and their 1,10-phenanthroline analogs **39b**,[250] (Scheme 6) are decomposed quickly by methanol when X, Y = H, alkyl, or aryl, but much more slowly when X, Y = Cl or OMe. Complexes where X = Y = Cl or X = Me, Y = Cl undergo substitution of Cl by OMe in methanol solution.[250]

B. Neutral Complexes

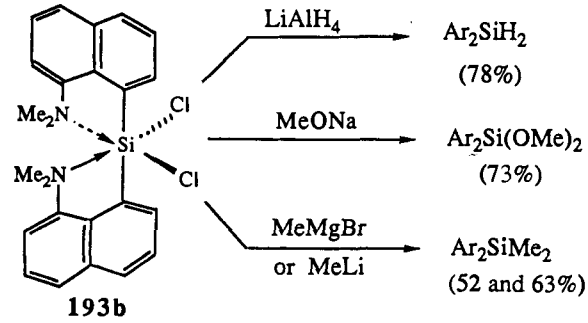
The reactivities of compounds **193a** and **193b** were surprisingly very different: difluorosilane **193a**[251] is apparently totally inert to attack even by powerful nucleophilic reagents ($LiAlH_4$, RMgBr, RLi, ROH, RONa). In contrast the dichloro compound **193b** is



193 a : X = F
b : X = Cl

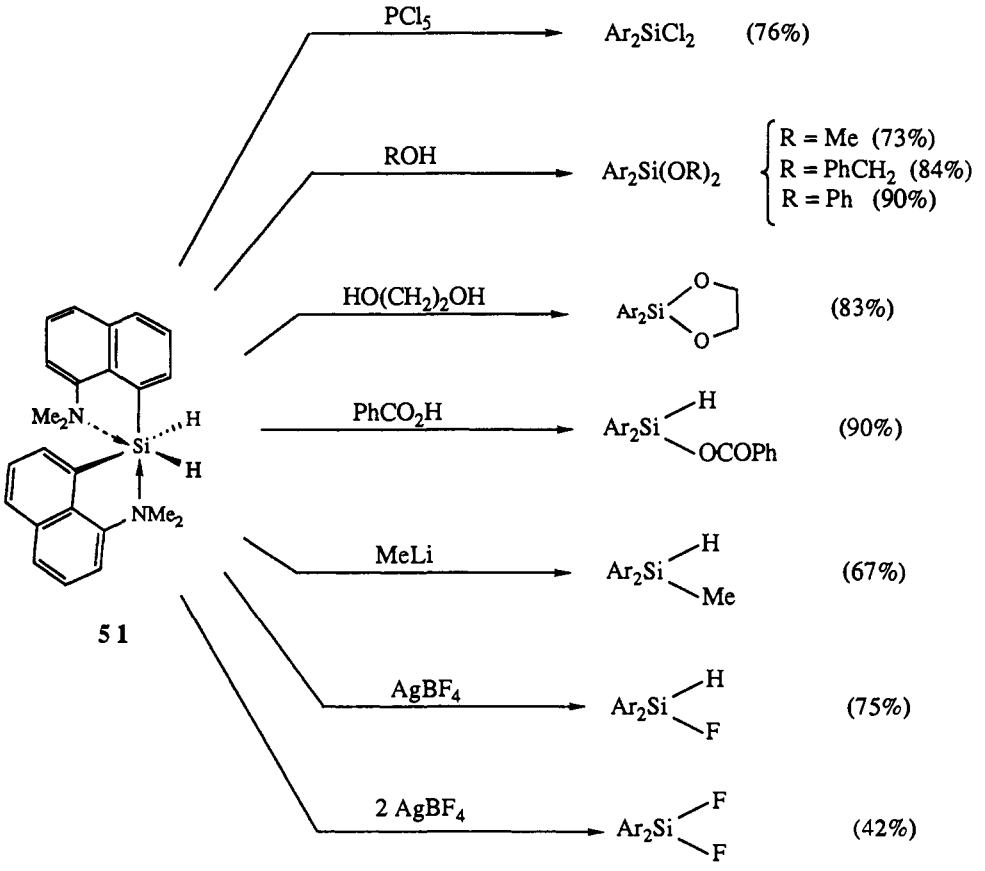
readily substituted by nucleophiles[251] (Scheme 45). The structures of the two halides **193a** and **193b** are however basically similar: both are hexacoordinated with a NMe_2 group opposite to each halogen. A possible explanation for the high reactivity of the dichlorosilane **193b** could

Scheme 45

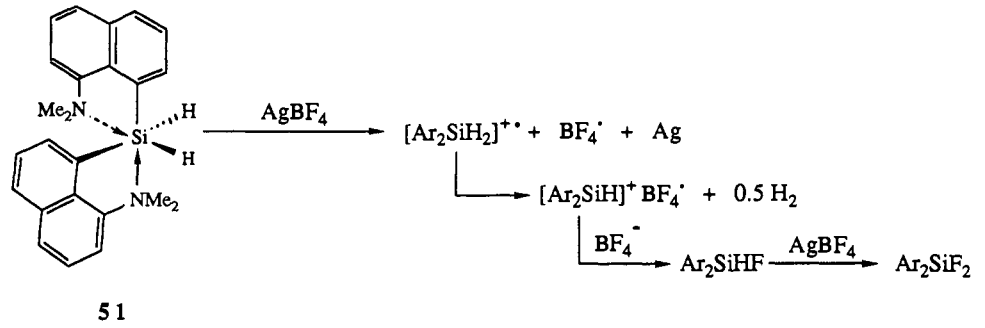


193b

Scheme 46



Scheme 47



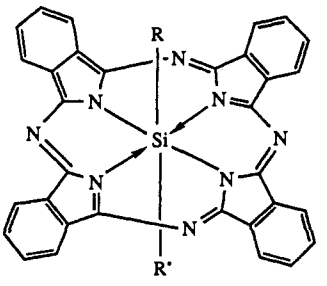
be the ease of dissociation of the Si–Cl bond compared to that of the Si–F bond. Bassindale and Borbaruah have recently pointed out that the Si–Cl bond exhibits an enhanced ability to favor intermolecular coordination in comparison with the Si–F bond.[252] The lack of reactivity of difluorosilane **193a** toward nucleophilic reagents is in marked contrast to the high reactivity of pentacoordinate fluorosilicates,[33,182] which have been shown to be more reactive than the corresponding tetracoordinates ones toward nucleophilic reagents. This lack of reactivity could be associated with the small elongation of the Si–F bonds, as shown for the analogous difluorosilane **53**.[107]

The reactivity of the dihydrosilane **51** is also unexpected.[251] Treatment with hydroxyl-containing compounds leads to alkoxysilanes (Scheme 46), whereas alkoxides (MeONa and PhONa) do not react. **51** may however be chlorinated by means of an exchange reaction with PCl_5 (Scheme 46) in a similar reaction to that observed with neutral pentacoordinate dihydrosilanes.[237] These reactions probably proceed by electrophilic attack on hydrogen, since **51** does not react with nucleophiles such as Grignard reagents. In the case of lithium compounds, monosubstitution by MeLi was observed after long reaction times. Furthermore, although pentacoordinate dihydrogenosilanes react with acid chlorides,[224] sulfur,[232] and CS_2,[232] compound **51** is inert toward these reagents.

51 is also susceptible to oxidation. Reaction with $AgBF_4$ leads to stepwise replacement of hydrogen by fluorine, with precipitation of silver and evolution of dihydrogen.[251] This reaction can be explained by the formation of a transient pentacoordinate siliconium ion via initial one electron transfer (Schem 47). It is worth noting that there is no evolution of dihydrogen when Ph_3SiH and Ph_2SiH_2 are treated with $AgBF_4$ under the same conditions.

The chemistry of diorgano(phthalocyaninato)silicon compounds **194** has also been investigated.[253] Alkyl- and aryl-silicon bonds in **194** are cleaved by NBS,

Scheme 48



194

NBS → RBr + R'Br

R = R' = p-$MeOC_6H_4$	88%	
R = n-C_8H_{17}, R'= p-$MeOC_6H_4$	20%	81%
R = n-C_8H_{17}, R' = p-MeC_6H_4	72%	17%
R = C_6H_5, R' = p-$MeOC_6H_4$	4%	88%

Br_2 → 2 RBr

R = R' = C_8H_{17}	61%
R = R' = p-$MeOC_6H_4$	74%

$CuBr_2$ → 2 RBr

R = R' = n-C_8H_{17}	70%
R = R'= p-$MeOC_6H_4$	23%

halogens, and copper(II) halides. In the case of cleavage by NBS (Scheme 48) the electronic effects observed may be summarized as follows: (1) The reactivity of the R–Si bond toward NBS decreases in the order 4-$MeOC_6H_4$ > *n*-C_8H_{17} > 4-MeC_6H_4 > Ph ≫ 3-$CF_3C_6H_4$.

(2) The reactivity of the alkyl–silicon bond is lowered by the trans group (trans effect) in the order 4-$MeOC_6H_4$ > Ph > 3-$CF_3C_6H_4$ > Cl.

A significant electronic effect was also observed (Scheme 48) in the cleavage of aryl–silicon bonds by bromine, the reactivity of the aryl–Si bonds decreasing in the order 4-$MeOC_6H_4$ > 4-MeC_6H_4 > Ph ≫ 3-$CF_3C_6H_4$.

Alkyl–silicon bonds in these compounds are readily cleaved by CuX_2 (Scheme 48) while aryl–silicon bonds are much less reactive toward this reagent. The reactivity of the 4-$MeOC_6H_4$–Si bond is much lower than that of the alkyl silicon bond, in contrast to observations on cleavage by NBS and halogens.

The experimental results suggest that at least two distinct mechanisms operate for the electrophilic cleavage of diorgano(phthalocyaninato)silicon compounds. In alkyl–silicon cleavage, one electron transfer appears to be the initial step, whereas aryl–silicon fission is probably initiated by electrophilic attack on the aryl moiety, consistent with the higher reactivity of the 4-$MeOC_6H_4$ derivative toward bromine.

C. Anionic Complexes

1. Organopentafluorosilicates

Organopentafluorosilicates are compounds which are easy to isolate and air-stable. The pioneer work of Müller[17,18] demonstrated the potential of such complexes, but the development of this chemistry, particularly the numerous applications in organic synthesis, is due to Kumada and co-workers.[19]

a. Organopentafluorosilicates as Fluorinating Reagents. Chlorosilanes take part in exchange reactions with organopentafluorosilicates.[254] These reactions occur in water (eq 84) or in the absence of solvent (eq 85).

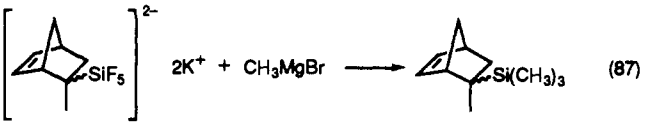
$$[MeSiF_5]^{2-}2Na^+ + 2Me_3SiCl \xrightarrow{H_2O} 2Me_3SiF + MeSiF_3 + 2NaCl \quad (84)$$
(71%) (80%)

$$[PhSiF_5]^{2-}2Na^+ + 2MeSiHCl_2 \rightarrow 2MeSiHF_2 + PhSiF_3 + 2NaCl \quad (85)$$
(70%)

b. Reactions with Grignard Reagents. Organopentafluorosilicates react with Grignard reagents[255,256] to give the corresponding tetraorganosilanes but the yields are generally poor (eqs 86 and 87). The hexafluorosilicate anion $[SiF_6]^{2-}$ also reacts with Grignard reagents[257] (eq 88), but heating and long reaction times are necessary and the yield is also poor.

$$[MeSiF_5]^{2-}\,2M^+ + 3C_2H_5MgBr \xrightarrow{80\,°C} MeSi(C_2H_5)_3 + 3MgBrF + 2MF \quad (86)$$

M = K (25%); M = Na (31%); M = NH_4 (12%)



$$2K^+ + CH_3MgBr \longrightarrow \quad (87)$$

exo/endo = 58/42
exo/endo = 5/95

60% exo/endo = 62/38
60% exo/endo = 8/92

$$[SiF_6]^{2-}2Na^+ + 4C_2H_5MgBr \xrightarrow{160\,°C} Si(C_2H_5)_4 \quad (88)$$
(21%)

c. Cleavage Reactions of Si–C Bonds by Inorganic Salts. Organopentafluorosilicates react with $HgCl_2$ to give organomercury compounds[258] (eqs 89 and 90). A similar exchange reaction takes place with antimony salts[259] (eqs 91 and 92) and with bismuth and lead salts.

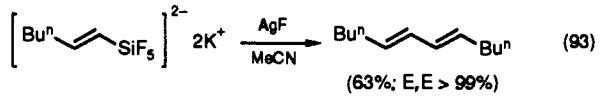
$$[MeSiF_5]^{2-}2NH_4^+ + HgCl_2 \xrightarrow[\text{room temp}]{H_2O} MeHgCl + [ClSiF_5]^{2-}2NH_4^+ \quad (89)$$
(92%)

$$[MeSiF_5]^{2-}2NH_4^+ + MeHgCl \xrightarrow[\text{room temp}]{H_2O} Me_2Hg + 2[ClSiF_5]^{2-}2NH_4^+ \quad (90)$$
(83%)

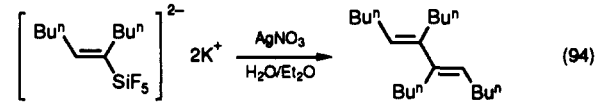
$$3[MeSiF_5]^{2-}2NH_4^+ + SbF_3 \xrightarrow{H_2O} Me_3Sb + 3[SiF_6]^{2-}2NH_4^+ \quad (91)$$
(79%)

$$2[PhSiF_5]^{2-}2NH_4^+ + SbF_3 \xrightarrow{H_2O} Ph_2SbF + 2[SiF_6]^{2-}2NH_4^+ \quad (92)$$
(43%)

d. Homocoupling Reactions Promoted by Silver (I) or Copper (I) Salts. Symmetrical (*E*,*E*)-1,3-dienes can be prepared stereoselectively in good yields from (*E*)-alkenylsilicates either by treatment with silver fluoride in acetonitrile or by stirring with silver nitrate in water/ether.[260] Representative results are given in eqs 93 and 94. Earlier, Müller et al. had noted that a



(93)
(63%; E,E > 99%)



(94)
(72%)

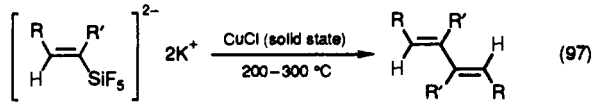
characteristic color appears when an organopentafluorosilicate is mixed with a silver(I) salt.[261] They had also reported the homocoupling reaction of vinylpentafluorosilicates induced by silver nitrate in water, giving 1,3-dienes[281] (eq 95), whereas in the case of

$$[CH_2{=}CHSiF_5]^{2-}2K^+ \xrightarrow[AgNO_3]{H_2O} CH_2{=}CH{-}CH{=}CH_2 \quad (95)$$

perfluorovinylpentafluorosilicates under the same conditions, the hydrolysis product was obtained (eq 96).

$$[CF_2{=}CFSiF_5]^{2-}2K^+ \xrightarrow[AgNO_3]{H_2O} CF_2{=}CFH \quad (96)$$

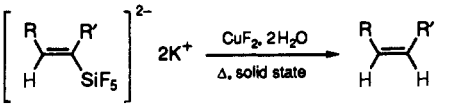
The homocoupling reaction could also be promoted by copper(I) chloride, without solvent.[262] This solid-state reaction requires heating (200–300 °C) (eq 97). In



(97)

R = Ph; R′ = H (64%)
R = Bu^n; R′ = H (30%)
R = R′ = Bu^n (43%)

contrast, copper(II) fluoride dihydrate gave almost exclusively protonolysis products from both alkyl and alkenyl silicates[262] (eq 98).

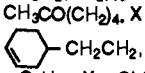


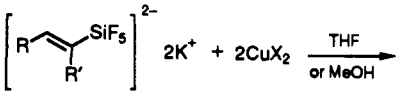
(98)

(R′ = H or R)

e. Copper(II) Oxidation of Organopentafluorosilicates. The carbon–silicon bond in organopentafluorosilicates $[RSiF_5]^{2-}2K^+$ (R = alkyl, alkenyl, and phenyl) is cleaved by copper(II) chloride or bromide to give the corresponding organic halides with good yields.[263] The reaction follows strictly the stoichiometry shown in equation 99. (*E*)-Alkenyl halides are obtained stereoselectively from (*E*)-alkenyl silicates (eq 100). Loss

$$[RSiF_5]^{2-}2K^+ + 2CuX_2 \xrightarrow{Et_2O \text{ or } THF} RX + 2CuX + [XSiF_5]^{2-}2K^+ \quad (99)$$

R = *n*-C_8H_{17}, X = Cl (70%), X = Br (70%)
R = $CH_3O_2(CH_2)_{10}$, X = Cl (70%)
R = $CH_3CO(CH_2)_4$, X = Cl (46%)
R =  CH_2CH_2, X = Cl (51%)
R = c-C_6H_{11}, X = Cl (18%)
R = Ph, X = Cl (75%), X = Br (79%)



(100)

R = Ph, R′ = H, X = Br (59%, 100% *E*)
R = Bu^n, R′ = H, X = Br (61%, 99% *E*)
R = R′ = Bu^n, X = Br (55%, >95% *E*)

of stereospecificity was observed in the case of *endo*- and *exo*-norbornyl pentafluorosilicates.

The reaction seems to proceed by an initial one-electron oxidation, with formation of a free alkyl radical which undergoes racemization before conversion to halide (Scheme 49). Such a mechanism is supported

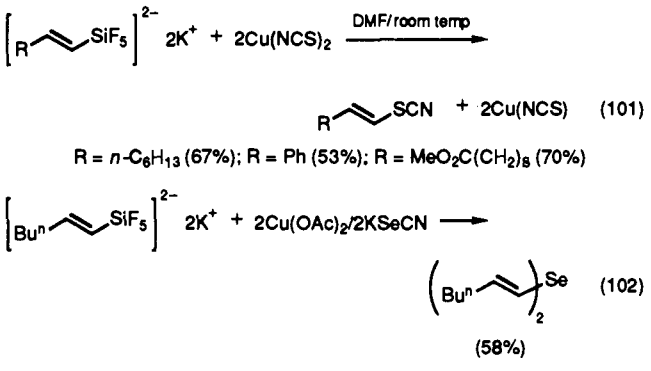
Scheme 49

$$[RSiF_5]^{2\cdot} + Cu^{II}X_2 \longrightarrow R^\cdot + [XSiF_5]^{2\cdot} + Cu^{I}X$$

$$R^\cdot + Cu^{II}X_2 \longrightarrow RX + Cu^{I}X$$

(1) by the formation of an aldehyde, at the expense of the halide, in the presence of oxygen; (2) by the loss of stereospecificity in the case of *exo*- and *endo*-2-norbornylsilicates; (3) by the observation of an ESR spectrum in the presence of a nitroso radical trap.

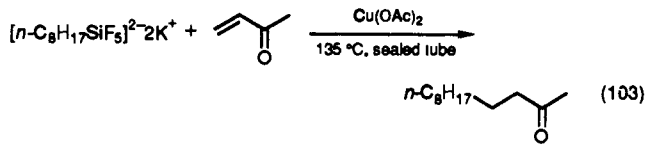
Alkenyl- (but not alkyl-) pentafluorosilicates react with copper(II) thiocyanate to give the corresponding alkenyl thiocyanates[263] (eq 101) and with copper(II) selenocyanates prepared in situ, to give dialkenyl selenide[263] (eq 102).



R = n-C_6H_{13} (67%); R = Ph (53%); R = $MeO_2C(CH_2)_8$ (70%)

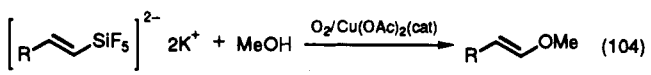
(58%)

f. Cleavage of the Si–C Bond by Copper(II) Acetate. In the presence of copper(II) acetate, 1,4-addition of alkylpentafluorosilicates to α,β-unsaturated ketones takes place under severe conditions and without solvent[263] (eq 103). In methanol as solvent and under



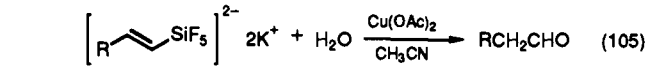
(70%)

an oxygen atmosphere a catalytic amount of copper(II) acetate promotes the cleavage of the Si–C bond of alkenylpentafluorosilicates to give alkenyl ethers.[263] The reaction is highly stereospecific and gives the (E)-alkenyl ether with an isomeric purity of over 99% from an (E)-alkenylpentafluorosilicate (eq 104). The yield of alkenyl ether decreases with the steric bulk of the alcohol.



R = n-C_6H_{13}	(56%)
R = Ph	(51%)
R = $MeO_2C(CH_2)_8$	(67%)

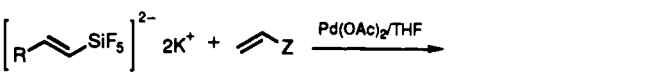
Oxidative hydrolysis of alkenylsilicates takes place in air in the presence of a catalytic amount of copper(II) acetate in solution in acetonitrile to give aldehydes[263] (eq 105).



R = n-C_6H_{13}	(52%)
R = $MeO_2C(CH_2)_8$	(50%)

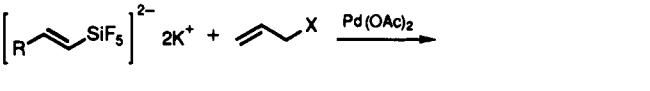
g. Carbon–Carbon Bond Formation Promoted by Palladium Salts. Alkenyl- and phenylpentafluorosilicates react with activated alkenes such as methyl acrylate, acrylonitrile, acrolein, and methyl crotonate in the presence of a stoichiometric amount of palladium acetate to give 1,3-dienes and phenyl-substituted alkenes, respectively.[264] The reaction is highly stereoselective, except with acrylonitrile. From (E)-alkenylsilicates only (E,E)-dienes are obtained (eq 106).

With allylic halides, (E)-alkenylsilicates react in the presence of a catalytic amount of palladium salt to give the corresponding cross-coupled products, (E)-1,4-



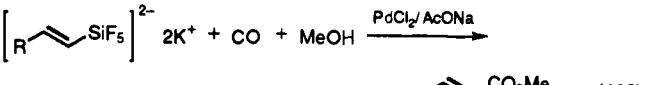
R = n-C_4H_9; Z = CHO	(20%)
Z = CO_2Me	(37%)
Z = CN	(43%)
R = Ph; Z = CO_2Me	(35%)

dienes, in good yield.[264] The reaction is stereoselective, the E stereochemistry of the alkenylsilicate being retained during the reaction. In all cases the reaction is highly regioselective, the allyl group being introduced onto the carbon atom which was originally attached to the silicon atom (eq 107).



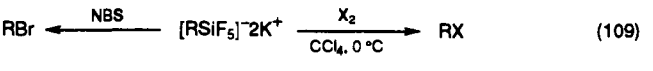
R = n-C_4H_9; X = Cl	(71%)
X = Br	(60%)
X = OTs	(24%)
R = Ph; X = Cl	(40%)

h. Carbonylation. (E)-Alkenylpentafluorosilicates react readily with carbon monoxide (under atmospheric pressure), in the presence of a palladium salt and sodium acetate in methanol, to give (E)-α,β-unsaturated carboxylic esters, in good yield.[264] This reaction constitutes the first reported case of carbonylation of an organosilicon compound (eq 108).



R = n-C_6H_{13}	(83%)
R = Ph	(76%)
R = CH_3OCH_2	(61%)

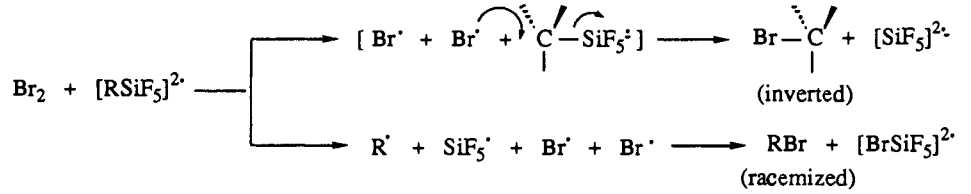
i. Cleavage of Organopentafluorosilicates by Halogens and by N-Bromosuccinimide. N-Bromosuccinimide, IBr, and elemental halogens (Cl_2, Br_2, I_2) induce cleavage of alkyl-, alkenyl-, and arylpentafluorosilicates with formation of the corresponding organic halide[91,265] (eq 109). In all cases the halogen atom is



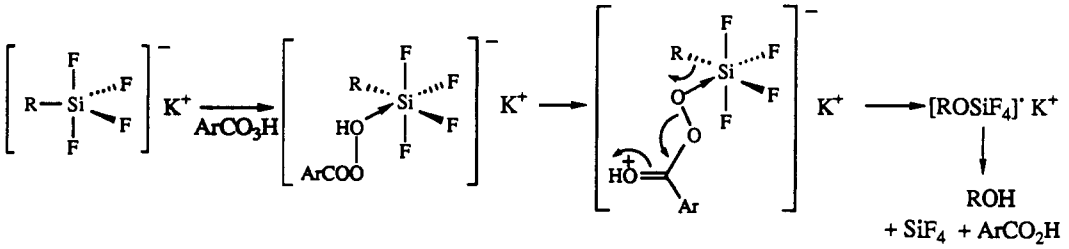
77% (in C_6H_6)	R = n-C_8H_{17}	73% (X = Cl)	
		69% (X = Br)	
		73% (X = I)	
79% (in MeOH)	R = c-C_6H_{11}	54% (X = Cl)	at 35 °C
		63% (X = Br)	at 35 °C
		32% (X = I)	at 50 °C
74% (in MeOH)	R = Ph	59% (X = Br)	

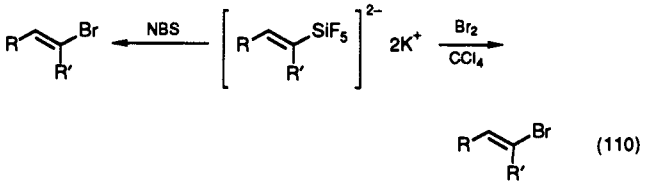
regioselectively introduced onto the carbon atom which was attached to the silicon atom. The stereoselectivity of the reaction of alkenylsilicates is higher with NBS than with bromine (eq 110). The NBS cleavage reaction is compatible with various functional groups, including alkoxycarbonyl, oxo, halo, and alkenyl groups. Cleavage of alkenylpentafluorosilicates by halogen or NBS occurs with retention of configuration. The stereospecificity

Scheme 50



Scheme 51

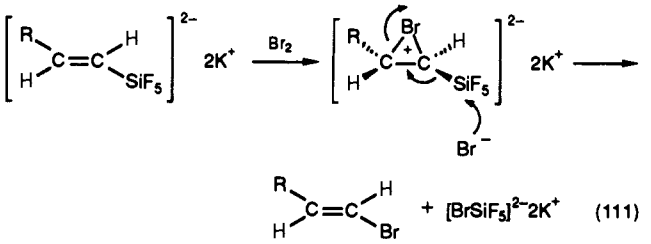




(110)

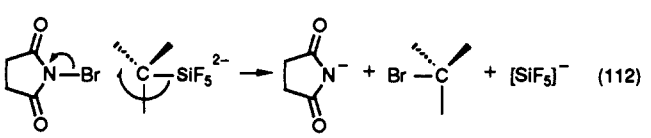
75% (91% *E*) (in C_6H_6) R = Bu^n, R′ = H 61% (67% *E*)
83% (100% *E*) (in MeOH) R = Ph, R′ = H
70% (>99% *E*) (in C_6H_6) R = R′ = Bu^n

of the reaction was explained by direct electrophilic displacement of silicon by attack at the α-carbon atom (eq 111).



(111)

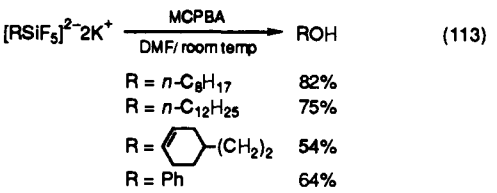
The stereochemistry of the cleavage of *exo*- and *endo*-2-norbornylpentafluorosilicates by bromine and NBS was examined in different solvents. In polar solvents the cleavage of both isomers proceeded with greater than 95% inversion of configuration at the carbon atom, both with NBS and with bromine. In nonpolar solvents, loss of stereoselectivity was observed in the reaction of the exo isomer with bromine. The inversion of configuration in the reaction with NBS was explained by direct electrophilic displacement (eq 112), but the



(112)

reaction with bromine was considered to proceed by an initial electron-transfer step, followed by nucleophilic attack of bromide ion on the resulting organopentafluorosilicate radical ion (Scheme 50). Steric factors or a reduction in the polarity of the solvent would facilitate dissociation of the radical ion to a free alkyl radical and loss of stereoselectivity, as observed (Scheme 50).

j. Oxidative Cleavage of Silicon–Carbon Bonds in Organopentafluorosilicates. Organopentafluorosilicates are cleaved by *m*-chloroperbenzoic acid (MCPBA) in DMF to give the corresponding alcohols in high yields[266] (eq 113). The reaction is stereospecific



(113)

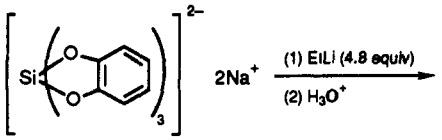
and proceeds with retention of configuration. It was observed that the cleavage of silicates was almost completely inhibited by added LiF or KF in diglyme. This observation suggests a mechanism involving prior dissociation of the organopentafluorosilicate, probably to the organotetrafluorosilicate, since organofluorosilanes, R_2SiF_2, and R_3SiF may also be oxidized, but only in the presence of increasing amounts of potassium fluoride (Scheme 51).

2. Hexacoordinate Tris(1,2-benzenediolato)silicates

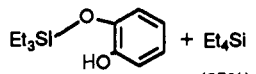
Although it had been known for sometime that catechol reacts in aqueous alkaline solution with silica gel, colloidal silica, and even finely divided quartz to form the anionic tris(1,2-benzenediolato)silicates **62**[116,117] the reactivity of these complexes had not been studied until recently.[115] Barnum[118] observed that complex **62** (M = NH_4) was stable in water and dilute aqueous ammonia, but immediately gave a precipitate of hydrated silica in aqueous acid.

a. Reactions with Nucleophiles. Surprisingly, complexes **62a** and **62b** react very rapidly with Grignard or organolithium reagents[115] in ether, even though they are insoluble in the solvent. The reaction products depend on the nature of the organometallic compound:

(1) When RM is an alkyllithium reagent a mixture of tri- and tetraorganosilane is obtained (for example eq 114).



62a

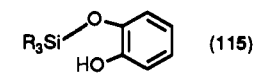


(114)

(2) When RM is an alkyl, vinyl, phenyl, or alkynyl Grignard reagent, R_4Si is formed directly whatever the ratio 62a/RM (Scheme 52). Di-Grignard reagents give spirosilanes in acceptable yield (Scheme 52).

(3) When RM is an alkyl (except MeMgBr) or benzyl Grignard reagent, the reaction results in formation of only three silicon–carbon bonds, whatever the ratio 62a/RM (eq 115) and the experimental conditions. In contrast MeMgBr leads only to Me_4Si in good yield. Further organosilanes can be obtained by subsequent addition of nucleophiles to the intermediate **195** (Scheme 52), formed in the reaction mixture. Thus, addition of $LiAlH_4$ gives monohydrogenosilanes, and "reactive Grignard reagents" including methyl, allyl, phenyl, vinyl, or alkynyl magnesium bromide slowly react to give mixed tetraorganosilanes. Reaction of HCl or HBr leads to chloro or bromosilanes. From all these

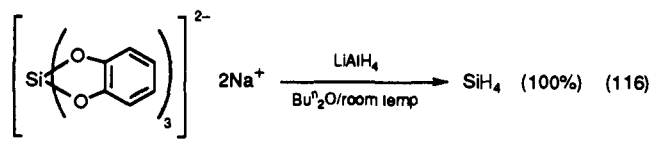
62a 195



(115)

(x = 1–5; R = alkyl)

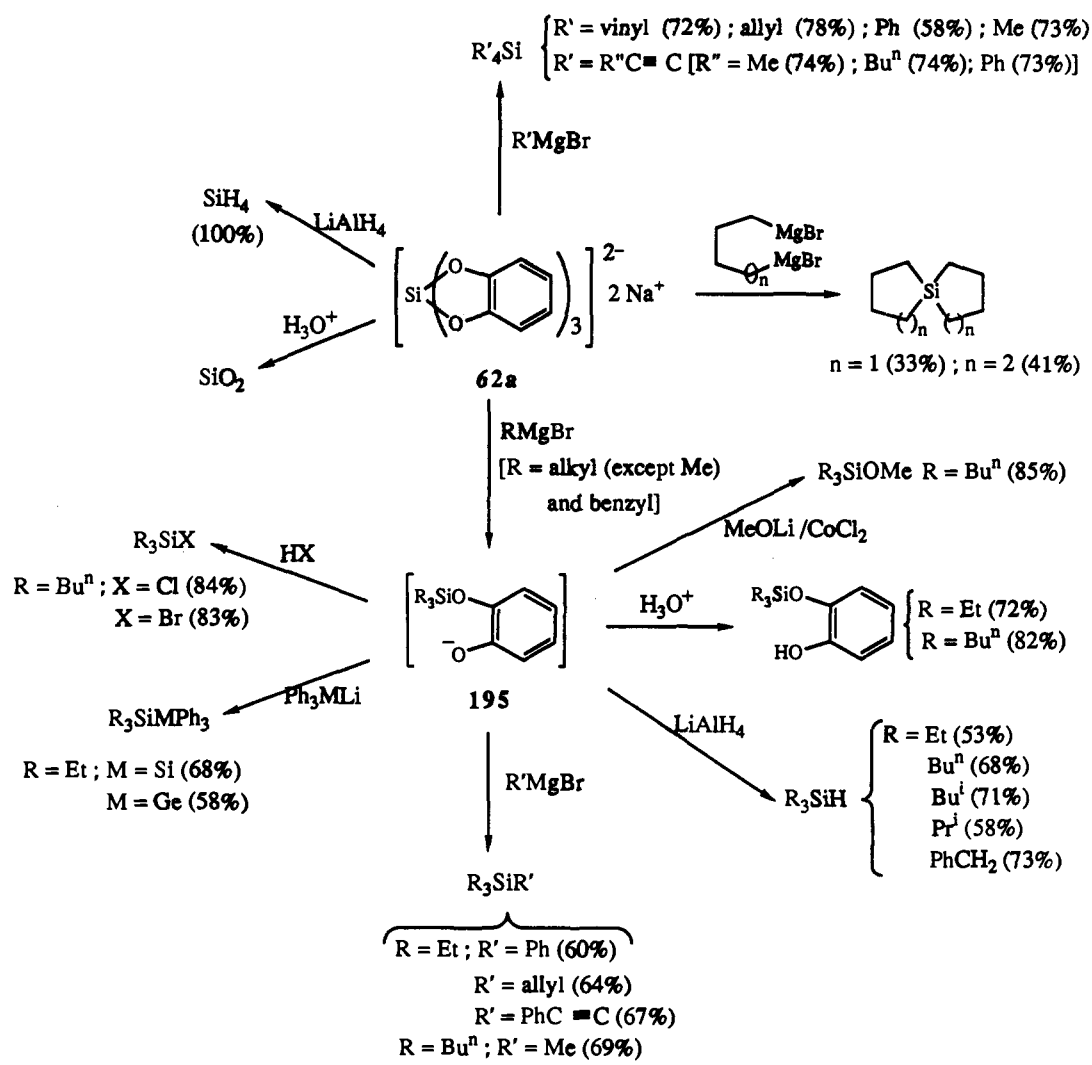
reactions pure products may be isolated in good yield (from 65 to 85%) (Scheme 52). Complex **62a** can also be treated under mild conditions by reducing agents such as $LiAlH_4$ to give SiH_4 in quantitative yield (eq 116).



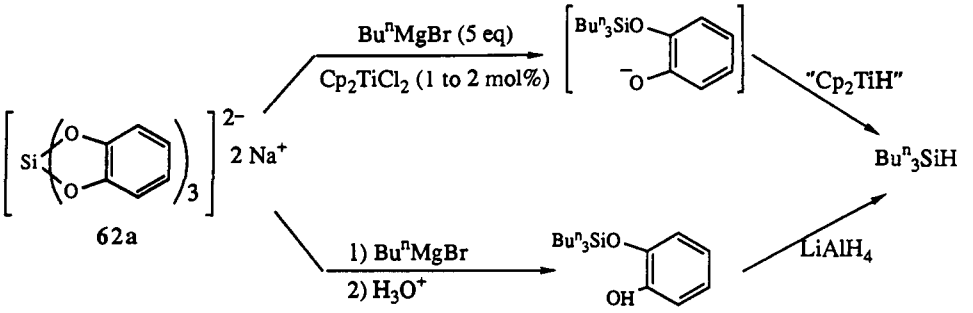
62a (116)

The reactivity of **62a** toward reducing alkyl Grignard reagents activated by Cp_2TiCl_2 has been studied under the same conditions as for the anionic pentacoordinate complexes.[187] It was found that treatment of complex

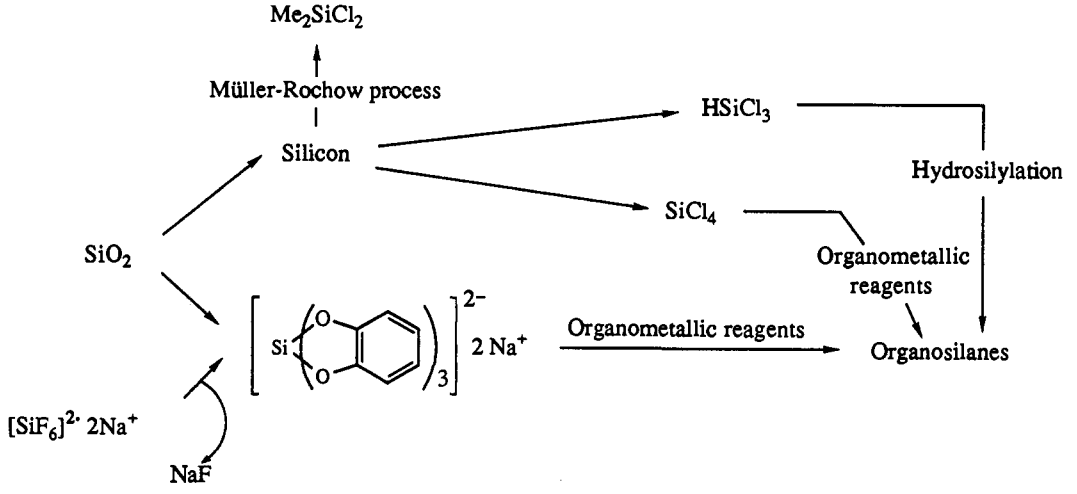
Scheme 52



Scheme 53

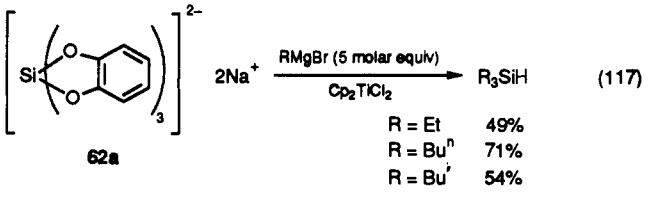


Scheme 54



62a with an excess of a reducing Grignard reagent in the presence of Cp_2TiCl_2 (1–2 mol % with respect to the Grignard reagent) gave hydrogenosilanes directly. The reaction product again depends on the nature of the alkyl Grignard reagent:

(1) With primary Grignard reagents, the main product is a monohydrogenosilane R_3SiH (eq 117). With

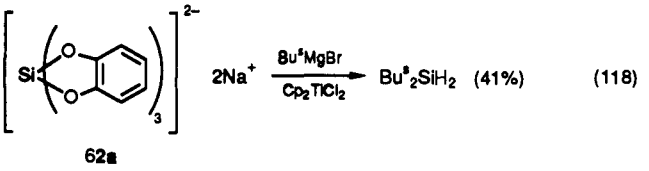


(117)

Bu^{n}MgBr, it was found that using 2 molar equiv instead of an excess (5 molar equiv) provided a mixture of tri-*n*-butylsilane (34%) and tri-*n*-butyl(2-hydroxyphenoxy)silane (25%) after hydrolysis. Thus R_3SiH results from the initial substitution of Si–O bonds, followed by reduction of the intermediate **195** (R = Bu^n) (Scheme 53) by "Cp_2TiH" formed in situ.[267]

(2) With Bu^{t}MgBr, no reaction product was isolated, neither a substitution product nor silica (resulting from the hydrolysis of the starting material). By analogy with the reaction of Bu^{t}MgBr with pentacoordinate silicon complexes under similar conditions,[187] it is suggested that in this case there is reduction of Si–O bonds by "Cp_2TiH" before substitution and subsequent loss of the very volatile SiH_4.

(3) With secondary alkyl Grignard reagents, the main product is the dihydrogenosilane (eq 118). The low yield of dihydrogenosilane is consistent with a mechanism involving competition between reduction of **62a**



(118)

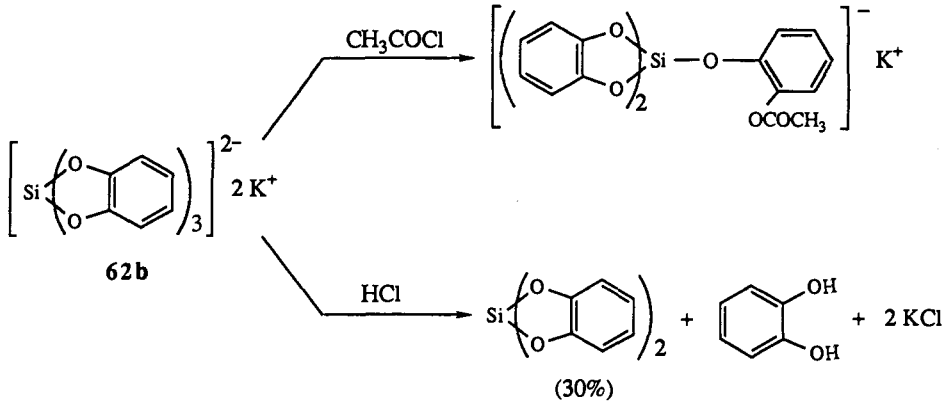
with formation and loss of SiH_4 and disubstitution of **62a** followed by reduction of the intermediate giving the dihydrogenosilane.

These reactions constitute a new way of obtaining organosilanes, since complexes **62** can be prepared from the various forms of silica and also from hexafluorosilicates which are byproducts of the fertilizer industry.[119] Moreover, in the latter case, the fluoride can be quantitatively recovered. This new chemical route is very convenient for the preparation of monofunctional organosilanes and tetraorganosilanes since no byproducts are formed in the reaction (Scheme 54). A limitation of this new process is the inability to stop the reaction of **62a** with organometallic reagents after a single substitution.

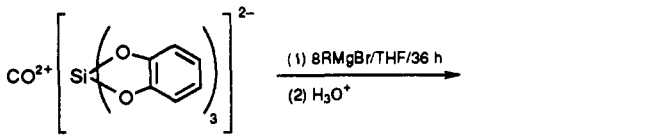
b. Reaction with Electrophiles. Tris(1,2-benzenediolato)silicate **62b** also reacts with electrophiles.[268] Monoacetylation of the complex may be achieved by reaction of **62b** with acetyl chloride (Scheme 55). Treatment of **62b** by HCl in anhydrous conditions gives catechol and spirosiloxane (Scheme 55).

c. Reactions Involving Single Electron Transfer. The cobalt salt **62c** undergoes a very slow substitution reaction,[269] with poor yields, on treatment with Grignard reagents. Nevertheless a large amount of Grignard reagent is consumed (eq 119). Silica and catechol are partially recovered in this process. In the

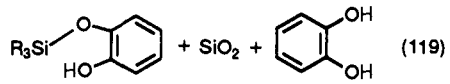
Scheme 55



62b



62c

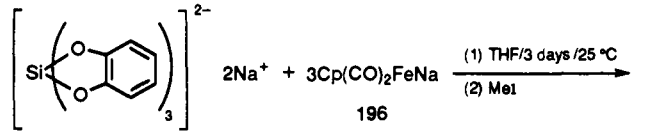


R = n-C_4H_9	17%
R = n-C_8H_{17}	20%
R = $PhCH_2$	25%

(119)

case of the benzyl Grignard reagent, toluene was obtained by distillation, prior to hydrolysis. The reaction also affords bibenzyl. So though one part of toluene (2 equiv) should originate from the Kharasch reaction, the formation of toluene and of bibenzyl is nevertheless indicative of a electron transfer between the Grignard reagent and the anionic part of the complex **62c**. The subsequent formation of the intermediate benzyl radical $PhCH_2^{\bullet}$ gives either dimerization (formation of $PhCH_2CH_2Ph$) or abstraction of a hydrogen atom from the reaction mixture (formation of $PhCH_3$).

An electron transfer is possibly involved also in the reaction of the (η^5-cyclopentadienyl)dicarbonyliron anion **196** with **62a**[269] (eq 120). Indeed in this case



62a

196

197

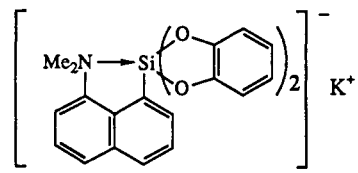
$$[Cp(CO)_2Fe]_2 + Cp(CO)_2FeMe \quad (120)$$

nucleophilic substitution is not observed; only formation of the dimer **197**. The excess of **196** was trapped with MeI[270] (eq 120).

These results show that although anionic hexacoordinate silicon compounds **62** can undergo substitution by nucleophiles leading to formation of Si–C bonds, they also display an unusual pattern of reactivity in which single electron-transfer processes can be operative.

d. Mechanistic Studies. In order to shed some light on the mechanism of the reaction of organometallic reagents with hexacoordinate silicates **62**, a comparative study of the reactivity of the hexacoordinate silicate **62b** and the pentacoordinate silicates **198a** and **198b** was made.[271] Grignard reagents were chosen so that the same organosilane would be obtained, starting from **62b** or **198** (Scheme 56). As indicated in Table 18, hexa- and pentacoordinate silicon compounds react with comparable rates toward these Grignard reagents. These results show that the pentacoordinate silicon compound is not an intermediate in the transformation of hexacoordinate complexes into organosilanes (Scheme 56). Indeed, the formation of the trisubstituted organosilane, whatever the ratio of substrate to Grignard reagent, implies that the second and the third substitutions are faster than the first one. Consequently, if **198a** (or **198b**) was formed during the first substitution of **62b** by Bu^nMgBr (or $PhCH_2MgBr$), it would exhibit a higher reactivity than **62b** toward Bu^nMgBr (or $PhCH_2MgBr$), which is not the case.

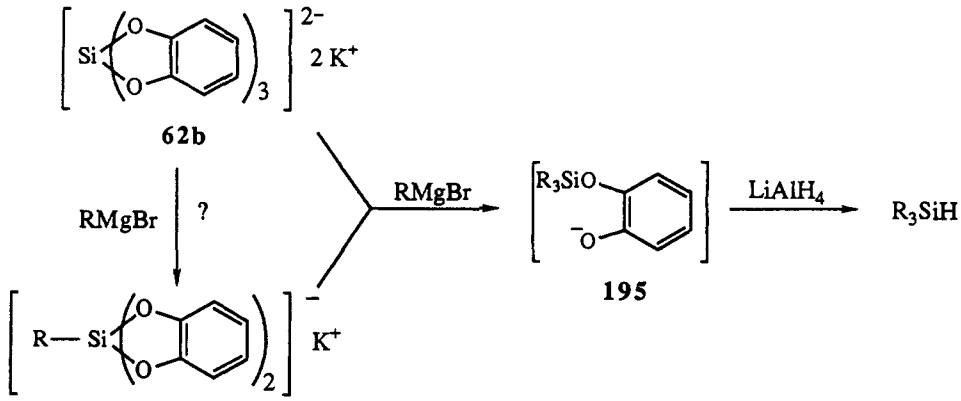
To obtain more information on the mechanism of nucleophilic substitution of hexacoordinate silicates, the reactivity of compounds **199** and **84**, with MeLi, MeMgBr, and $LiAlH_4$ was compared[167] to that of the pentacoordinate complex **115b**. As shown in Table 19,



199

115b reacts easily with organometallic compounds but **199** reacts only slowly with MeLi and MeMgBr to give the expected silane **200** (R = Me, Table 19). No reaction occurred with compound **84** after 3 days at 20 °C. Since **62b** and **115b** presents a very similar reactivity toward Grignard reagents, the reactivity of hexacoordinate silicon complexes apparently decreases in the following order: **62b** > **199** ≫ **84**. The difference in reactivity between **62b**, **199**, and **84** appears to be connected to the number of 1,2-benzenediolato ligands around the silicon atom: the more 1,2-benzenediolato ligands there are, the more reactive the complex is toward nucleophilic reagents. Since the 1,2-benzenediolato ligand is electron-withdrawing and consequently tends to increase the electrophilic character of the silicon atom, the reactivity of hexacoordinate silicon species toward nucleophilic reagents can be explained by nucleophilic

Scheme 56



62b

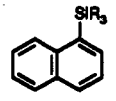
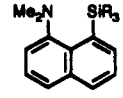
198 a : R = Bu^n
b : R = $PhCH_2$

195

Table 18. Comparison of the Reactivity of 62b and 198 toward Grignard Reagents in Ether Followed by $LiAlH_4$ Reduction

	yield (%) of R_3SiH		
organometallic reagent	from 62b	from 198a	from 198b
Bu^nMgBr (0 °C, 15 min)	63	64	
$PhCH_2MgBr$ (35 °C, 1 h)	60		45

Table 19. Reactivity of Compounds 115b and 199 in Ether at 20 °C

compound	organometallic reagent	reaction product		half-reaction time
115b	$LiAlH_4$		R = H	1.5 h
	MeLi		R = Me	20 min
	MeMgBr		R = Me	40 min
199	$LiAlH_4$		R = H	*a*
	MeLi		R = Me	65 h
	MeMgBr		R = Me	22 h

200

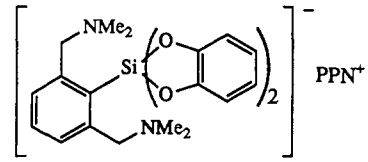
[a] Only 8% of reaction after 3 days.

attack at the silicon center, which involves a heptacoordinate silicon intermediate (or transition state); at the present time there is no information which allows the elimination of such a mechanism.

D. Heptacoordination at Silicon

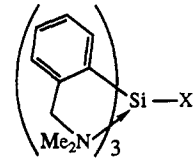
The involvement of a heptacoordinate silicon intermediate was first suggested by Pearson et al.[247] in 1962. These authors studied the hydrolysis of the tris(acetylacetonato)silicon cation, following the work of Dhar, Doron, and Kirschner[246] on this reaction, and deduced from kinetic data that attack occurred by an SN_2 mechanism on an octahedral complex. However Muetterties and Wright[245,272] subsequently reported that when the tris(tropolonato)silicon cation was hydrolyzed with $^{18}OH^-$, the dissociated ligands were enriched with ^{18}O to an extent consistent with initial hydroxide attack on the ligand. Thus direct nucleophilic attack at a hexacoordinate silicon atom seemed to be a possibility which deserved further study, since the early results were inconclusive.

Recently the complex **201** was prepared[273] in order to obtain more information about the reactivity of hexacoordinate silicon complexes toward nucleophilic reagents. In solution the ^{29}Si chemical shift of **201** (δ = −129.8 ppm) is upfield of that of **81** (δ = −121.2 ppm) and the ^1H NMR spectrum of **201** shows the resonance of the NMe_2 groups as a sharp singlet at room temperature. Since the silicon atom is at least hexacoordinated,[165] the equivalence of the two NMe_2 groups is due to reversible attack of the free NMe_2 group on the silicon atom, with displacement of the chelated one. Thus this complex can be considered as the first to model an intramolecular nucleophilic attack on a hexacoordinate silicon species which could occur via a heptacoordinate intermediate (or transition state).

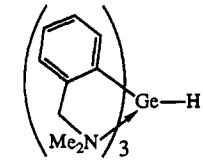


201

Some attempts to obtain heptacoordinate silicon species have been made and the X-ray crystallographic analysis of silicon compounds **202a**[274] and **202b**[275] have



202 a : X = F
b : X = H



203

revealed an unusual geometry which corresponds to a tricapped tetrahedron. The main features of the structure of **202a** (Figure 2) are the following: (1) the basic tetrahedral geometry of the fluorosilane is retained; (2) the lone pairs of the three NMe_2 groups are oriented toward the silicon atom even though there is no geometric restraint to force these groups into this conformation, since the NMe_2 groups in the benzylic positions are free to rotate around the carbon–carbon bond; (3) the nitrogen–silicon distances vary from 3.00 to 3.49 Å, which correspond to weak intramolecular interactions. Nevertheless the system prefers three

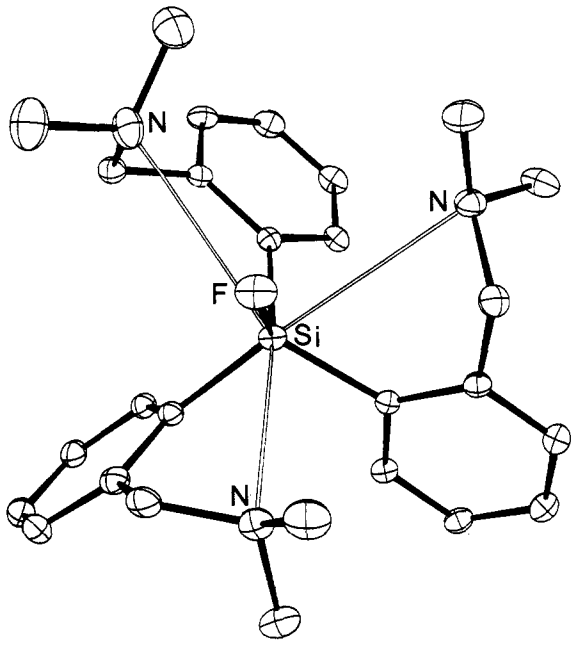


Figure 2. ORTEP drawing of the molecular structure of **202a**.

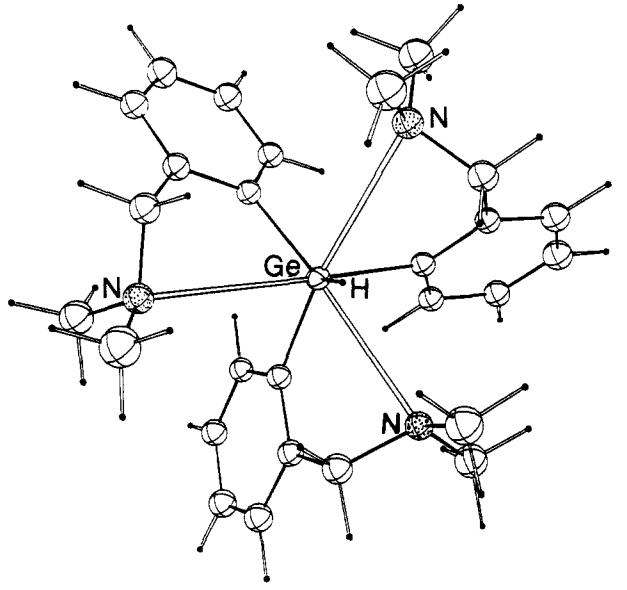


Figure 3. ORTEP drawing of the molecular structure of 203.

weak intramolecular interactions to either a single one (resulting in pentacoordination at silicon) or to two (resulting in hexacoordination).

This geometry is completely original since none of the three weak intramolecular coordinations occurs opposite to the Si–F bond as it has been observed in structures of pentacoordinate fluorosilanes.[64,65]

Interestingly, the single-crystal X-ray diffraction analysis[275] of the germane **203** (Figure 3), which is isomorphous with the silane **202b**, has revealed the same geometry.

Thus it can be concluded that mechanisms with participation of heptacoordinate silicon intermediates (or transition states) in the course of nucleophilic reactions at hexacoordinate silicon species cannot be ruled out since the tricapped tetrahedron geometry around silicon has been observed.

VIII. Synthetic Methods Involving Hypervalent Silicon Intermediates

Synthetic methods using the efficiency of nucleophilic reagents to coordinate to a silicon center have been known for more than 20 years. Fluoride ion used as a simple and efficient means of removing a silyl-protecting group[276,277] was the first example of a reaction with nucleophilic activation at silicon.

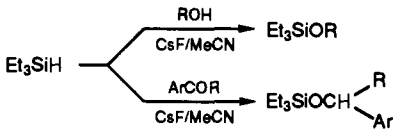
Following these initial reports many reactions involving the activation of Si–X bonds (X = H, O, N, C, Si) have been developed. Because of the considerable strength of the Si–F bond (590 ± 13 kJ mol^{-1}), fluoride anion, originating from a variety of sources [KF, CsF, KHF_2, R_4NF, $(Et_2N)_3S^+Me_3SiF_2^-$ (TAS $TMSF_2$)], is the nucleophilic reagent the most used to activate silicon bonds.

Since the synthetic uses of organosilicon compounds with catalysis by nucleophiles were extensively reviewed recently[20] only a short survey of the area will be given. Then a mechanistic interpretation will be proposed and the role of penta and hexacoordinate silicon species discussed.

A. Activation of the Si–H Bond

1. Activation of Alkyl- or Arylsilanes

a. Silylation of Alcohols and Hydrosilylation of Carbonyl Compounds. The cesium fluoride-catalyzed reactions of trialkylsilanes with alcohols and aromatic carbonyl compounds were first reported by Vol'pin et al.[278] (eq 121). The silylation of alcohols[279] and carbonyl

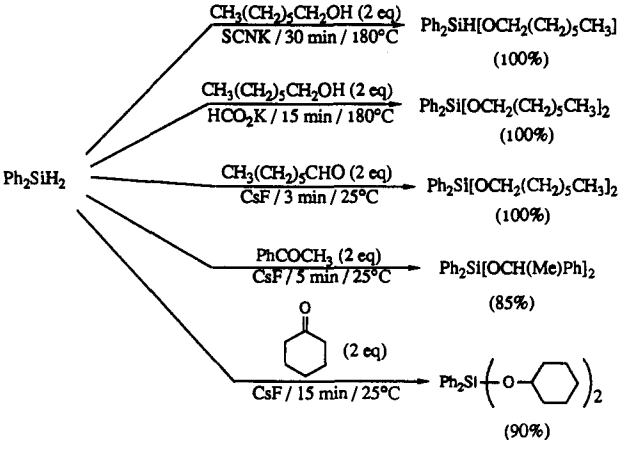


(121)

compounds[280] was then shown to proceed more readily with arylsilanes, and to take place at the surface of a variety of salts without solvent in heterogeneous conditions (Scheme 57). Ph_2SiH_2 adds to α,β-unsaturated aldehydes and ketones only at the 1,2-positions in the presence of CsF, as previously observed by Vol'pin et al.[278] with cinnamaldehyde.

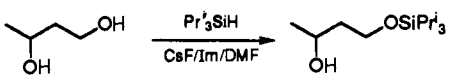
The order of reactivity of silanes used for silylation of alcohols and carbonyl compounds was found to be

Scheme 57



αNpSiH$_3$ > Ph$_2$SiH$_2$ > PhMeSiH$_2$, and the efficiency of salts to be CsF > KF > KHCO$_3$ > KSCN.

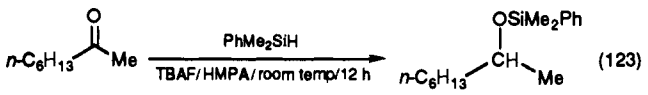
Organosilanes such as Ph$_3$SiH, PhMe$_2$SiH, Ph$_2$MeSiH, and Pr$^i_3$SiH react with alcohols in the presence of CsF, and also under homogeneous conditions to give the corresponding silyl ether.[281] It was shown that the addition of imidazole (Im) accelerates the reaction, and under these conditions, primary alcohols are silylated much faster than secondary alcohols (eq 122), and tertiary alcohols and ketones do not react at all. In



(122)

>95%

contrast aldehydes and ketones are reduced by PhMe$_2$SiH, in the presence of a catalytic amount of TBAF or TAS TMSF$_2$ in aprotic solvents[282] (eq 123).

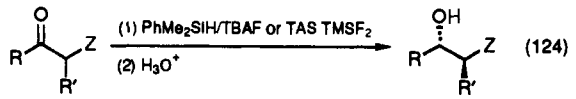


(123)

(81%)

The efficiency of solvents was found to be the following HMPA > DMF > THF ≫ CH_2Cl_2. Use of 18-crown-6 ether increases the efficiency of CsF and allows the reduction of aromatic carbonyl compounds in solvents of low polarity such as dichloromethane.[283]

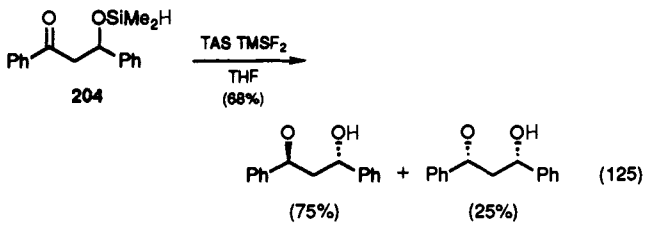
This method of reduction is stereoselective. It was used to synthesize optically active 1,2-diols and 2-amino alcohols of threo configuration[190a,b,282] (eq 124). The



(124)

Z = Ph, OAc, OBz, OEE, OTHP, NMe$_2$, CONEt$_2$, CON, CON

threo selectivity is consistent with the Felkin–Anh model[234] in which interaction of the carbonyl oxygen with a countercation is suppressed. However, the reduction of β-dimethylsiloxy ketone **204** affords the *anti*-diol preferentially[282] (eq 125).



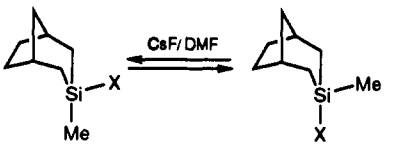
(125)

Recently, formation of Si–N bonds by dehydrocoupling of Si–H and N–H bonds in the presence of TBAF has been reported[285] (eq 126).

$$Ph_2SiH_2 + Me_2NH \xrightarrow[THF]{TBAF} Ph_2SiHNMe_2 \quad (126)$$

b. Fluorination of Hydrogenosilanes. Fluorination of triphenylsilane in the presence of CsF is another example of the activation of the Si–H bond by fluoride anion. The reaction occurs either in DMF or in MeCN within 5 min, to give the corresponding fluorosilane in nearly quantitative yield.[286] The reaction takes longer with KF in DMF and does not proceed with LiF in DMF or CsF in benzene. The fluorination of triethylsilane occurs also with CsF in DMF.

c. Isomerization of Hydrosilanes. CsF in dry DMF also promotes exo/endo isomerization[287] of 3-methyl-3-silabicyclo[3.2.1]octane (**205**, X = H) (eq 127). No



(127)

205 (X = H, OMe, F, Ph)

isomerization was observed when CsF was replaced by KF but KF with 18-crown-6 ether gives the equilibrium mixture. This nucleophile-induced isomerization also takes place with other derivatives of 3-silabicyclo[3.2.1]-octane (**205**, X = OMe, F)[286] and interestingly even with tetraorganosilanes **205** (X = C_6H_5). The order of reactivity of alkali–metal fluorides was found to be CsF > KF > LiF.

The racemization of optically active methyl(α-naphthyl)phenylsilane was shown to take place rapidly in the presence of CsF in dry DMF[286] and also in the presence of hydrides (KH, LiAlH$_4$ or LiAlD$_4$) in THF.[288]

These reactions of isomerization and of racemization have been explained by reversible coordination of a nucleophile (fluoride or hydride) to give a pentacoordinate intermediate which then undergoes intramolecular ligand rearrangement around the Si center via pseudorotation.

d. Redistribution Reactions of Hydrosilanes. Redistribution reactions observed[289] for di- and trihydrogenosilanes in the presence of hydrides (LiAlH$_4$, KH, NaH) as catalysts have also been explained by the formation of a pentavalent hydridoorganosilyl anion in the initial step, through which the redistribution reaction probably takes place (Scheme 58).

Scheme 58

$$PhSiH_3 + H^- \rightleftharpoons [PhSiH_4]^-$$

$$[PhSiH_4]^- + PhSiH_3 \rightleftharpoons [Ph_2SiH_3]^- + SiH_4$$

$$[Ph_2SiH_3]^- \rightleftharpoons Ph_2SiH_2 + H^-$$

2. Activation of Alkoxysilanes

A general and very efficient method for the reduction of carbonyl compounds is to use (EtO)$_3$SiH, (EtO)$_2$SiMeH, or Me$_3$SiO(HSiMeO)$_n$SiMe$_3$ (PMHS) which is a byproduct of the silicones industry, activated by KF or CsF (Table 20). The reaction takes place satisfactorily without solvent,[290] but is accelerated by polar solvents[291] (DMF or DMSO). The observed silane reactivity sequence is (EtO)$_3$SiH > (EtO)$_2$Si(Me)H > PMHS.

The reaction is selective for the carbonyl group so that aldehydes and ketones having another functional group, including a C–C double bond, bromo, nitro, amido, or ester group are reduced selectively.[292] Moreover it is possible to reduce aldehydes selectively in the presence of ketones, and ketones in the presence of esters (Table 21).

Table 20. Reduction of Carbonyl Compounds by Hydrosilylation Catalyzed by Fluoride Anions

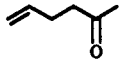
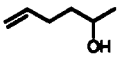
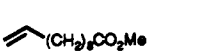
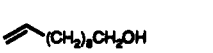
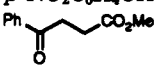
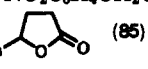
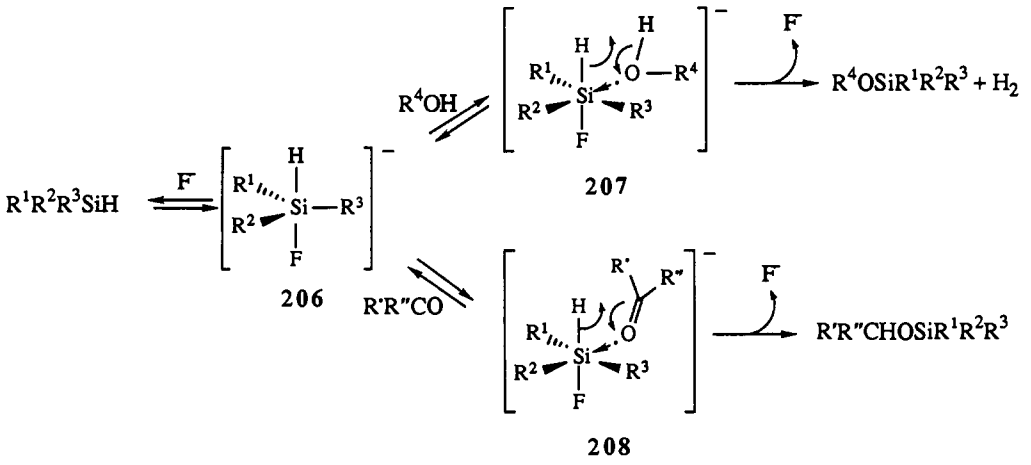
carbonyl compound	reducing system	solvent	reaction conditions: t (h)	reaction conditions: T (°C)	alcohol [yield (%)]	
$nC_6H_{13}CHO$	$(EtO)_3SiH/KF$	none	4	25	n-$C_6H_{13}CH_2OH$	(70)
	$Me(EtO)_2SiH/KF$	DMF	1.75	10		(85)
	$(EtO)_3SiH/CsF$	none	0.25	0		(90)
	$Me(EtO)_2SiH/KF$	DMF	5	60		(85)
	$(EtO)_3SiH/CsF$	none	0.5	60		(70)
	PMHS/KF, 2 equiv H_2O	DMSO	6	80		(73)

Table 21. Selective Reduction of Bifunctional Compounds by Hydrosilylation Catalyzed by Fluoride or Formate Anion

carbonyl compound	reducing system	solvent	reaction conditions: t (h)	reaction conditions: T (°C)	isolated product [yield (%)]
p-$NO_2C_6H_4CHO$	$(EtO)_3SiH/KF$	none	2	100	p-$NO_2C_6H_4CH_2OH$ (80)
	$Me(EtO)_2SiH/CsF$	none	2.5	25	 (85)
$MeCOCH_2CONHPh$	$(EtO)_3SiH/CsF$	none	0.2	25	$MeCHOHCH_2CONHPh$ (90)
$OHC(CH_2)_8COMe$	$PMHS/HCO_2K$	DMF	2	100	$HOCH_2(CH_2)_8COMe$ (63)

Scheme 59



208

3. Mechanism

All the nucleophile-catalyzed reactions can be explained by a mechanism which involves as the first step the coordination of the nucleophile to the silicon atom to give a more reactive pentacoordinate species **206**[16] (Scheme 59). Intermediate **206** is then attacked by the alcohol or the carbonyl compound giving hexacoordinate silicon intermediates (or transition states) **207** and **208** within which the hydride transfer may take place. This mechanism requires first that a pentacoordinate silicon species be more reactive than a tetracoordinate silicon species and also that a pentacoordinate silicon species may undergo nucleophilic attack. These two points have been amply demonstrated in section VI. Moreover the great reactivity of isolated anionic hydridosilicates[36] toward carbonyl compounds in the absence of catalyst (section VI.B.1), whereas the corresponding tetracoordinate hydride does not react at all, support completely the mechanism proposed.

The alcoholysis of potassium hydridosilicates in the presence of 18-crown-6, giving another pentacoordinate species[194] (eq 36) also supports this mechanism very well since this reaction—a nucleophilic displacement at a pentacoordinate silicon species—would also reasonably be expected to take place through a hexacoordinate intermediate.

The loss of stereoselectivity observed for the reduction of **204**[282] (eq 125) agrees also with the formation of hexacoordinate intermediates **209** and **210** (Scheme 60).

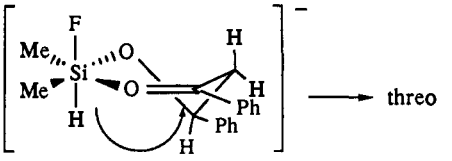
Hiyama and Fujita[190c,282] observed that the TBAF-catalyzed reduction of aldehydes and ketones with hydrosilanes are accelerated by polar solvents such as HMPA. These data suggest the involvement of the hexacoordinated silicate $[HSiR_3F(HMPA)]^-$ as the active hydride species. However only aldehydes and ketones are reduced under these conditions.

B. Activation of the Si–O Bond

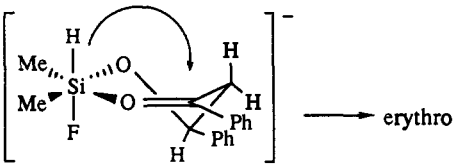
1. Hydrolysis of Tetramethoxysilane

The application of nucleophilic catalysis in the sol–gel process has been investigated[293] by comparing the gel times of $(MeO)_4Si$ with various acidic, basic, and nucleophilic catalysts in different solvents (methanol, dioxan, and acetone). Among the catalysts which have been studied, Bu^n_4NF is the most effective, with regard to gel times. In methanol it reduces the gel time of $(MeO)_4Si$ about 3600-fold with respect to the noncat-

Scheme 60



209

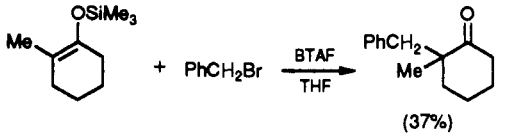


210

alyzed process. The efficiency of the catalysts studied decreases as follows: Bu^n_4NF > NaF > NH_4F > CsF > DMAP > NmI > NH_4OH > no catalyst > HCl.

2. Reaction of Silyl Enol Ethers with Organic Halides

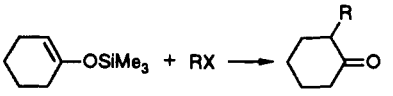
In the presence of a stoichiometric amount of benzyltrimethylammonium fluoride (BTAF), silyl enol ethers react with primary alkyl iodides and allylic or benzylic bromides to give the corresponding monoalkylated product regiospecifically[294] (eq 128). This reaction



(37%) (128)

occurs also in the presence of a stoichiometric amount of TAS $TMSF_2$[295] which proved to be the most efficient source of fluoride for the alkylation of ketones (Table 22). No reaction is observed with CsF.[296]

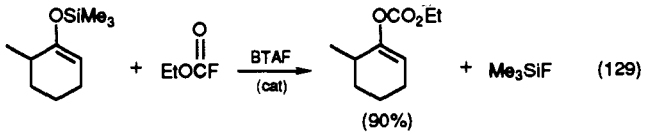
Table 22. Yield and Reaction Conditions of Fluoride Ion-Promoted Alkylation of 1-(Trimethylsiloxy)cyclohexene



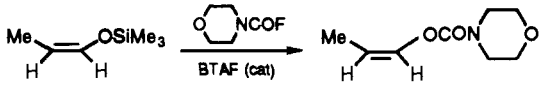
RX	TBAF[a]	TAS $TMSF_2$[b]
MeI	0 °C/6 h (91%)	−78 °C/4 h (95%)
Bu^nI	20 °C/24 h (50%)	−30 °C/3 h (59%)
$BrCH_2CO_2Me$	20 °C/1 h (80%)	−78 °C/2 h (83%)
$PhCH_2Br$	0 °C/14 h, then 25 °C/4 h (69%)	−78 °C/3 h (72%)

[a] Taken from ref 294b. [b] Taken from ref 295b.

Silyl enol ethers activated by a catalytic amount of benzyltrimethylammonium fluoride also react with fluoroformate or carbamoyl fluorides[297] to yield enol carbonates (eq 129) or enol carbamates, respectively (eq 130).



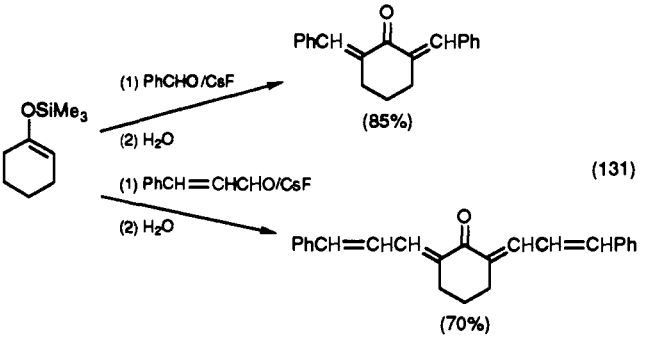
(90%) (129)



(130)

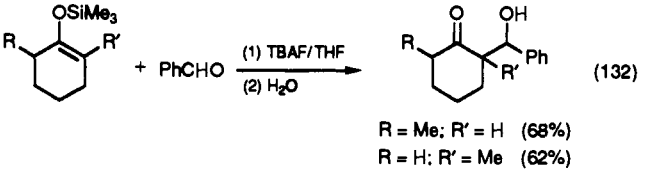
3. Aldol Reactions

a. Aldol Products from Silyl Enol Ethers. In the presence of CsF and without solvent, silyl enol ethers react under heterogeneous conditions with aldehydes to give α,β-unsaturated ketones[298] (eq 131). Under



(131)

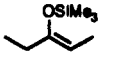
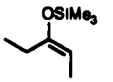
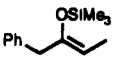
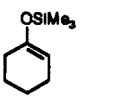
homogeneous conditions, aldol condensation occurs between silyl enol ethers and aliphatic or aromatic aldehydes in the presence of a catalytic amount of TBAF[299] or of TAS $TMSF_2$.[295b] The reaction proceeds in a regiospecific manner (eq 132) with respect to the silyl enol ether. In most cases the reaction is kinetically



(132)

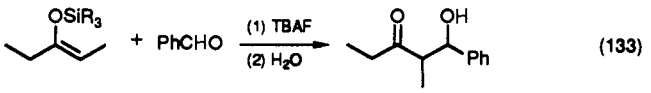
controlled and the major product has the erythro configuration with either catalyst regardless of the enolate configuration[295,299-301] (Table 23). This aldol

Table 23. TBAF (at −72 °C) and TAS $TMSF_2$ (at −78 °C) Catalyzed Aldol Reaction of Enol Silyl Ethers with Aldehydes (See Eq 132)

		time, yield (erythro/threo)	
enol silyl ether	aldehyde	TBAF[a]	TAS $TMSF_2$[b]
	PhCHO	2 h, 72% (86/14)	2 h, 89% (86/14)
	PhCHO	2 h, 89% (44/56)	2 h, 84% (63/37)
	PhCHO	1 h, 89% (93/7)	1 h, 75% (95/5)
	PriCHO	13 h, 35% (97/3)	8 h, 67% (100/0)

[a] Taken from ref 301. [b] Taken from ref 295b.

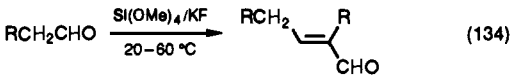
reaction is postulated to proceed by attack of the free enolate on the aldehyde via an acyclic, extended transition state.[295,301,302] It was found that the diastereoselectivity of the reaction was the same whatever the nature of the silyl group of the silyl enol ether, thus confirming the participation of a free enolate in this reaction[301] (eq 133).



(133)

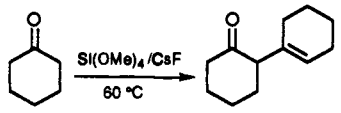
$R_3 = Me_3$	72%	erythro/threo = 86/14
$R_3 = Me_2Ph$	87%	erythro/threo = 85/15
$R_3 = Ph_3$	6%	erythro/threo = >9/1

b. Aldolization Promoted by $(RO)_4Si/F^-$. The system $(RO)_4Si/KF$ or CsF is sufficiently basic to promote self-condensation of aldehydes and ketones.[303] The reaction takes place without solvent in heterogeneous conditions. Self-condensation of aldehydes is fast in the presence of $(MeO)_4Si/KF$, whereas that of ketones requires the use of $(MeO)_4Si/CsF$ (eqs 134 and 135). Cross-aldolization between nonenolizable alde-



(134)

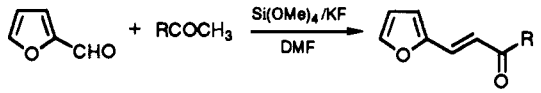
R = Me (32%); R = Et (69%); R = n-C_5H_{11} (70%); R = $PhCH_2$ (72%)



(135)

(65%)

hydes and ketones takes place in the presence of $(RO)_4Si/CsF$ without solvent or in the presence of $(RO)_4Si/KF$ in dimethylformamide (eq 136). With



(136)

R = Me (20%); R = Pr^n (43%); R = Pr^i (78%)

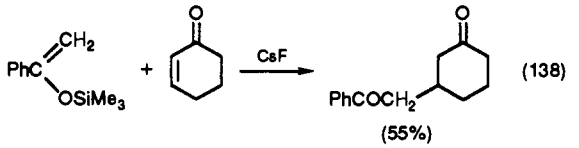
symmetrical ketones such as cyclohexanone double aldolization occurs, whereas with unsymmetrical ketones reaction occurs only at the less-hindered site, as is usually observed with base-catalyzed aldolization (eq 137).

(137)

(85%)

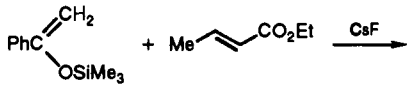
4. Michael Reactions

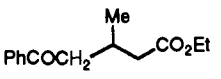
a. Michael Reactions with Silyl Enol Ethers. Silyl enol ethers activated by CsF react under heterogeneous conditions with α,β-unsaturated ketones and esters to give 1,4-addition products[298] (eqs 138 and 139).



(138)

(55%)

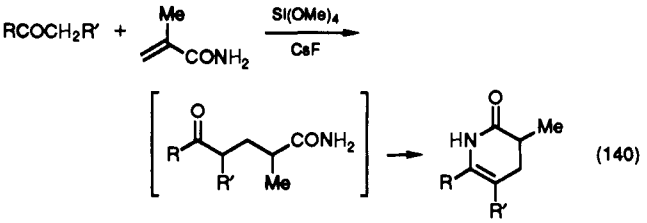




(139)

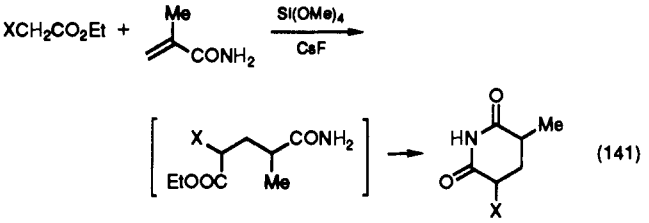
(70%)

b. Michael Reactions Promoted by $(RO)_4Si/F^-$. In the presence of a stoichiometric amount of $(MeO)_4Si/CsF$, ketones and aryl acetonitriles add to α,β-unsaturated ketones, esters, nitriles, and amides[304,305] (Table 24). The 1,4-addition product is obtained without hydrolysis. With primary methacrylamides as Michael acceptors, 3,4-dihydro-2(1*H*)-pyridinones or 3,5-disubstituted glutarimides are obtained[306] in a one-pot process, also without hydrolysis and in good yield (eqs 140 and 141).



(140)

R = R' = Ph (76%); $RCOCH_2R'$ = α-tetralone (94%)



(141)

X = CH_3CO (83%); X = CN (84%)

c. Michael Reactions with Silyl Ketene Acetals. Trimethylsilyl ketene acetals in the presence of a catalytic amount of TAS $TMSF_2$ add to α,β-unsaturated ketones to give after hydrolysis the corresponding 1,5-dicarbonyl compound exclusively.[307] This compound can be further alkylated in the presence of a stoichiometric amount of TAS $TMSF_2$ (Scheme 61). The addition is not stereoselective with respect to the newly created chiral centers.

Scheme 61

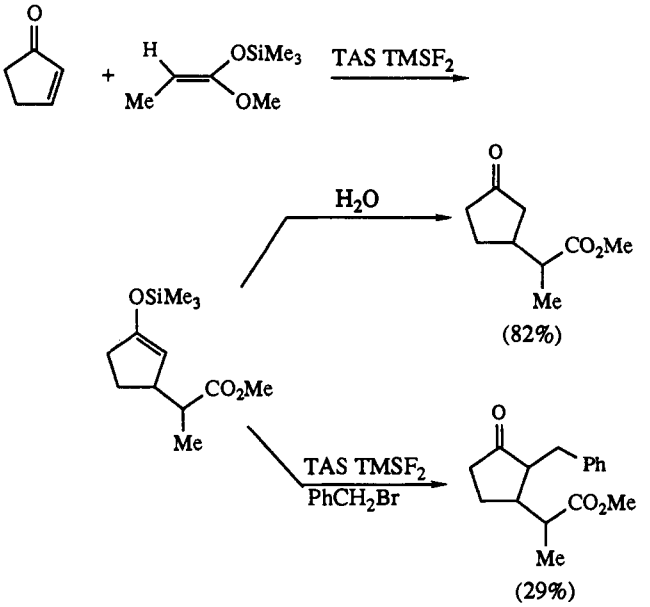
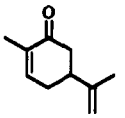
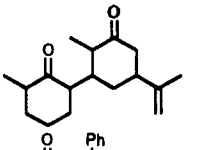
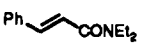
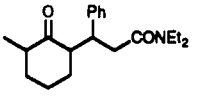
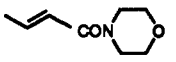
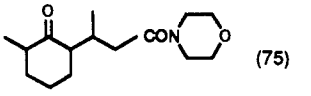
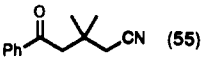
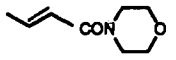
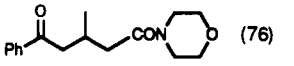
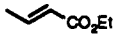
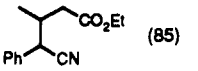
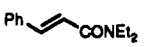
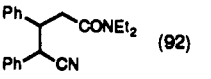
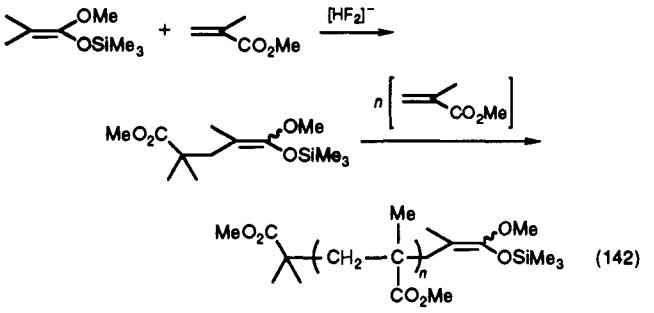


Table 24. Michael Additions in the Presence of $Si(OMe)_4/CsF$

Michael donor	Michael acceptor	reaction conditions: time (h)	reaction conditions: T (°C)	isolated product [yield (%)]
		4	25	 (70)
		5	80	 (86)
		5	70	 (75)
PhCOMe		3	80	 (55)
		7	80	 (76)
$PhCH_2CN$		1	25	 (85)
		1	65	 (92)

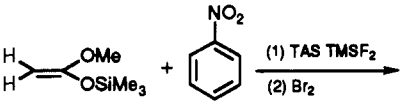
Most importantly silyl ketene acetals activated by a suitable anionic catalyst add to α,β-unsaturated esters in a controlled polymerization[209,210,306,309] (eq 142). This polymerization has been shown to proceed by repeated

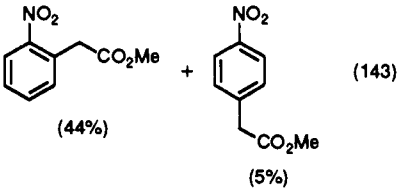


(142)

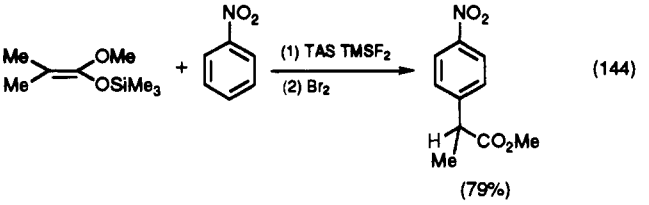
Michael additions of monomer to a growing chain end carrying the silyl ketene acetal functionality. This fundamentally new method of controlled addition polymerization has been termed "group-transfer polymerization" (GTP).[209] An anionic catalyst is required for the polymerization, and surprisingly bifluoride anion is one of the most generally used. Other anions that catalyst GTP are for example $Me_3SiF_2^-$, CN^-, and N_3^-. Monodisperse polymers of high molecular weight can be obtained by adjusting the monomer/initiator ratio.

Another unusual Michael reaction occurs with aromatic nitro compounds.[310] Silyl enol ethers and ketene silyl acetals add to aromatic nitro compounds in the presence of a stoichiometric amount of TAS $TMSF_2$ to give dihydroaromatic nitronates which can be oxidized with bromine to yield α-nitroarylacetate esters in moderate to high yield (eq 143). Substitution ortho to the nitro group predominates with sterically undemanding silyl reagents, while para substitution products are exclusively obtained with bulky reagents (eq 144).





(143)



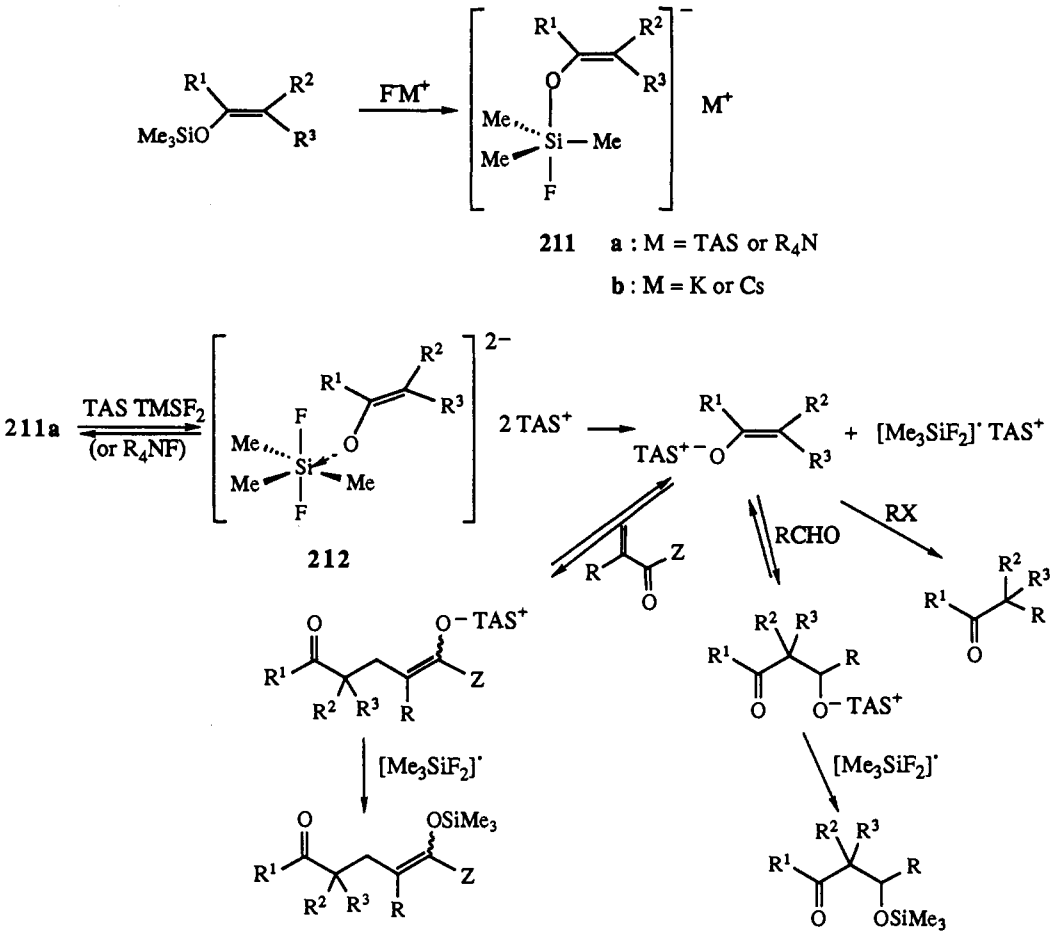
(144)

5. Mechanism

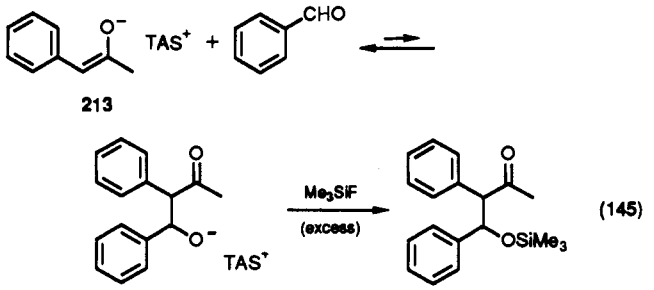
To explain the anionic activation of Si–O bonds two mechanisms have been proposed[311] both involving in the first step the same pentacoordinate silicon intermediate **211**, formed by coordination of the nucleophilic catalyst to the silicon center (Scheme 62). Subsequently two different processes may be envisaged according to the source of fluoride anion, but in each case nucleophilic attack on the pentacoordinate silicon species **211** is involved.

First, attack of reactive fluoride anion (from R_4NF or TAS $TMSF_2$) on complex **211a** would give a hexacoordinate difluoride complex **212** from which "free enolate" and $Me_3SiF_2^-$ may be formed.[295,299,312] The "free enolate" is capable of reacting with aldehydes[295b,299,300] or Michael acceptors[307,310] and also with organic halides[294,295] (Scheme 62). An important feature of this

Scheme 62

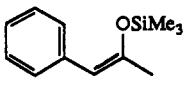


mechanism is that $[Me_3SiF_2]^-$ appears as the silylating agent instead of Me_3SiF. The lack of reactivity of the isolated enolate **213** toward benzaldehyde, observed by Noyori et al.[295b] supports this hypothesis (eq 145).



(145)

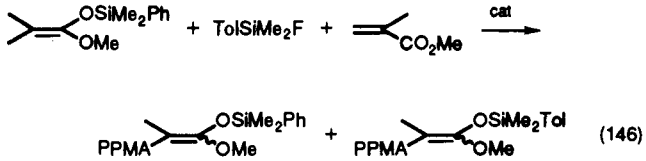
Furthermore it was shown[295b] that when an excess of Me_3SiF (5 molar equiv), or of the silyl enol ether **214**,



was added to the reaction mixture, the aldol condensation occurred smoothly to give the corresponding β-trimethylsiloxy ketone (eq 145) demonstrating that Me_3SiF is not a good silylating agent.

Second, with less reactive fluoride anion, from KF or CsF under heterogeneous conditions, or from KHF_2 (used in the GTP process) the initial attack at the silicon center giving the pentacoordinate silicon intermediate **211b** still occurs, but the reactivity of fluoride anion from these sources is not sufficient to displace the enolate ion. Under these conditions, the intermediate **211b** reacts with compounds having two reactive centers, such as carbonyl compounds,[16,210,308] leading to hexacoordinate intermediates **215** or **216** (Scheme 63). However **211b** cannot react with compounds having no nucleophilic center such as organic halides[296] (in contrast to the enolate formed from very reactive fluoride anions).

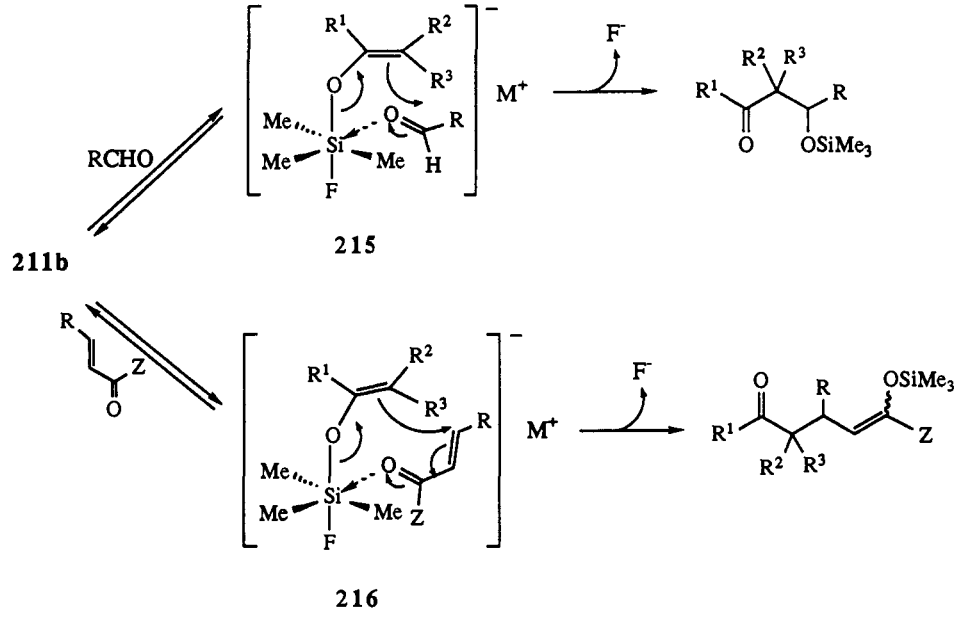
Studies[210] of the mechanism of GTP have clearly revealed the existence of these two mechanisms as a function of the fluoride anion source. Polymerization of methyl methacrylate in the presence of an equimolar quantity of tolyldimethylsilyl fluoride, with $HF_2^-TAS^+$ as catalyst (eq 146) (25–75 °C, 0.75 **h**) provides an



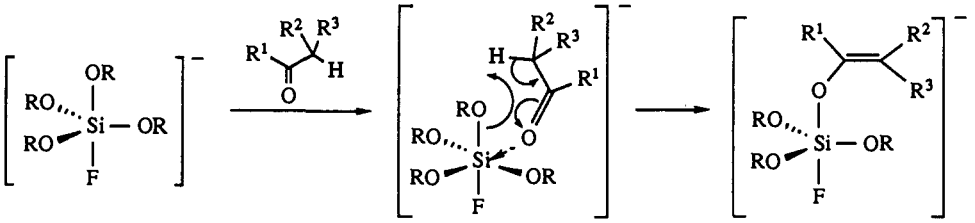
(146)

oligomer which contains no detectable tolyldimethylsilyl end groups. This result shows that the polymerization process does not involve a reversible, dissociative step. In contrast, with TAS $TMSF_2$ as catalyst, silyl group exchange occurs proving the formation of "free enolate" in this case. To suppress the silyl group exchange, low temperatures and short reaction times are required. The nondissociative mechanism is favored under these conditions with respect to the mechanism involving "free enolate".

Scheme 63



Scheme 64

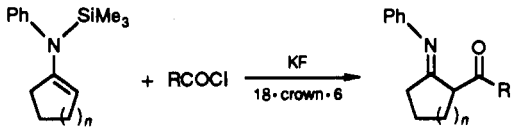


In the case of reactions promoted by the $(RO)_4Si/F^-$ system, the coordination of F^- to $(RO)_4Si$ gives a pentacoordinate species (Scheme 64), which is basic enough to promote silyl enol ether formation. The pentacoordinate complex **217**, similar to **211**, then reacts with carbonyl compounds as shown in Scheme 63.

C. Activation of the Si–N Bond

1. Silylenamines

N-Silylenamines react easily with acid chlorides in the presence of potassium fluoride and a catalytic amount of crown ether to afford β-keto imines in good yield[313] (eq 147).

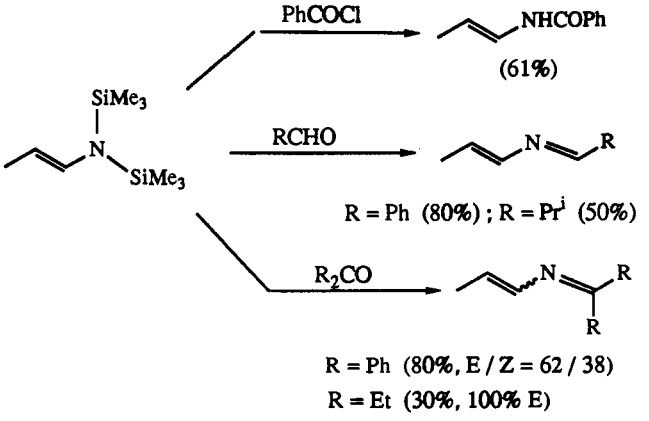


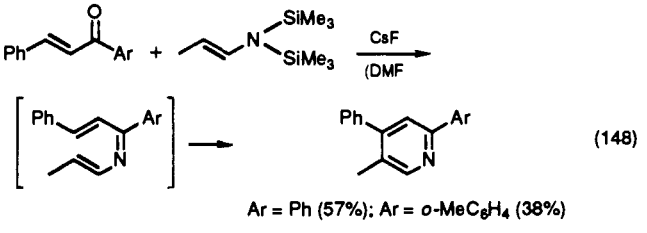
R = *n*-C_7H_{15}	*n* = 1 (82%)	*n* = 2 (92%)
R = $CH_3CH{=}CH_2$	*n* = 1 (71%)	*n* = 2 (81%)
R = EtO	*n* = 1 (88%)	*n* = 2 (84%)
R = Pr^i		*n* = 2 (93%)
R = Ph		*n* = 2 (90%)

(147)

N,N-Bis(silyl)enamines[314] also need a catalyst such as CsF or TBAF to react with electrophilic compounds but the reaction leads to the formation of carbon–nitrogen bonds. Thus enamides are obtained from acid chlorides and 2-aza 1,3-dienes from carbonyl compounds (Scheme 65). Interestingly, chalcone-type enones react with *N,N*-bis(silyl)enamines to yield substituted pyridines, probably through cyclization of an intermediate azatriene (eq 148).

Scheme 65



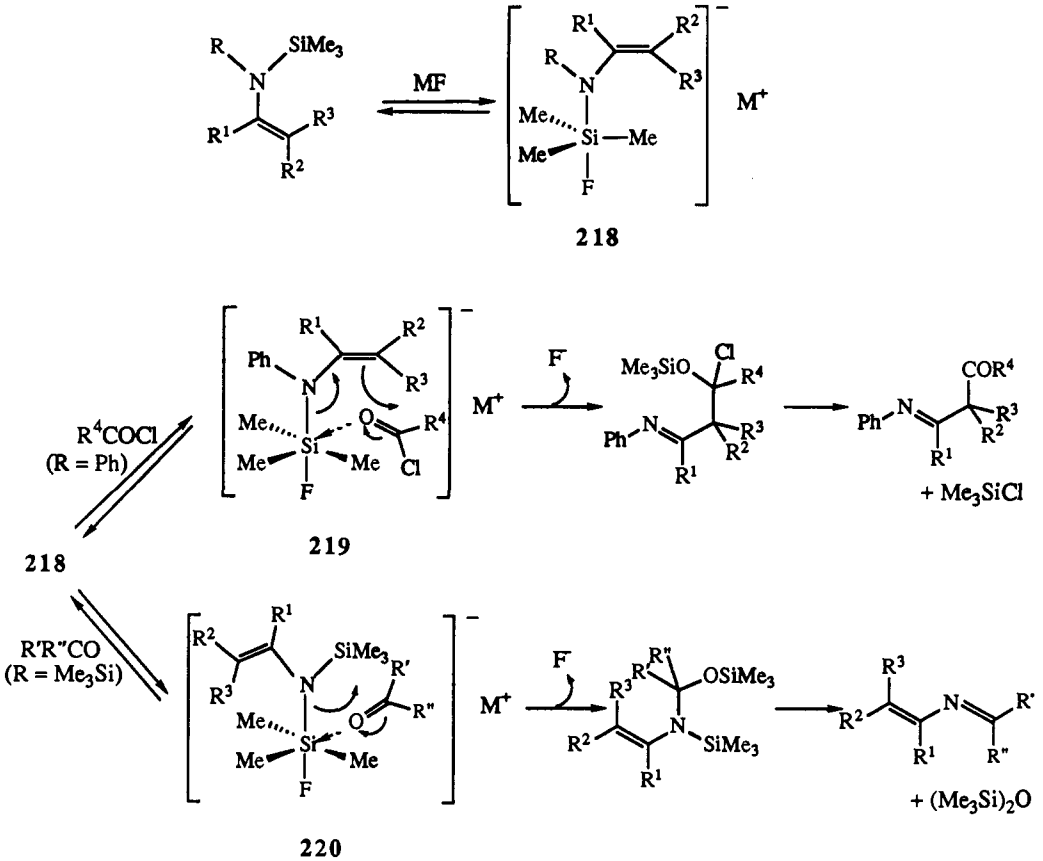


(148)

2. Mechanism

These results can be explained by the same mechanism as the one previously described (Scheme 66):

Scheme 66



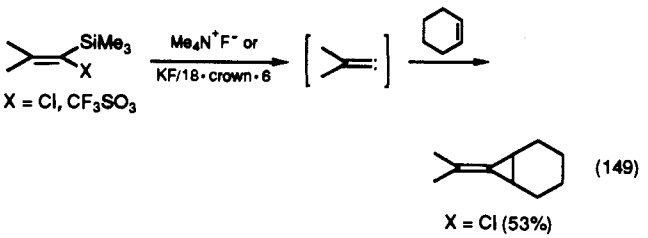
(1) Formation of pentacoordinate silicon species by coordination of F^- to the silicon center to give intermediate **218**.

(2) Reaction of **218** with compounds having two reactive centers such as acid chlorides or carbonyl compounds through hexacoordinate intermediates **219** and **220** leading to carbon–carbon bond formation from *N*-silyl enamines and carbon–nitrogen bond formation from *N,N*-bis(silyl) enamines.

D. Activation of the Si–C Bond

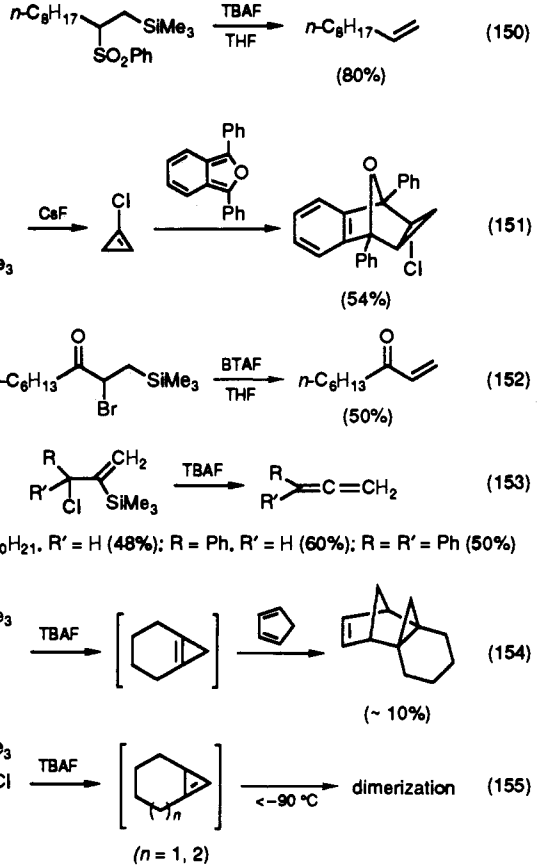
1. Elimination Reactions

a. α-Elimination. Fluoride ion-promoted decomposition of (α-chlorovinyl)trimethylsilane[315] and of trimethylsilylvinyl triflate[316] provide alkylidene carbene under mild conditions and in good yield (eq 149).



X = Cl (53%) (149)

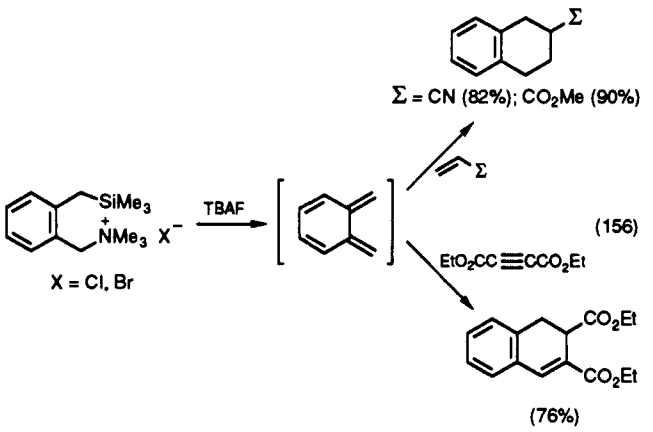
b. β-Elimination. β-Elimination of β-functionalized organosilicon compounds is also promoted by fluoride ion to give alkenes[317] (eq 150), cyclopropene[318] (eq 151), activated alkenes[319] (eq 152), or allenes[320] (eq 153). This β-elimination reaction has recently been effected in the gas-phase, using a solid fluoride deposited on glass helices, to prepare 1,3-bridged cyclopropenes[321,322] (eqs 154 and 155).



(150) (151) (152) (153) (154) (155)

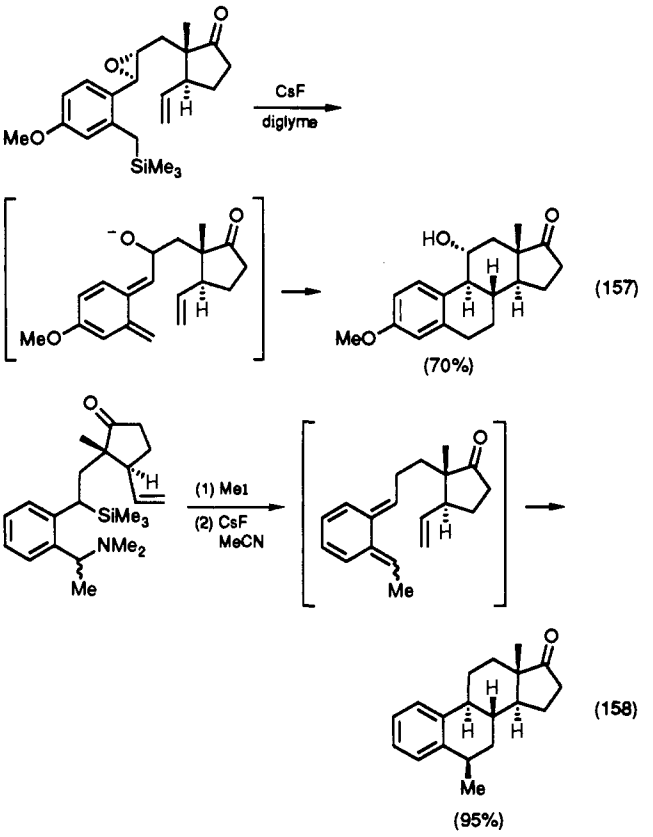
c. 1,4-Elimination. *o*-Xylylenes are efficiently prepared by fluoride anion-induced 1,4-elimination of [*o*-[(α-trimethylsilyl)alkyl]benzyl]trimethylammonium halides.[323] They can be trapped by electron-

deficient olefins or acetylenes (eq 156). These reactions



(156)

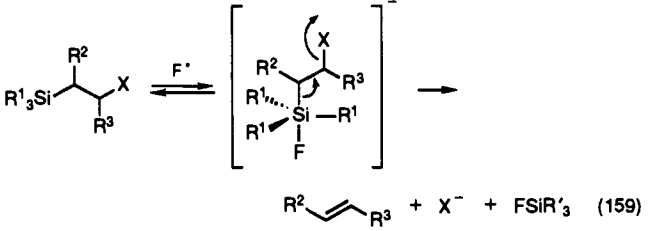
constitute a new approach to the synthesis of polycyclic ring systems, including natural products (eqs 157[324] and 158[325]).



(157)

(158)

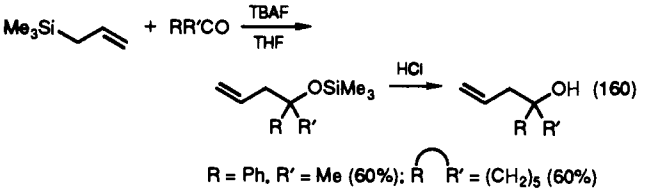
d. Mechanism. These reactions can be rationalized by a mechanism which involves, in the rate-determining step, the formation of a pentacoordinate silicon complex concerted with the cleavage of the silicon–carbon bond and the departure of the leaving group (eq 159).



(159)

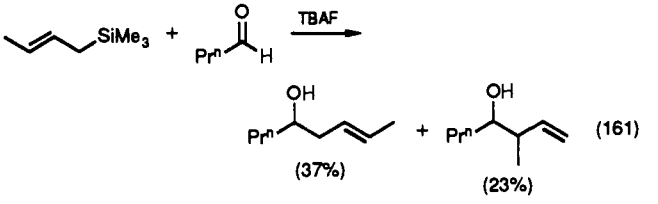
2. Activation of Allylsilanes

a. Reaction with Carbonyl Compounds. Considerable attention has been focused on the use of allylsilanes in organic synthesis.[203,326,327] Sakurai et al. were the first to report the F-catalyzed reaction of allyltrimethylsilanes with aldehydes and ketones[328] (eq 160). Crotyltrimethylsilane gives the two regioisomers



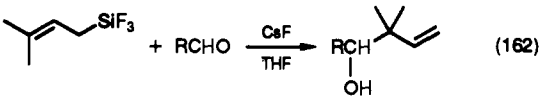
(160)

(eq 161) while (γ,γ'-dimethylallyl)trimethylsilane reacts without allylic rearrangement.[328]

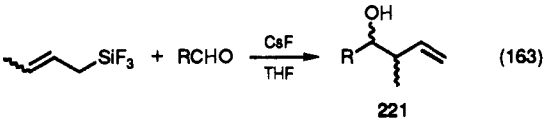


(161)

The substituents on the silicon atom were found to affect the course of the reaction. Allylation of aldehydes with allyltrifluorosilanes activated by cesium fluoride gives in excellent yields, a single isomer resulting from allylic rearrangement[329] (eq 162). Tetrabutylammonium fluoride can also be used as a fluoride ion source, whereas potassium fluoride is less effective. The reaction is stereospecific. (*E*)-Crotyltrifluorosilane reacts with aldehydes to give threo isomers, while erythro isomers are formed from (*Z*)-crotyltrifluorosilanes[211] (eq 163 and Table 25). However, 20% of



(162)



(163)

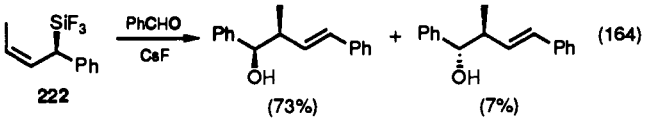
Table 25. Addition of (*E*)- and (*Z*)-Crotyltrifluorosilanes to Aldehydes RCHO in the Presence of CsF

		alcohol 221	
aldehydes	allylsilane	yield (%)	erythro/threo
R = Ph	*E*	92	99/1
	Z	96	1/99
R = n-C_6H_{17}	*E*	96	99/1
	Z	89	2/98
R = Bun, Et, CH	*E*	68	99/1
	Z	90	10/90
R = PhCH=CH	*E*	77	98/2
	Z	77	3/97
R = Ph, Me, CH	*E*	91	99/1
	Z	92	10/90

Table 26. Addition of (*E*)- and (*Z*)-Crotyltrifluorosilanes to Aldimines R^1CHNR^2 in the Presence of CsF

aldimines	allylsilane	amine 223 yield	amine 223 erythro/threo
$R^1 = R^2 = Ph$	*E*	94	71/29
	Z	91	40/60
$R^1 = Ph, R^2 = PhCH_2$	*E*	91	73/27
	Z	85	28/72
$R^1 = Ph, R^2 = Pr^n$	*E*	81	71/29
	Z	75	28/72
$R^1 = R^2 = Pr^n$	*E*	20	71/29
	Z	20	42/58
$R^1 = Pr^i, R^2 = Pr^n$	*E*	67	77/23
	Z	66	57/43

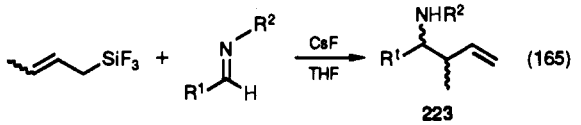
products without allylic rearrangement have been obtained from the chiral derivative **222**[207] (eq 164).



(164)

222

Crotyltrifluorosilanes react with aldimines[330] in the presence of cesium fluoride to afford the corresponding homoallylamines in high yields (eq 165 and Table 26).

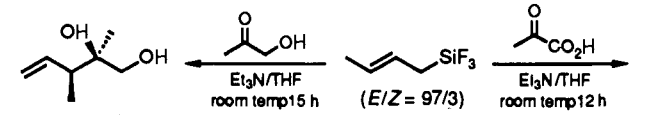


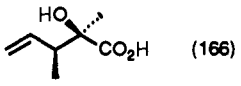
(165)

223

Carbon–carbon bond formation occurs exclusively at the γ-carbon of the crotylsilanes. The stereoselectivity is low,[330] nevertheless (*E*)-allylsilanes give mostly erythro isomers and (*Z*)-allylsilanes threo isomers.

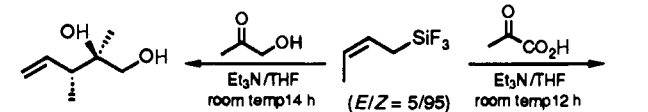
Allyltrifluorosilanes and allyltrialkoxysilanes react with α-hydroxyketones[331] or α-keto carboxylic acids[204] in the presence of triethylamine to give the corresponding homoallyl alcohols. Protection of the hydroxyl group or the carboxyl group is not necessary. The reaction is highly regio- and stereoselective (eqs 166 and 167). Allyltrialkoxysilanes are less reactive

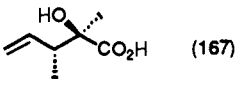




(166)

94% (syn/anti = 97/3)



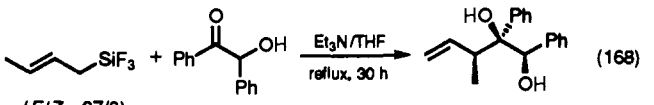


(167)

96% (syn/anti = 4/96)

than allyltrifluorosilanes and require a rather longer reaction time. In contrast to α-hydroxy ketones, aliphatic β- and γ-hydroxy ketones do not react under similar conditions.[331]

Crotyltrifluorosilanes react with α-substituted α-hydroxy ketones to give the corresponding 1,2-diol with high 1,2-syn selectivity[204,331] (eqs 168 and 169).



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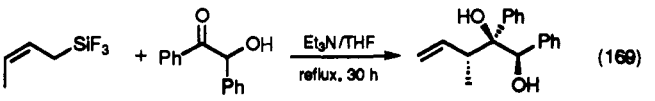


(169)

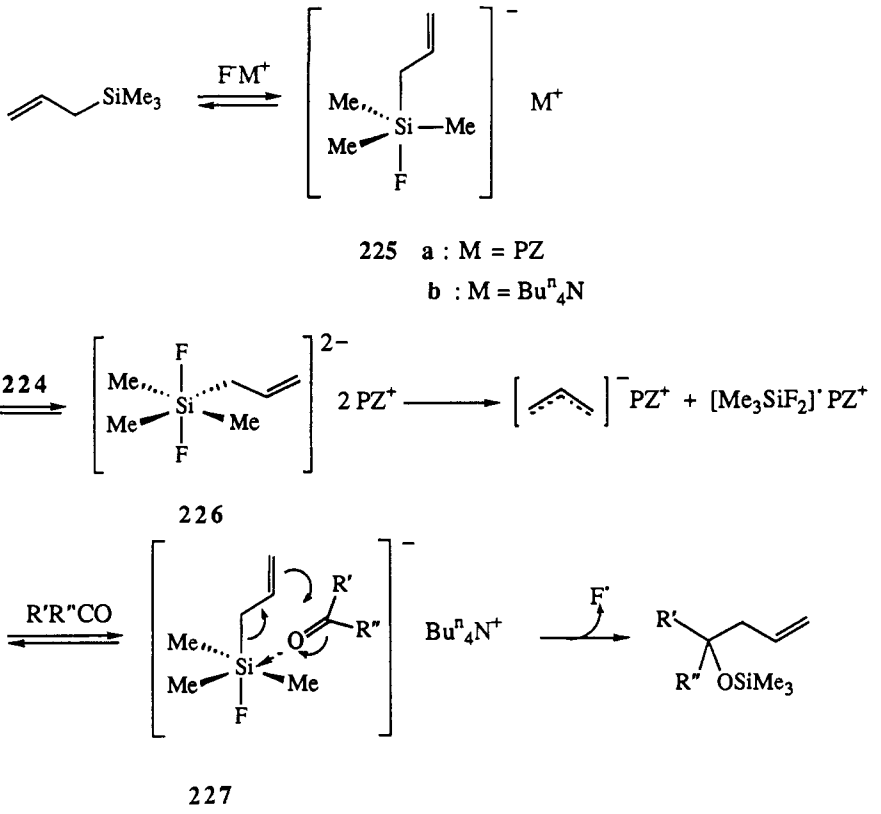
b. Reactions with α,β-Unsaturated Compounds. Allylation of a variety of Michael acceptors using trimethylallylsilane and fluoride catalysis has been investigated in detail.[332] It was found that the 1,2-/1,4-adduct ratio depends on the electrophile. With α,β-unsaturated ketones, both conjugate addition and 1,2-addition take place competitively. Cinnamaldehyde and α-methylcinnamaldehyde give only the 1,2-adduct, while α,β-unsaturated esters, nitriles, or amides without an acidic proton afford exclusively the 1,4-adduct (Table 27). Remarkably, the fluoride-induced allylation of polyene esters and nitriles provides 1,4-addition product exclusively, whereas cuprates prefer 1,6-conjugate addition.

Intramolecular allylation of various Michael acceptors with fluoride catalysis has been exploited.[333] The

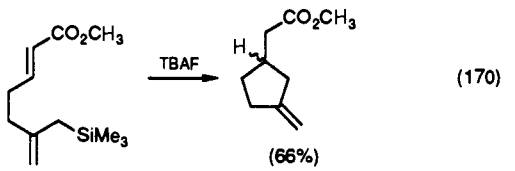
Table 27. TBAF-Catalyzed Reaction of Allyltrimethylsilane with αβ-Ethylenic Carbonyl Compounds and Nitriles

Michael acceptor	product [yield (%)]	
Ph–CH=CH–CHO	Ph–CH(OH)–CH=CH–Ph	(86)
Ph–CH=CH–COR	Ph–CH(COR)–CH=CH$_2$	Ph–CH=CH–C(OH)(R)–CH=CH$_2$
R = Me	(25)	(50)
R = Bu^i	(57)	(20)
R = Bu^t	(58)	(26)
Ph–CH=CH–CN	Ph–CH(CN)–CH=CH$_2$	(65)
Ph–CH=CH–COZ	Ph–CH(COZ)–CH=CH$_2$	
Z = OMe	(90)	
Z = NEt$_2$	(80)	
Ph–CH=CH–Σ	Ph–CH=CH–CH(Σ)–CH=CH$_2$	
Σ = CO$_2$Et	(63)	
Σ = CN	(37)	

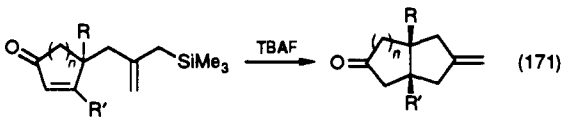
Scheme 67



annelation takes place with both acyclic (eq 170) and cyclic (eq 171) unsaturated esters, nitriles, amides, and



(170)

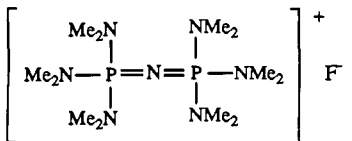


(171)

R = R' = H n = 1 (64%) n = 2 (69%)
R = Me, R' = H n = 1 (55%) n = 2 (63%)
R = R' = Me n = 1 (10%) n = 2 (65%)

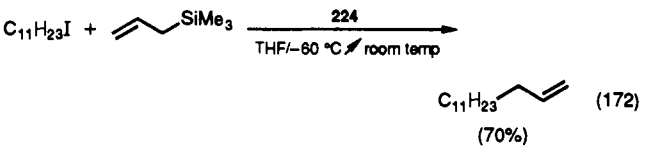
enones in contrast to the Lewis acid-catalyzed procedure. Moreover these intramolecular Michael condensations occur despite both enolizable protons and severe steric interactions. It was shown that optimum conditions for both inter- and intramolecular additions require only a catalytic quantity (ca. 0.2 equiv) of tetrabutylammonium fluoride (TBAF) as the fluoride source, with *N,N*-dimethylformamide as the solvent.[333]

c. Reaction with Organic Halides. For the first time, allyltrimethylsilane has been found to react with alkyl iodides[334] in the presence of the very reactive phosphazenium fluoride (PZ^+F^-) **224** (eq 172). Two



224

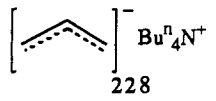
equivalents of **224** are necessary to perform the reaction and only minimal conversion can be achieved with 1 equiv of **224**.



(172)

d. Mechanism. To rationalize these allylation reactions two mechanisms may be proposed, as for the fluoride-catalyzed Si–O bond activation. In both cases the first step is the coordination of fluoride ion to the silicon atom to give the pentacoordinate species **225** (Scheme 67). Then the course of the reaction depends on the fluoride ion source. With the very reactive fluoride ion from the salt **224**[334] further coordination occurs to give the hexacoordinate complex **226**, which decomposes to allyl anion and $[Me_3SiF_2]^-$. The allyl anion then reacts with alkyl halide.[334] The fact that 2 equiv of **224** are necessary to give a good yield of the coupling product supports this mechanism.

With less reactive fluoride ion (CsF, TBAF), displacement of the allyl anion does not occur. Instead, there is coordination of the carbonyl group to the silicon atom to give the hexacoordinate intermediate **227** which involves a six-membered cyclic transition state (Scheme 67). This geometry explains the high stereoselectivity observed. With trifluoroallylsilane the reaction is regiospecific, with carbon–carbon bond formation occurring exclusively at the γ-carbon atom,[329] whereas with trimethylsilane the reaction is not regioselective.[328] In the case of allylation by trimethylallylsilane–TBAF, the formation of the allyl anion **228** was invoked.[328] This seems to be unlikely since the reactive allyl anion

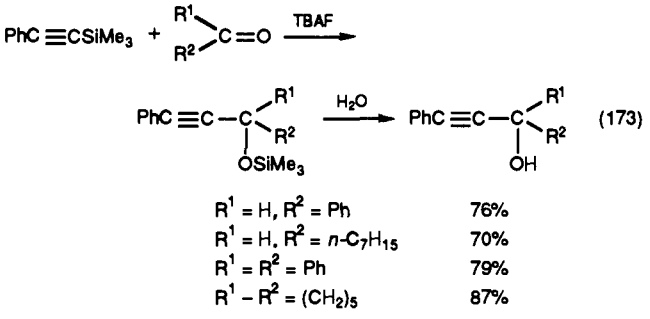


228

would react with the tetrabutylammonium ion. Moreover, it is important to note that, whereas TBAF acts as a source of reactive fluoride ion toward the Si–O bond, it does not show the same reactivity toward the Si–C bond, which is more difficult to cleave.

3. Activation of Alkynyl-, Propargyl-, Benzyl-, and Arylsilanes

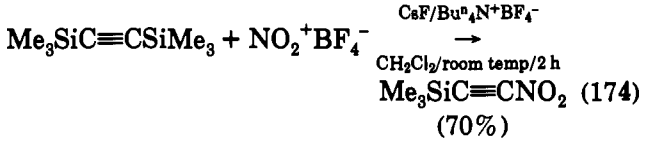
1-Phenyl-2-(trimethylsilyl)acetylene adds to carbonyl compounds in the presence of a catalytic amount of fluoride ion (eq 173).[335,336] Yields are generally good.



$R^1 = H, R^2 = Ph$	76%
$R^1 = H, R^2 = n\text{-}C_7H_{15}$	70%
$R^1 = R^2 = Ph$	79%
$R^1 - R^2 = (CH_2)_5$	87%

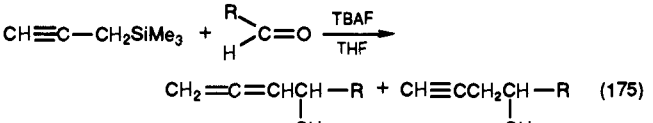
The source of fluoride can be TBAF in THF[335,336] or KF/18-crown-6 ether in CH_2Cl_2 or THF.[337]

Nitro(trimethylsilyl)acetylene has been prepared by reaction of bis(trimethylsilyl)acetylene and nitronium tetrafluoroborate. The reaction rate appears to depend on the fluoride ion source. A combination of added $Bu^n_4N^+BF_4^-$ and CsF increases the nitration rate 4-fold (eq 174).[338]

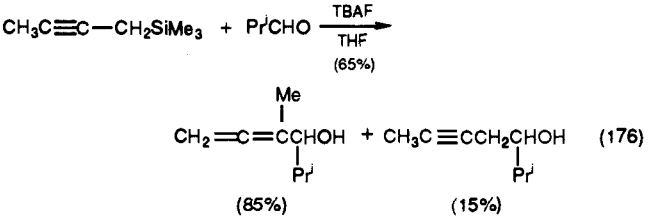


(70%) (174)

Propargyltrimethylsilane reacts with aliphatic aldehydes in the presence of TBAF to give α-allenic alcohols (eq 175). With α,β-unsaturated aldehydes and aromatic aldehydes a mixture of α-allenic and β-acetylenic alcohols was obtained[339] (eq 175). A mixture of alcohols was also obtained[340] from 1-(trimethylsilyl)-2-butyne (eq 176).



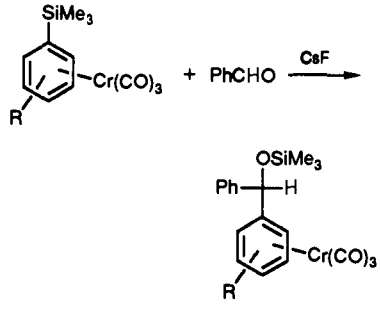
R = Me	65%	
R = n-C_6H_{13}	70%	
R = Pr^i	53%	
R = Ph	31.5%	13.5%



(85%) (15%) (176)

The transfer of a benzyl group from the corresponding organosilanes to various electrophiles has been reported. This reaction can be catalyzed by KF/18-crown-6, silica-supported TBAF,[341,342] and TBAF.[343] (Trimethylsilyl)benzenes activated in the 2-position by electron-withdrawing groups react with aldehydes, ketones, acid fluorides, acid anhydrides, and CO_2 in the presence of a catalytic amount of potassium *tert*-butoxide or fluoride anion in HMPA[344] (Scheme 68).

In the same way, tricarbonylchromium complexes of (trimethylsilyl)benzene react[345] with aromatic aldehydes and ketones in the presence of a catalytic amount of CsF (eq 177). The reaction takes place also with aliphatic aldehydes and enolizable ketones, but yields are lower.

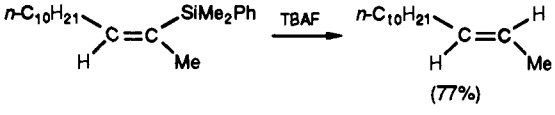


(177)

R = H (88%); R = *o*-Me (81%); R = *o*-Cl (83%); R = *m*-Me (83%); R = *m*-Cl (70%); R = *p*-Me (81%); R = *p*-Cl (57%)

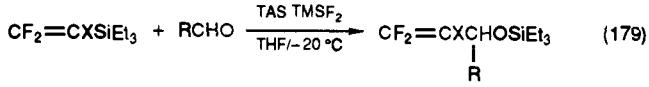
4. Activation of Alkenylsilanes

Bu^n_4NF proved to be effective in cleaving $PhMe_2Si$– and Ph_2MeSi–vinyl carbon bonds not only in vinylsilanes having a hydroxyl group at the β-carbon atom[346] but also in simpler compounds[347] (eq 178). The reaction

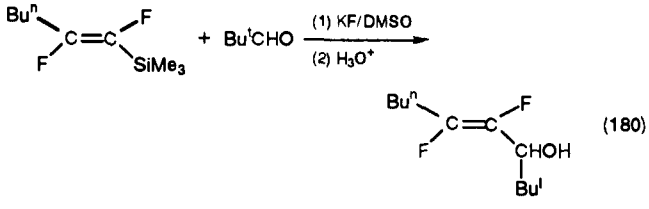


(77%) (178)

is highly stereospecific. Substitution of the silyl group by hydrogen proceeds with retention of configuration. All attempts to trap a supposed vinyl anion intermediate failed. Under the same conditions vinyltrimethylsilane is recovered unchanged. However (polyhalovinyl)silanes add to aldehydes in the presence of a catalytic amount of TAS $TMSF_2$ (eq 179)[346] or with KF/DMSO (eq 180).[349]



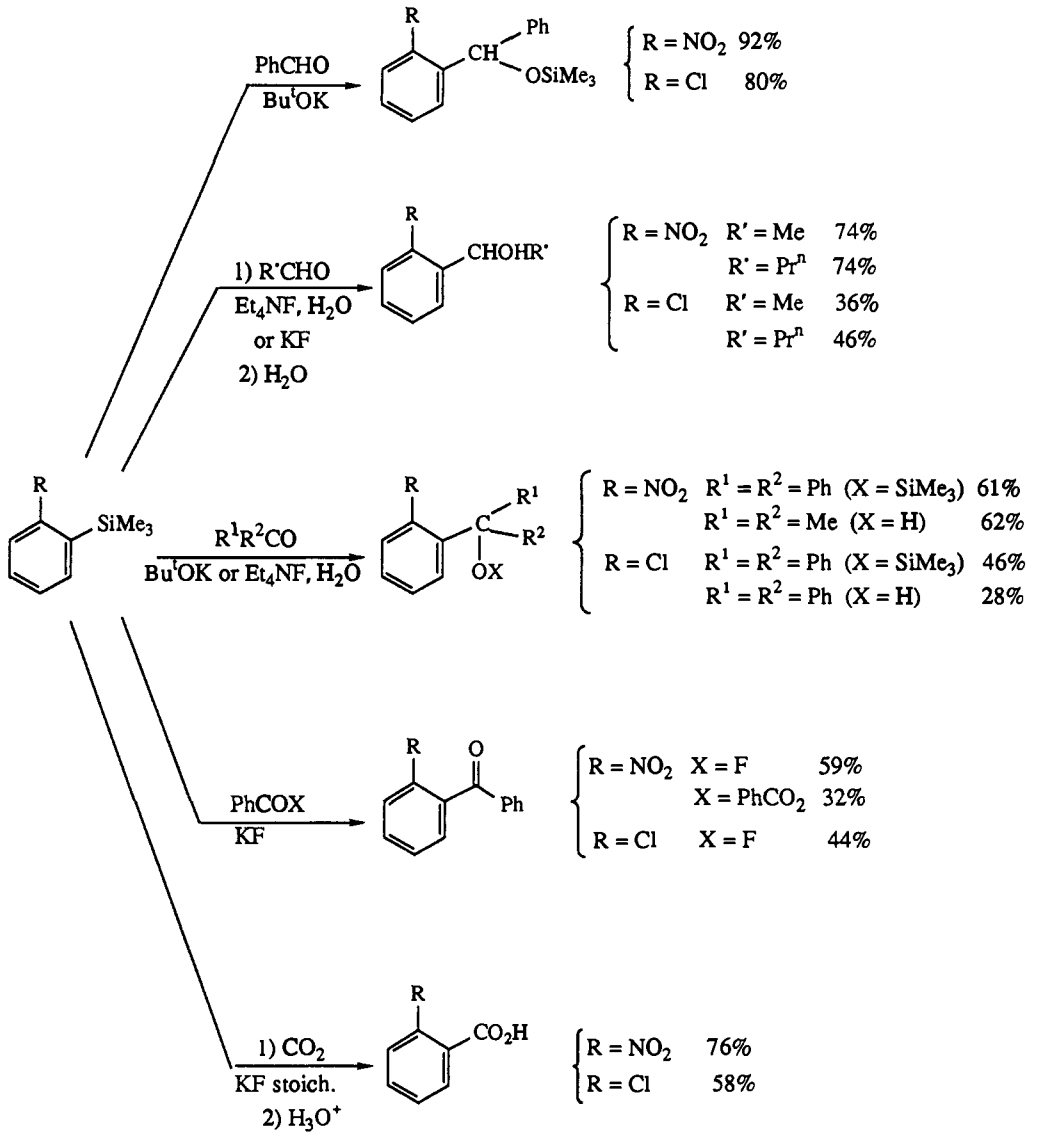
R = Ph, X = F	66%
R = Ph, X = Cl	38%
R = n-$C_{10}H_{21}$, X = F	59%



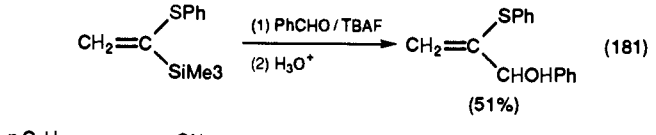
(180)

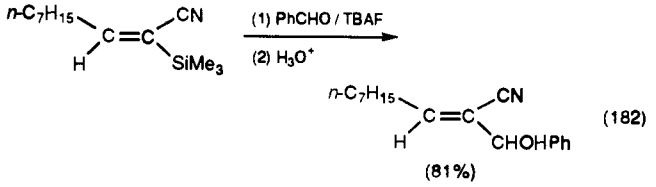
Vinylsilanes, having an anion-stabilizing group on the carbon bearing the silyl group, react with aldehydes

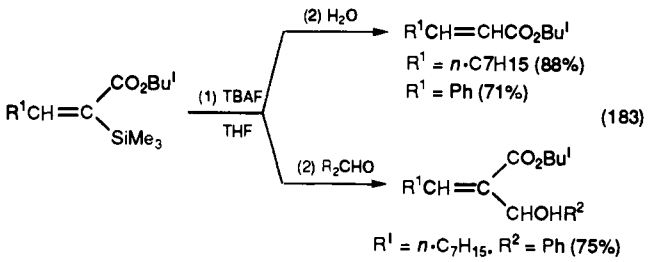
Scheme 68



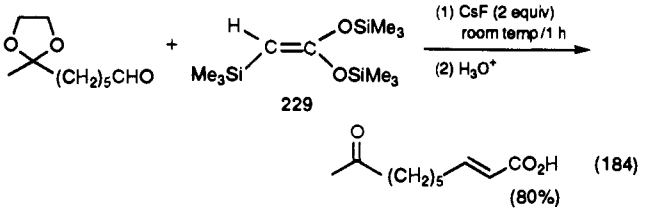
and ketones in the presence of TBAF. The cleavage of the Si–C bond always proceeds with retention of configuration (eqs 181,[347] 182,[350] and 183[351]).





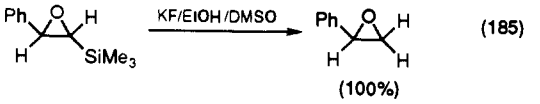


Recently, the tris(trimethylsilyl)ketene acetal **229** activated by CsF has been used[352] in the last step of the synthesis of the pheromone **230** (eq 184).

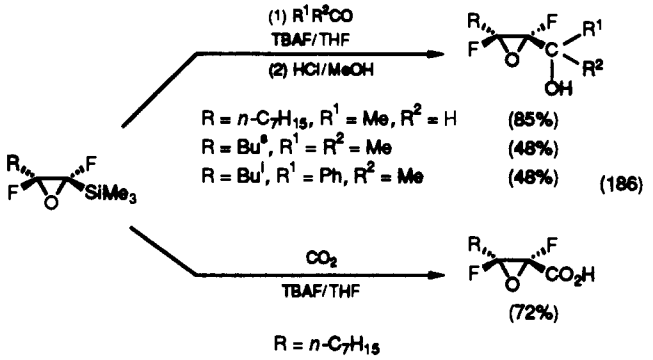


5. Activation of Silicon–Carbon Bonds in the α-Position of a Three-Membered Ring

a. **Oxiranylsilanes.** The protodesilylation of some oxiranylsilanes by fluoride ion has been studied. It occurs with quantitative formation of the corresponding oxirane[353] (eq 185) and with retention of configuration.[354]

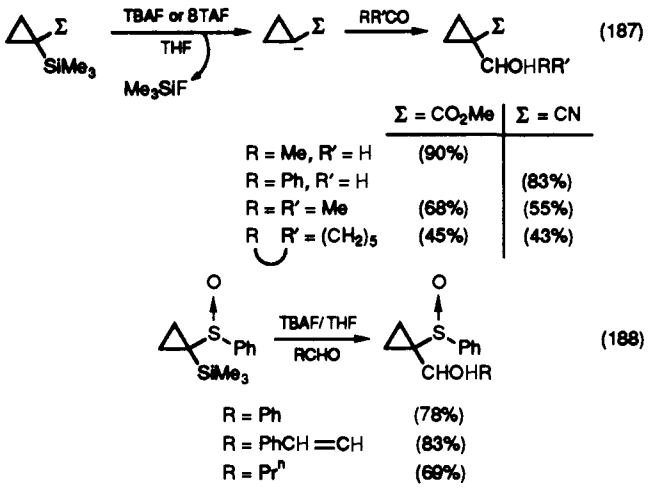


The cleavage of the Si–C bond by fluoride ion occurs more easily in oxiranylsilanes than in vinylsilanes of corresponding structure,[353] and some addition reactions of oxiranylsilanes to carbonyl compounds have been carried out[355] (eq 186).



(186)

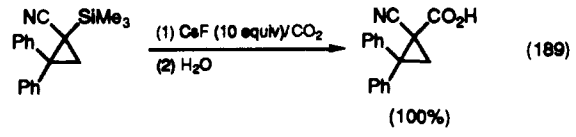
b. Cyclopropylsilanes. α-Trimethylsilyl-substituted cyclopropanes bearing an electron-withdrawing group (CO_2Et,[356] CN,[356] PhSO,[357] $N(NO_2)Me$[358]) are desilylated by fluoride ion to give condensation products with ketones (eqs 187[356] and 188[357]).



(187)

(188)

The desilylation–carboxylation reaction of α-trimethylsilyl-substituted cyanocyclopropanes is quantitative[359] in the presence of an excess of CsF (10 equiv) in DMF (eq 189).



(189)

6. Activation of Trimethylsilyl Derivatives Bearing an Anion-Stabilizing Group in the α-Position

Silicon compounds with an anion-stabilizing group in the α-position can readily be activated by nucleophiles to give reactions of the carbanion resulting from Si–C cleavage.

a. Generation of Anion Equivalents. *i. Activation of α-Halogenosilanes.* (Dichloromethyl)- and (trichloromethyl)trimethylsilanes react with aldehydes at room temperature in the presence of a catalytic amount of TAS $TMSF_2$[360] (eqs 190 and 191).

$$Me_3SiCHCl_2 + RCHO \xrightarrow[(2)\ H_3O^+]{(1)\ TAS\ TMSF_2/THF} RCHOHCHCl_2$$

R = Ph (77%); R = n-$C_{10}H_{21}$ (72%); R = PhCH=CH (95%) (190)

$$Me_3SiCCl_3 + RCHO \xrightarrow[(2)\ H_3O^+]{(1)\ TAS\ TMSF_2/THF} RCHOHCCl_3$$

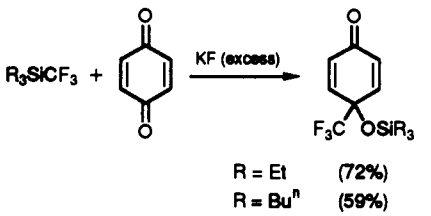
R = Ph (77%); R = n-$C_{10}H_{21}$ (79%) (191)

In the same way, trifluoromethylation of carbonyl compounds is effected by (trifluoromethyl)trimethylsilane activated by a catalytic amount of TBAF[361] (eq 192). (Trifluoromethyl)trialkylsilanes also react with

$$Me_3SiCF_3 + R^1R^2CO \xrightarrow[(2)\ H_3O^+]{(1)\ TBAF/THF/RT/1\ h} R^1R^2C(OH)CF_3$$

R^1 = H, R^2 = Ph (85%); R^1 = H, R^2 = c-C_6H_{11} (80%); R^1 = Me, R^2 = Ph (74%); R^1–R^2 = $(CH_2)_5$ (77%) (192)

benzoquinone in the presence of an excess of KF to give dienones containing geminal trifluoromethyl and trialkylsiloxy substituents (eq 193). Similar reactions



(193)

occur with 1,4-naphthoquinone, 9,10-anthraquinone, and 9,10-phenanthrenequinone, as well as with alkyl-substituted quinones, but not with halogen-substituted quinones.[362]

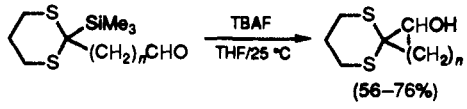
Fluoride ion induces cross-coupling of organic halides with (trifluoromethyl)trialkylsilane in the presence of Cu(I) salts[363] (eq 194).

$$RX + CF_3SiEt_3 \xrightarrow[CuI\ (1\ equiv)/DMF/NMP]{KF\ (1.2\ equiv)} RCF_3 \quad (194)$$

RX = βNpI (94%); o-MeC_6H_4I (86%); m-MeC_6H_4I (78%); p-MeC_6H_4I (82%); p-$MeOC_6H_4I$ (48%); p-ClC_6H_4I (35%); p-$EtO_2CC_6H_4I$ (94%); p-$CH_3COC_6H_4I$ (45%); (Z)-n-$C_8H_{17}CH$=CHI (90%); $PhCH_2Br$ (73%); PhCH=$CHCH_2Br$ (23%).

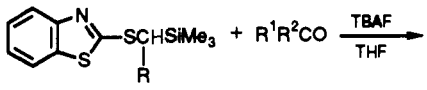
ii. Activation of [(Organothio)methyl]trimethylsilanes. (2-Trimethylsilyl-1,3-dithian-2-yl)alkanals un-

dergo cyclization in the presence of fluoride anion[364] (eq 195). Intermolecular transfer of the 2-(trimethylsilyl)-1,3-dithiane group may also be induced but with variable yields.

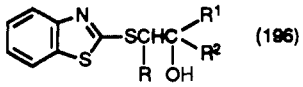


(195)

Compound **231** reacts in the presence of a catalytic amount of TBAF with aldehydes and ketones[365] (eq 196). Although (arylthio)methylsilanes are excellent



231



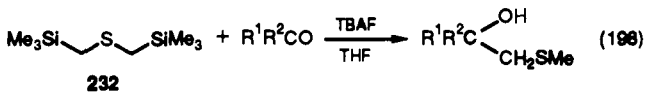
(196)

R = H, R^1 = *p*-MeC_6H_4, R^2 = H	(75%)
R = Me, R^1 = *p*-MeC_6H_4, R^2 = H	(75%)
R = Me, R^1 = Bu^n, R^2 = H	(65%)

reagents for (arylthio)methylation[366] (eq 197), fluoride ion promoted (alkylthio)methylation from (alkylthio)methylsilanes is ineffective. In contrast bis(trimethylsilyl)methyl]sulfide (**232**) reacts with aldehydes and ketones in the presence of TBAF to afford the corresponding β-hydroxyethyl sulfide[367] (eq 198).

(197)

R^1 = Ph, R^2 = H	(96%)
R^1 = Ph, R^2 = Me	(49%)
R^1 = R^2 = Me	(61%)

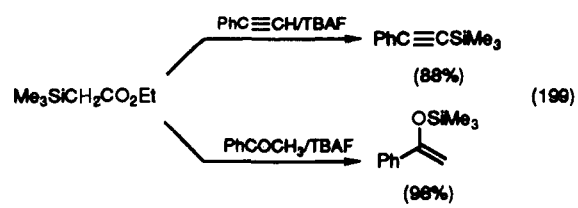


(198)

232

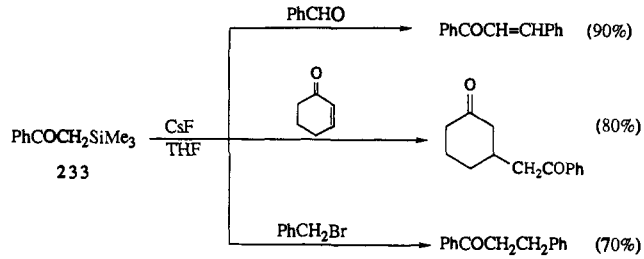
R^1 = H, R^2 = *p*-XC_6H_4 (X = Me 52%; MeO 71%; Cl 76%; Me_2N 56%)
R^1 = R^2 = Ph (30%)
R^1–R^2 = $(CH_2)_5$ (65%)

b. Activation of (Trimethylsilyl)acetate and (Trimethylsilyl)acetonitrile. In the presence of a catalytic amount of TBAF, ethyl (trimethylsilyl)acetate silylates compounds containing an acidic hydrogen in excellent yields[368] (eq 199). With nonenolizable carbonyl compounds, ethyl (trimethylsilyl)acetate in the presence of TBAF[369] and also (trimethylsilyl)acetonitrile in the presence of TAS $TMSF_2$[370] give β-hydroxy esters or nitriles respectively in good yields (eq 200). In the same way transfer of the $PhCOCH_2^-$ ion occurs on

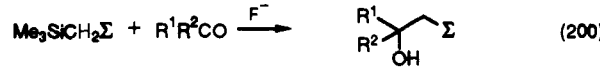


(199)

Scheme 69



reaction of **233** with various electrophiles (Scheme 69) in the presence of a stoichiometric amount of CsF.[371]

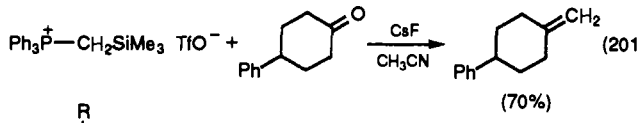


(200)

	Σ = CO_2Et	Σ = CN
R^1 = H, R^2 = Ph	(76%)	(93%)
R^1 = H, R^2 = PhCH=CH	(81%)	(45%)
R^1 = H, R^2 = MeCH=CH	(69%)	(45%)
R^1 = R^2 = Ph	(88%)	(95%)

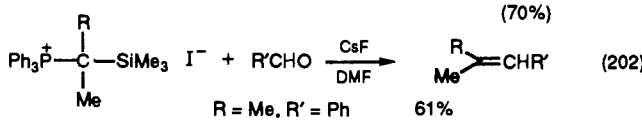
c. Generation of Ylide Equivalents. Cesium fluoride-induced desilylation also occurs readily with a variety of systems of the type $(CH_3)_3SiCH_2Y$ in which Y is a group containing a phosphorus, sulfur, or nitrogen atom.

i. Phosphorus Derivatives. CsF in acetonitrile induces a Wittig reaction between α-silylphosphonium salts and carbonyl compounds (eqs 201[372] and 202[373]).



(201)

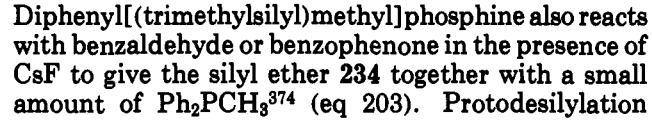
(70%)



(202)

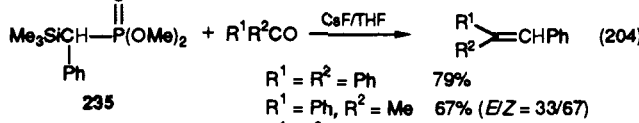
R = Me, R' = Ph	61%
R = Et, R' = *n*-C_8H_{17}	46% (*E*/*Z* = 58/42)
R = allyl, R' = *n*-C_8H_{17}	83% (*E*/*Z* = 53/47)
R = $PhCH_2$, R' = Ph	45% (*E*/*Z* = 11/89)

Diphenyl[(trimethylsilyl)methyl]phosphine also reacts with benzaldehyde or benzophenone in the presence of CsF to give the silyl ether **234** together with a small amount of Ph_2PCH_3[374] (eq 203). Protodesilylation occurs with enolizable carbonyl compounds. In the same way (α-silylalkyl)phosphonate **235** reacts with carbonyl compounds to give a Horner-Emmons type reaction[375,376] (eq 204) in the presence of a stoichiometric



(203)

234
(R = H, Ph)

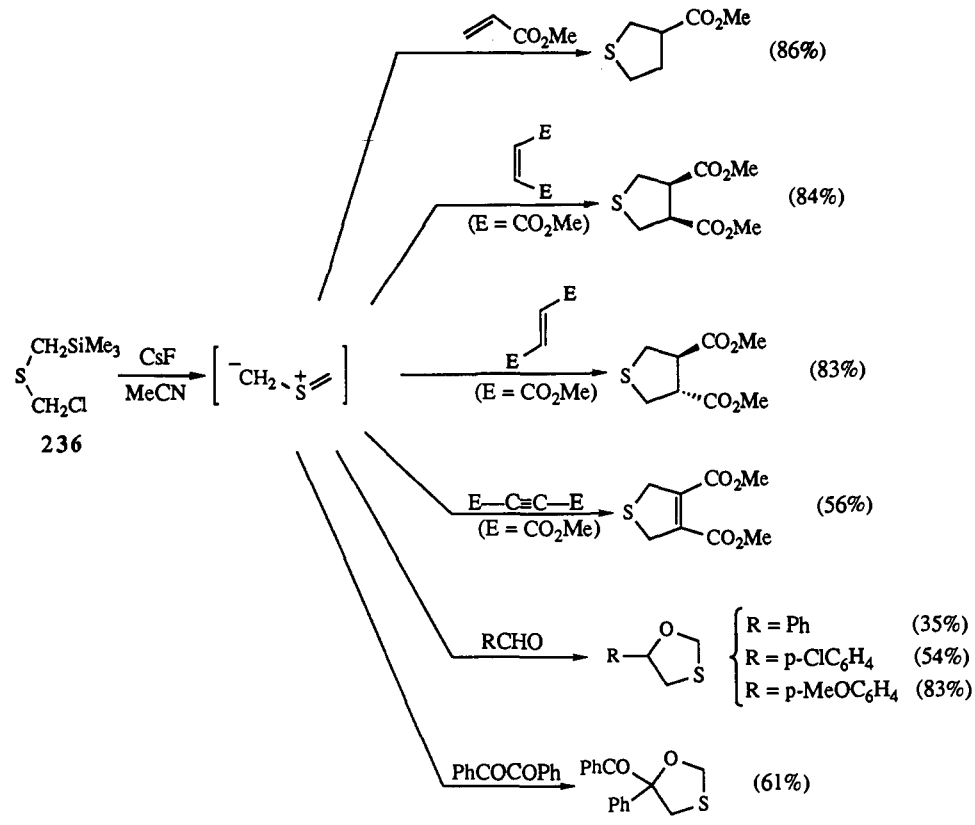


(204)

235

R^1 = R^2 = Ph	79%
R^1 = Ph, R^2 = Me	67% (*E*/*Z* = 33/67)
R^1–R^2 = $(CH_2)_5$	35%
R^1 = H, R^2 = Pr^i	35% (*E*/*Z* = 70/30)

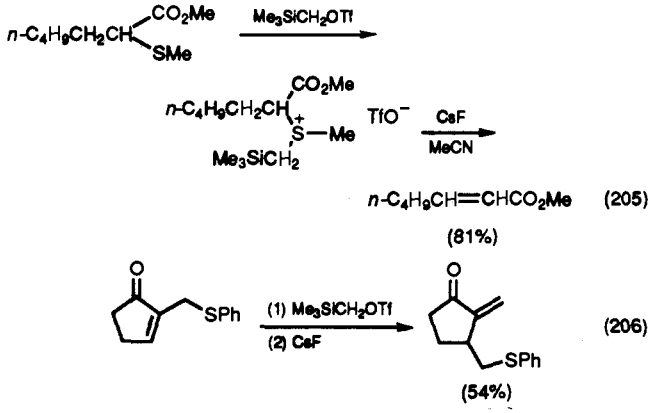
Scheme 70



amount of CsF, which is the best fluoride source for this reaction.

ii. Sulfur Derivatives. Chloromethyl (trimethylsilyl)methyl sulfide (**236**), activated by CsF, reacts with activated alkenes and alkynes as a thiocarbonyl ylide synthon to give tetrahydro and dihydrothiophen derivatives.[377] **236** reacts similarly with carbonyl compounds to give 1,3-oxathiolanes[378] (Scheme 70).

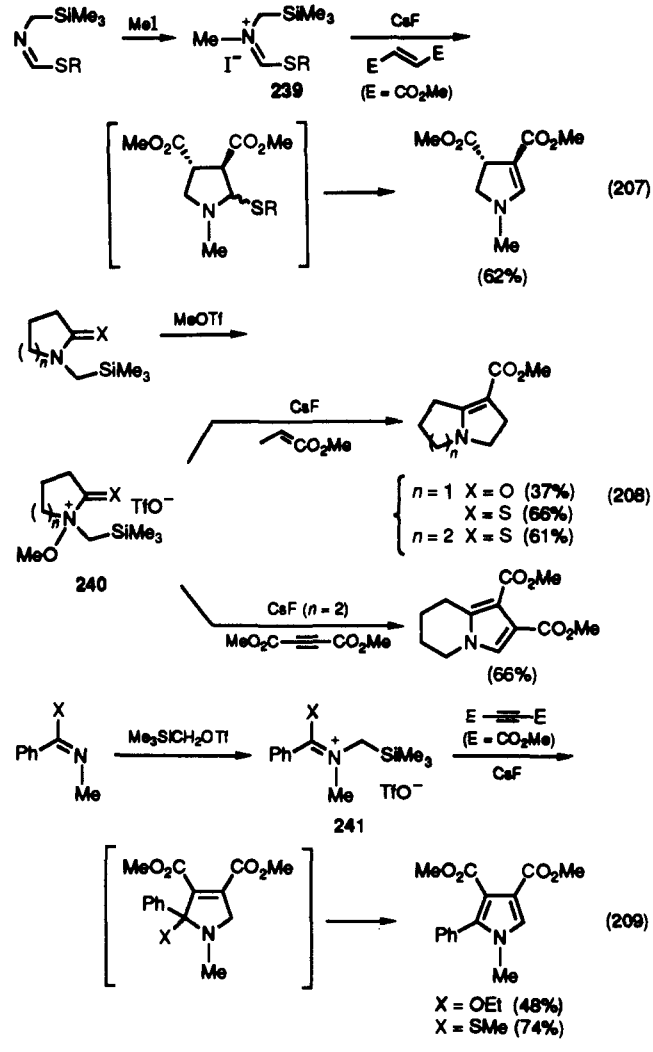
[(Trimethylsilyl)methyl]sulfonium salts when treated by CsF undergo apparent five-center fragmentation to alkenes (eqs 205[372] and 206[379]). In the presence of



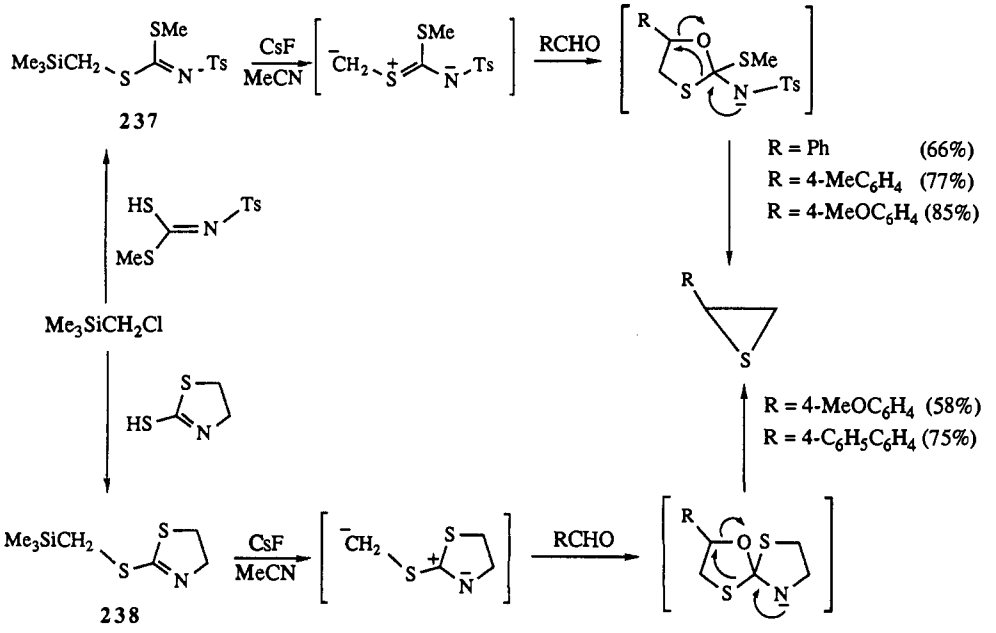
CsF, compounds **237** and **238**, easily obtained from (chloromethyl)trimethylsilane, react with aldehydes to give thiiranes[360] (Scheme 71).

iii. Nitrogen Derivatives. Compounds **239–242** react with electrophilic alkenes to give (3 + 2) cycloaddition reactions when activated by fluoride anion (eqs 207,[381] 208,[382] and 209[383] and Scheme 72[384]).

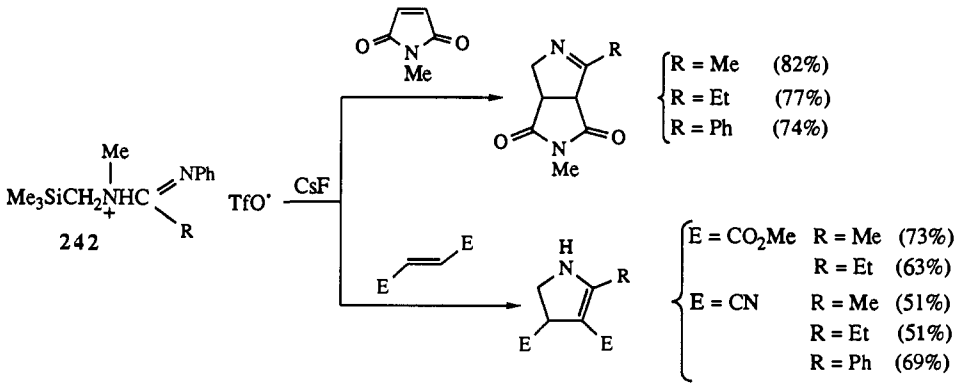
Compounds **243** and **244** are also activated by CsF to give azomethine ylide equivalents which react with



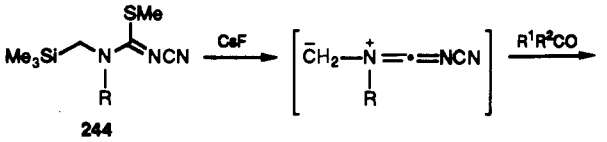
Scheme 71

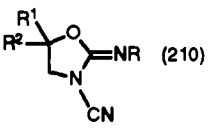


Scheme 72



electrophilic alkenes or carbonyl compounds (Scheme 73[385] and eq 210[386]).





(210)

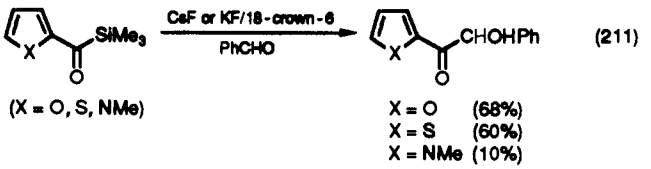
R = H, R¹ = H, R² = Ph 41%

R = Me, R¹ = H, R² = Ph 77%

R¹ = R² = Ph 40%

d. Activation of Acylsilanes. Benzoyltrimethylsilane, activated by KF/18-crown-6, CsF, or TBAF, reacts with water, organic halides, and carbonyl compounds to give aldehydes, ketones, and hydroxy ketones[387,388] (Scheme 74). This reaction has been extended to heteroacylsilanes. It proceeds with benzaldehyde (eq 211), $PhCOCH_2Br$, $PhCH_2Br$, and $PhCH=CHCH_2I$, but not with ketones or allyl bromide.[389]

Alkanoyltrimethylsilanes are less reactive than aroyltrimethylsilanes and require elevated temperatures and



(211)

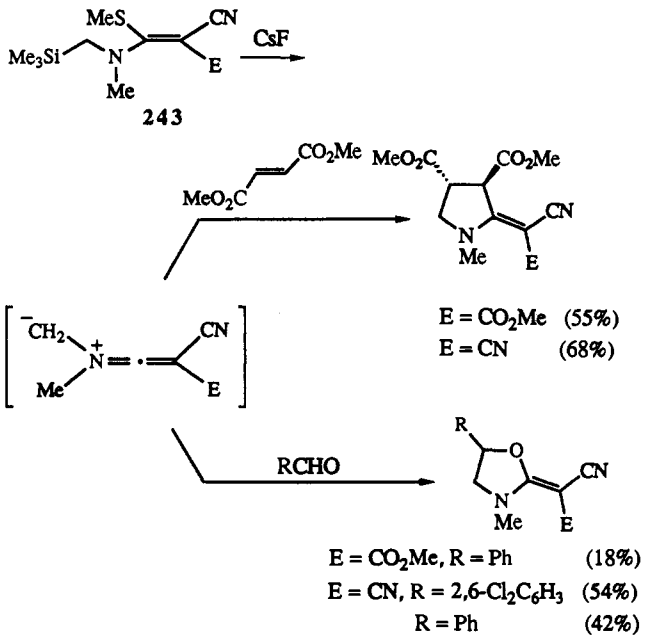
the presence of an acid to give an aldehyde.[390] In the absence of acid, an alcohol is obtained, arising from an unusual migration of the alkyl or aryl group from the silicon atom to the carbonyl carbon atom[390] (eq 212).

$$RCOSiMe_3 \xrightarrow{\text{TBAF/THF/room temp}} RCHOHMe \quad (212)$$

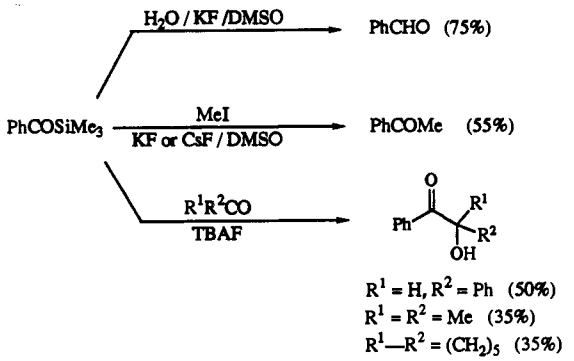
$R = n\text{-}C_5H_{11}$ (62%); $R = n\text{-}C_6H_{13}$ (68%)

e. Mechanism. The reactions described in sections 5 and 6 have not been studied from a mechanistic point of view. Most of them have been interpreted by the formation of a stabilized anion (for example, eq 187). However these reactions can also be rationalized by a mechanism similar to the one proposed for Si–H, Si–O, and Si–N activation and involving penta- and hexacoordinate intermediates. The nucleophilic catalyst coordinates to the silicon atom to provide a pentacoordinate species in which the Si–C bond is lengthened. This process induces a partial negative charge on one ligand which is stabilized by the α-electron-withdrawing substituent (halogen, sulfur, ester group, etc.). This

Scheme 73



Scheme 74



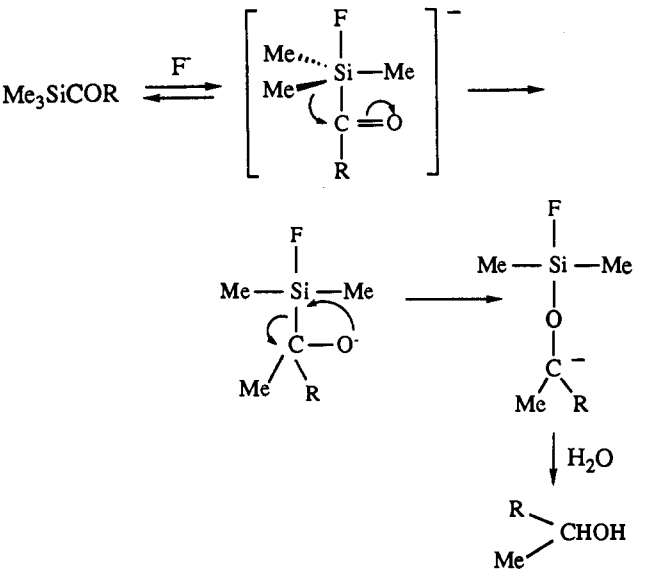
intermediate may then react with an electrophile via a hexacoordinate intermediate, with formation of a new C–C bond and cleavage of the Si–C bond. This interpretation although less classical agrees with the experimental results.

The migration of the methyl group of acylsilanes[390] from the silicon to the carbonyl group can take place as shown in Scheme 75.

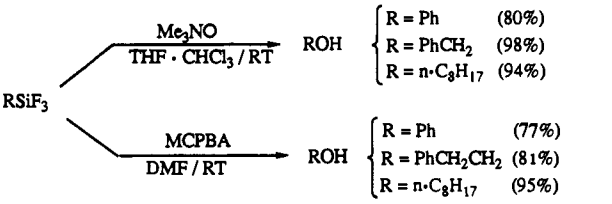
7. Oxidative Si–C Bond Cleavage of Organotrifluorosilanes

Trifluoroalkyl- and trifluoroarylsilanes are oxidized by trimethylamine *N*-oxide in a THF–$HCCl_3$ mixture[391] or by *m*-chloroperbenzoic acid[266] in DMF (Scheme 76). Both oxidizing reagents oxidize *exo*-norbornyltrifluorosilane with retention of configuration. It has been shown[391] that (*E*)- and (*Z*)-crotyltrifluorosilanes are oxidized stereospecifically by trimethylamine *N*-oxide into (*E*)- and (*Z*)-crotyl alcohols, respectively. The likely mechanism of these oxidative reactions is shown in Scheme 77. Complexation of trimethylamine *N*-oxide or of *m*-chloroperbenzoic acid gives pentacoordinate complexes **245** and **246** within which 1,2-migration of an organic group can occur. *m*-Chloroperbenzoic acid also oxidizes difluorodiorganosilanes[288] but more slowly, the reaction being greatly accelerated

Scheme 75



Scheme 76



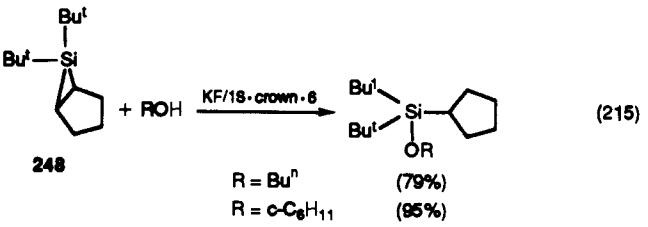
in the presence of a catalytic amount of KF (eq 213 and Scheme 78). Monofluorotriorganosilanes are also oxidized but in the presence of 2 equiv of KF (eq 214).

$$(n\text{-}C_8H_{17})_2SiF_2 \xrightarrow[\text{KF (0.1 equiv)}]{\text{MCPBA}} 2n\text{-}C_8H_{17}OH\ (92\%) \qquad (213)$$

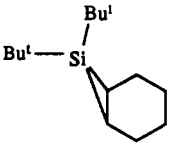
$$n\text{-}C_8H_{17}Me_2SiF \xrightarrow[\text{KF (2 equiv)}]{\text{MCPBA}} n\text{-}C_8H_{17}OH\ (76\%) \qquad (214)$$

8. Potassium Fluoride Activated Alcoholysis of Hindered Siliranes

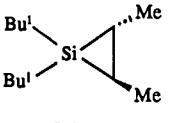
The rate of alcoholysis of 1,1-di-*tert*-butylsiliranes **247–249** was observed to be significantly accelerated in the presence of 10% KF and still further enhanced by the addition of 1% of 18-crown-6 ether[392] (eq 215). This



(215)



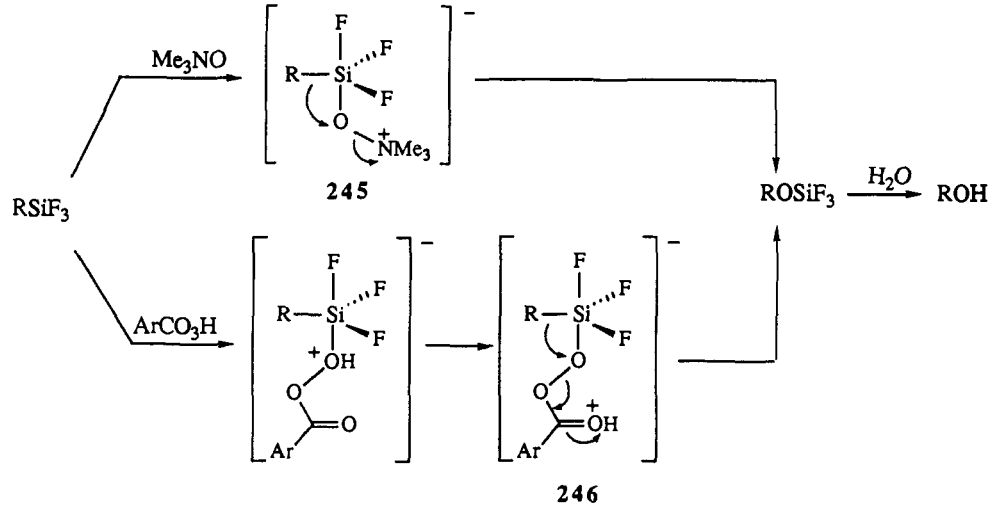
247



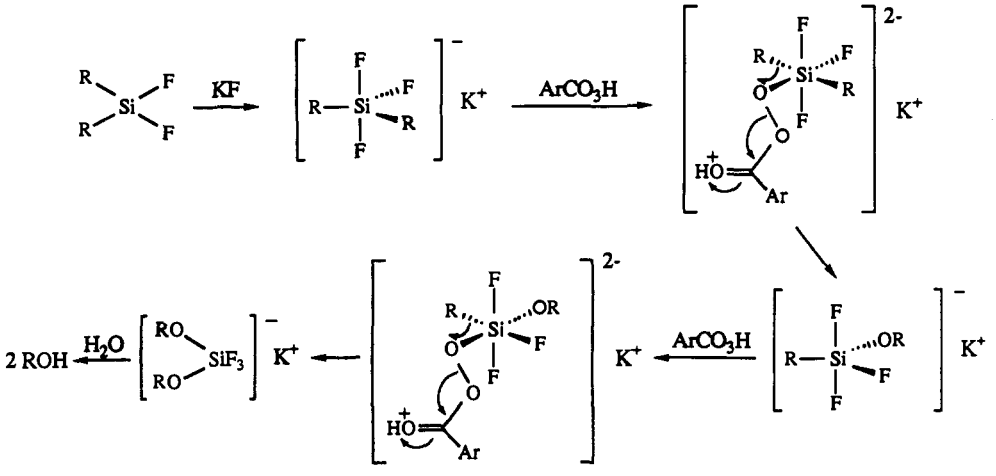
249

catalytic process may be explained by rapid coordination of fluoride to the siliranes, with formation of a

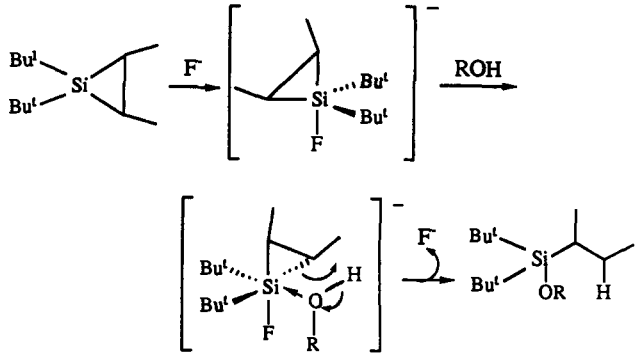
Scheme 77



Scheme 78



Scheme 79



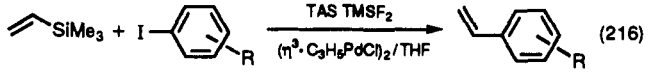
pentacoordinate species, followed by attack of the alcohol at silicon giving a hexacoordinate silicon intermediate (Scheme 79).

E. Palladium-Catalyzed Cross-Coupling Reactions of Organosilicon Compounds with Aryl and Vinyl Halides and Triflates in the Presence of Fluoride Ion

Hiyama and Hatanaka[393] found that organosilicon compounds react with aryl or alkenyl halides (or triflates) when activated by a stoichiometric amount of fluoride ion in the presence of a palladium catalyst.

1. Cross-Coupling Reactions of Vinylsilanes

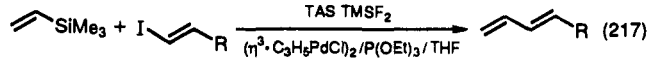
Trimethylvinylsilanes in the presence of TAS $TMSF_2$ and $(\eta^3\text{-}C_3H_5PdCl)_2$ couple the vinyl group with aryl iodides[394] (eq 216). HMPA is a satisfactory solvent.



(216)

R = *p*-Me (89%); R = *p*-NO_2 (83%); R = *p*-NH_2 (85%); R = *p*-$COCH_3$ (86%)

With vinyl iodides, $P(OEt)_3$ in THF is required to accelerate the reaction and improve the yield of the coupled products (eq 217). The reaction proceeds

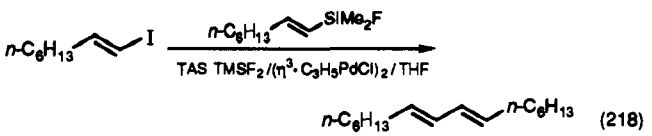


(217)

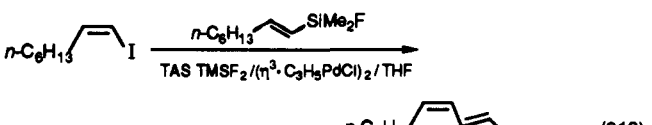
R = *n*-C_6H_{13} (100%); R = $(CH_2)_8CO_2CH_3$ (88%); R = $(CH_2)_8COCH_3$ (67%); R = $(CH_2)_8CHO$ (52%)

stereo- and chemoselectively in all cases. Introduction of one or two fluorine atoms onto the silyl group of vinylsilanes greatly accelerates the coupling reaction with alkenyl iodides.[395] Surprisingly, the effect is most marked on substitution of a single methyl group by fluorine, the SiF_3 group completely inhibiting the reaction. The reaction proceeds with retention of configuration for both the starting vinylsilane and the

iodoalkene, providing a general and highly stereospecific route to 1,3-dienes (eqs 218 and 219). It is worth noting

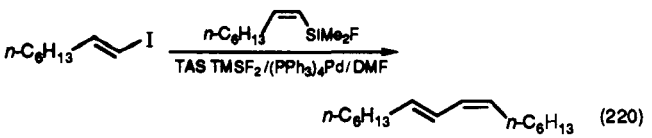


(218)



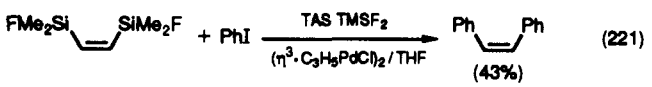
(219)

that a *Z* and *E* isomerization was observed in the coupling reaction between (*Z*)-1-(dimethylfluorosilyl)-1-decene with (*E*)-1-iodo-1-octene in THF and with $(\eta^3\text{-}C_3H_5PdCl)_2$ as catalyst. This isomerization can be avoided by using $(PPh_3)_4Pd$ as catalyst in DMF as solvent[395] (eq 220). Coupling at both ends of the double



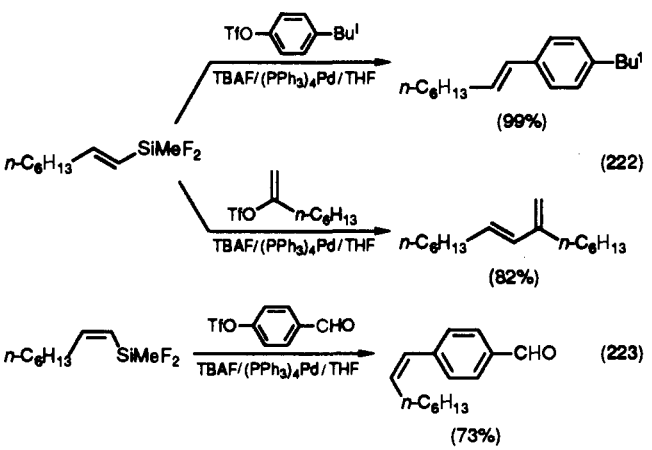
(220)

bond can be achieved in one step, starting from bis(dimethylfluorosilyl)ethene[395] (eq 221). Selective re-



(221)

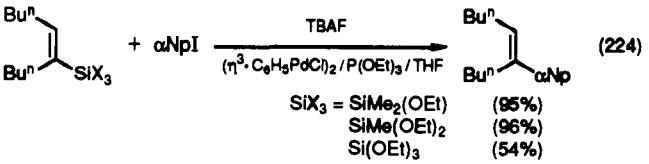
action of the FMe_2Si group in the bis(silyl)ethene **250** allows the preparation of substituted vinyltrimethylsilanes[395] (Scheme 80). Mono-, di-, and even trifluorovinylsilanes couple with aromatic and vinyl triflates with high stereospecificity and chemoselectivity. The reaction takes place in the presence of TBAF (but not in the presence of KF or TAS $TMSF_2$) as fluoride ion source, with $(PPh_3)_4Pd$ as catalyst[396] (eqs 222 and 223).



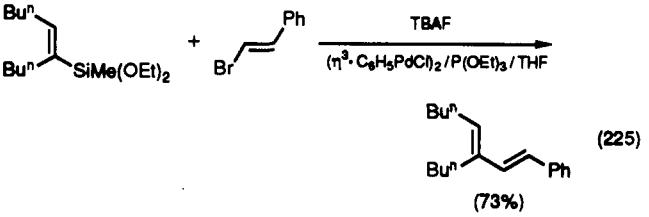
(222)

(223)

This reaction is not limited to vinylfluorosilanes. Indeed vinyl mono-, di-, and to a lesser degree trialkoxysilanes also couple with aromatic iodides and vinyl bromides[397] (eqs 224 and 225).



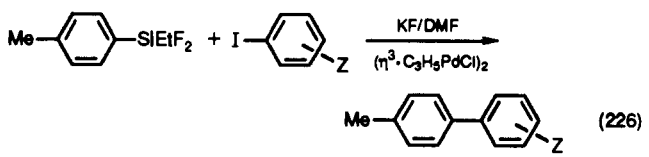
(224)



(225)

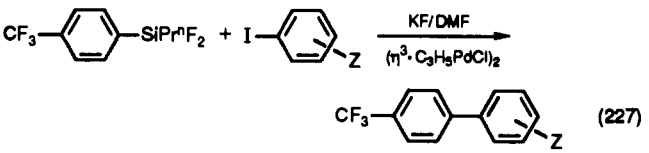
2. Cross-Coupling Reactions of Arylsilanes

Cross-coupling reactions occur between arylmonofluoro or difluoro (but not trifluoro) silanes and aryl iodides in the presence of a catalytic amount of $(\eta^3\text{-}C_3H_5PdCl)_2$ and 2 equiv of KF in DMF.[398] The reaction proceeds also with TBAF but not with TAS $TMSF_2$ (eqs 226 and 227). This reaction is highly chemose-



(226)

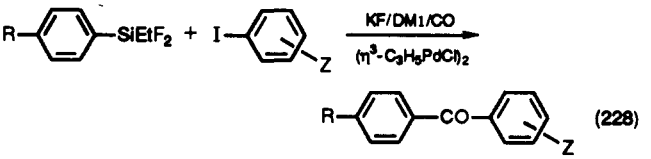
Z = *o*-MeO (45%); Z = *m*-MeO (83%); Z = *m*-CH_2OH (86%); Z = *p*-CN (67%)



(227)

Z = *m*-MeO (52%); Z = *m*-CH_2OH (67%); Z = *p*-OAc (47%)

lective since it takes place in the presence of a variety of reactive functional groups including ester, ketone, aldehyde, cyano, and even hydroxyl groups. With aryldifluoromethylsilanes, transfer of the methyl group is observed.[398] When the reaction is conducted under 1 atm of CO in *N*,*N*-dimethyl-2-imidazolidinone (DMI), diaryl ketones are obtained[399] (eq 228). This reaction is quite general.



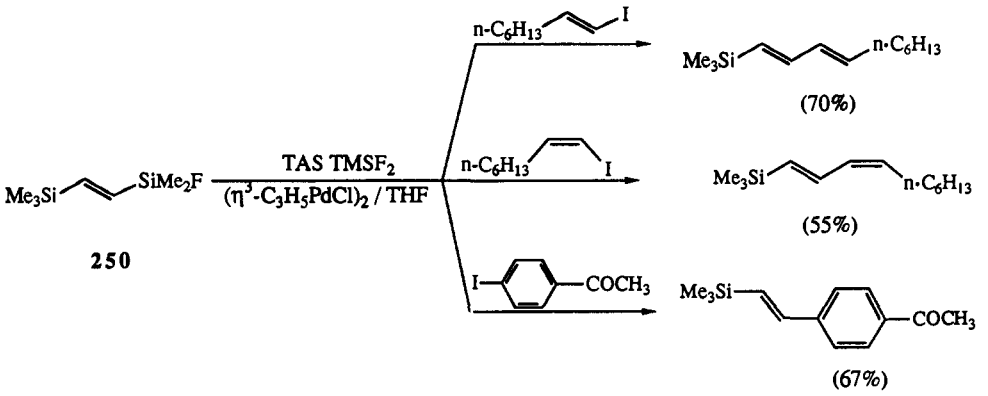
(228)

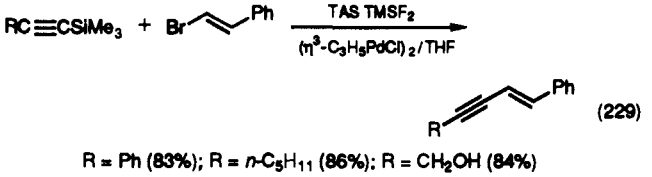
R = H: Z = *p*-CN (60%), Z = *p*-CO_2Me (61%)
R = Me: Z = *p*-COMe (91%), Z = *p*-OEt (69%)

3. Cross-Coupling Reactions of Alkynylsilanes

Alkynyltrimethylsilanes react with vinyl bromides to give 1,3-enynes[394] (eq 229). The reaction proceeds with retention of the double-bond geometry of the vinyl halide. Stereodefined 1,5-dien-3-ynes have been obtained[400] by the palladium-catalyzed cross-coupling reaction of $Me_3SnC{\equiv}CSiMe_3$ with successively an

Scheme 80



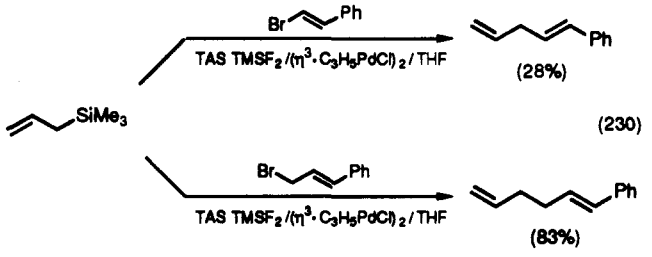


R = Ph (83%); R = n-C_5H_{11} (86%); R = CH_2OH (84%)

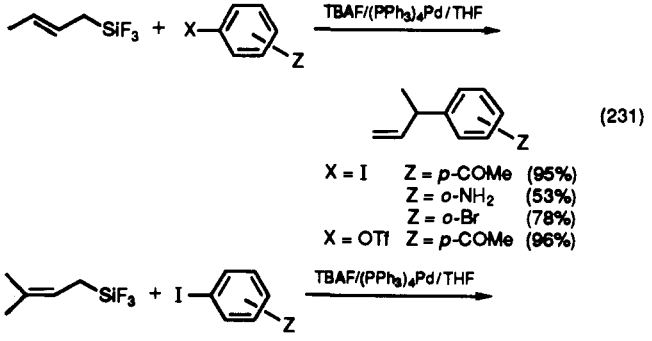
alkenyl iodide, and then another alkenyl iodide (or aryl iodide), in the presence of newly added TAS $TMSF_2$. This "one-pot" reaction takes advantage of the difference in reactivity of the C–Sn bond over the C–Si bond. The general process is illustrated in the Scheme 81.

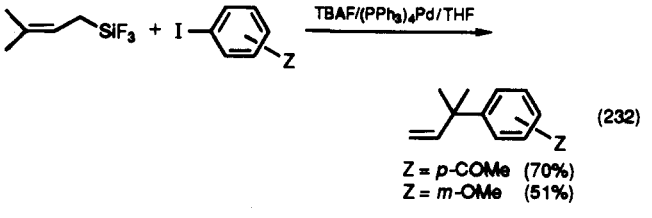
4. Cross-Coupling Reactions of Allylsilanes

Palladium-catalyzed cross-coupling reactions of allyltrimethylsilanes with vinyl and allyl bromides take place in the presence of TAS $TMSF_2$[394] (eq 230).



Allyltrifluorosilanes when activated by a stoichiometric amount of fluoride ion in the presence of a palladium catalyst undergo cross-coupling reactions with various electrophiles to give allyl compounds resulting exclusively from attack at the γ-carbon[401] (eqs 231 and 232).

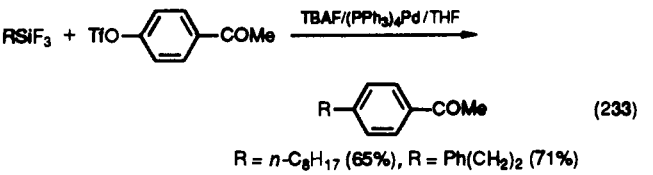




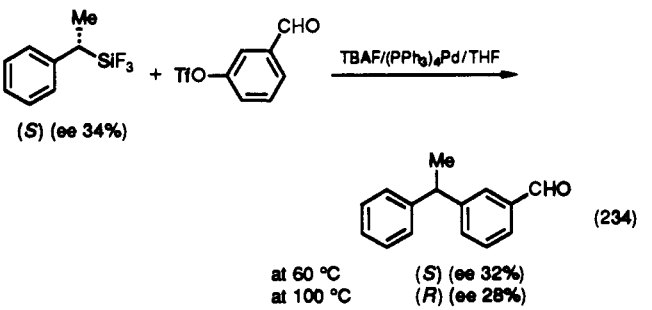
Z = p-COMe (70%)
Z = m-OMe (51%)

5. Cross-Coupling Reactions of Alkyltrifluorosilanes

Even alkyltrifluorosilanes couple with aromatic triflates[396] in the presence of TBAF and $(PPh_3)_4Pd$ (eq 233). The stereochemistry is a function of the temperature of the reaction[402] as shown in eq 234.



R = n-C_8H_{17} (65%), R = $Ph(CH_2)_2$ (71%)



F. Activation of the Si–Si Bond

It was found that disilanes in the presence of a catalytic amount of TBAF in HMPA react with aldehydes to give silylated alcohols and triorganylsilyl

$$\mathrm{RCHO + Me_3SiSiMe_3} \xrightarrow[\text{HMPA}]{\text{TBAF (5 mol \%)}} \mathrm{RCH(OSiMe_3)SiMe_3} \xrightarrow{H_3O^+} \mathrm{RCHOHSiMe_3} \quad (235)$$

R = n-$C_{10}H_{21}$ (67%)

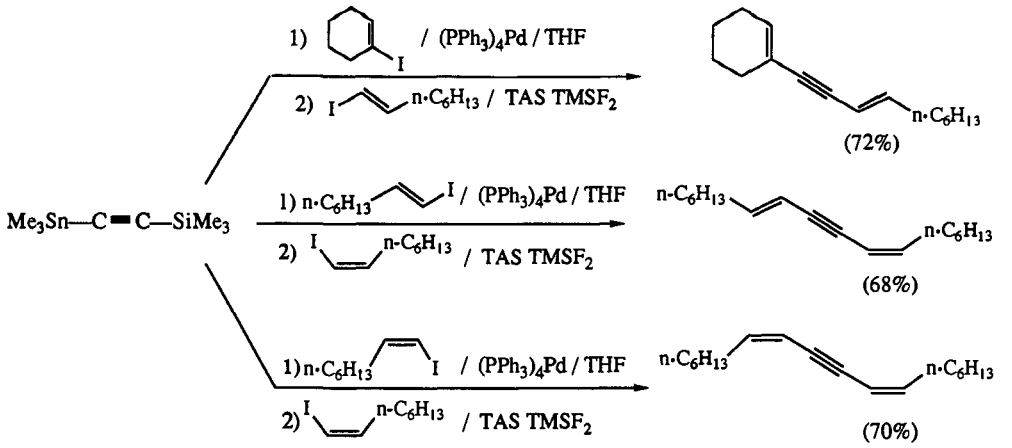
fluorides[403] (eq 235). It is worth noting that with an unsymmetrical disilane, fluoride ion cleaves selectively the disilane to give the more electronically favored silyl

$$\mathrm{RCHO + Me_3SiSiPh_3} \xrightarrow[(2)\ H_3O^+]{(1)\ \text{TBAF/HMPA}} \mathrm{RCHOHSiPh_3} \quad (236)$$

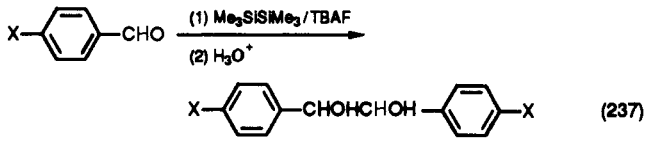
R = n-$C_{10}H_{21}$ (64%); R = n-C_3H_7 (60%); R = i-C_3H_7 (61%)

anion equivalent[403] (eq 236). Aromatic aldehydes react with hexamethyldisilane in the presence of a catalytic

Scheme 81

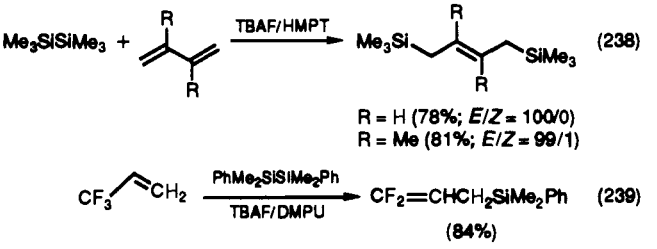


amount of TBAF to give 1,2-diarylethanediols after hydrolytic workup (eq 237). Cesium fluoride is also



X = H (94%); X = *p*-MeO (87%); X = *p*-Me_2N (61%)

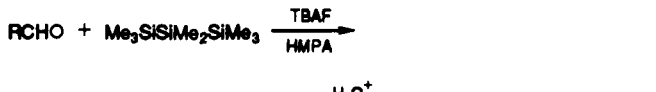
effective as a catalyst but not potassium fluoride.[403] The disilane/TBAF system also reacts with 1,3-dienes to give 1,4-disilyl-2-butenes (eq 238)[403] and with 3,3,3-trifluoropropene to afford (γ,γ-difluoroallyl)silanes[404] (eq 239).

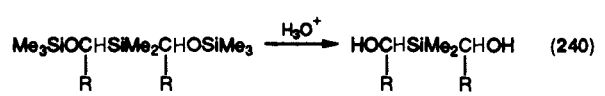


R = H (78%; *E*/*Z* = 100/0)
R = Me (81%; *E*/*Z* = 99/1)

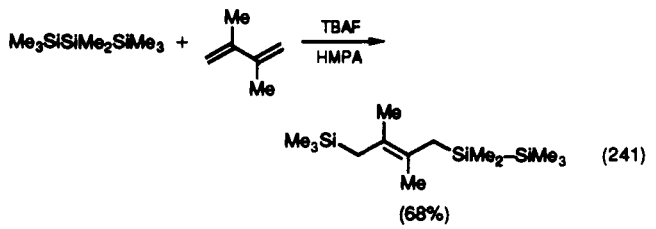
(84%)

Insertion of alkanals (eq 240) and 1,3-dienes (eq 241) into the Si–Si bond of trisilanes has also been observed under the same conditions.[405]



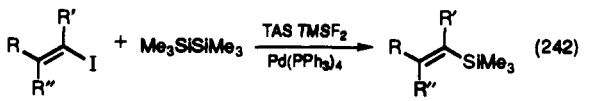


R = *n*-C_5H_{11} (66%); R = *n*-$C_{10}H_{21}$ (63%)



(68%)

$Me_3SiSiMe_3$ in the presence of fluoride ion and a catalytic amount of $Pd(PPh_3)_4$ react with vinyl halides to give the corresponding vinylsilanes in good yield (eq 242).[406] TAS $TMSF_2$ was found to be the most efficient catalyst, but a small excess of fluoride ion is required.



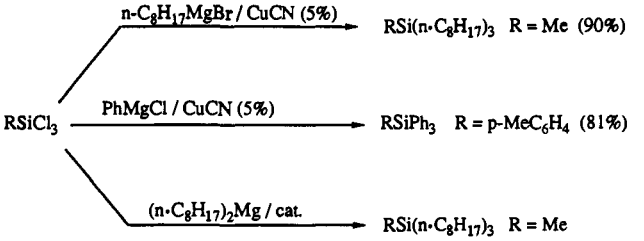
R = Ph, R′ = R″ = H (82%); R = R′ = H, R″ = Ph (84%);
R = *n*-C_6H_{13}, R′ = R″ = H (74%); R = R′ = H, R″ = *n*-C_6H_{13} (62%)

The reaction proceeds stereospecifically with retention of the C=C bond geometry. Moreover the reaction can be carried out without protection of a wide variety of functional groups, including ester and nitrile. The mechanism has not yet been elucidated, nevertheless it is likely that a pentacoordinate silicon species is involved.

G. Activation of the Si–Cl Bond

Catalytic quantities of cyanide or thiocyanate ion have been shown to facilitate the substitution of silyl chlorides by Grignard reagents and dialkylmagnesium reagents to afford high yields of tetraalkyl and tetraarylsilanes under extremely mild conditions[407] (Scheme 82).

Scheme 82



cat. = AgCN (80%) ; $Hg(CN)_2$ (97%) ; BrCN (94%)
Me_3SiCN (95%) ; CuCN (96%)

IX. Conclusion

Nucleophilic activation at silicon was first extensively used for synthetic purposes to cleave Si–O, Si–H, and Si–C bonds. The key to the rationalization of this catalytic process was provided by kinetic data obtained in studies of the racemization and hydrolysis (or alcoholysis) of chlorosilanes. The mechanism proposed[180,181] to explain these data postulates the coordination of the nucleophilic reagent to silicon with formation of a pentacoordinate silicon intermediate in a first step, followed by attack of a second molecule of nucleophile on the pentacoordinate species in the rate-determining step (Scheme 12). This mechanism carries

the implication that the pentacoordinate intermediate, even when anionic, reacts with nucleophiles faster than the starting tetracoordinate silane (Scheme 12). A similar mechanism has been proposed to explain some reactions in phosphorus chemistry such as alcoholysis of fluorophosphates,[408] chlorophosphates, and chlorophosphonates,[409] racemization and hydrolysis of chlorophosphonates,[410] as well as for the racemization of chlorogermanes.[411] This mechanism can also be expected to apply to other elements able to extend their coordination numbers.

In order to confirm these mechanistic implications, the synthesis of pentacoordinate silicon species was undertaken and their reactivity studied. It has been amply shown in this review that pentacoordinate silicon compounds are more reactive than tetracoordinate ones and exhibit their own pattern of reactivity. These studies have not only proved valuable from a fundamental point of view, but have led to unexpected applications in organic synthesis and even in polymer chemistry.

The reactivity of hexacoordinate silicon compounds has also been found to be quite varied and difficult to predict. Future research could well be aimed at improving understanding of the reactions of hexacoordinate compounds, since at present the mechanisms of nucleophilic substitution reactions at hexacoordinate silicon compounds are not well established. It is not clear if such reactions occur through a heptacoordinate intermediate (or transition state), or whether other modes of reaction, such as electron transfer, are common. It will be interesting to devise new structures, perhaps with different coordinating atoms, which might allow high coordination numbers and new geometries. In addition, since enhanced coordination numbers are also a prominent feature of the chemistry of phosphorus, the study of hypervalent phosphorus compounds is certainly another large field meriting further exploration.

The stabilization by intramolecular coordination of compounds containing a silicon atom which is formally unsaturated or in a low valence state is a most interesting development. The isolation of stable silanethiones, silanimines, and silanephosphimines and compounds containing silicon–transition metal multiple bonds, together with the probable formation by similar routes of silanones as reactive intermediates point to a rich new field of investigation. Other compound types which might perhaps be stabilized in this way include silylenes and silenes. Finally, the growing number of silicocations containing donor ligands now known holds out the hope of a better understanding of their chemistry.

Abbreviations

BTAF	benzyltrimethylammonium fluoride
Bz	benzoyl
DMI	*N,N*-dimethyl-2-imidazolidinone
DMAP	(dimethylamino)pyridine
EE	1-ethoxyethyl
HMPA	hexamethylphosphoric acid triamide
Im	imidazole
MCPBA	*m*-chloroperbenzoic acid
NmI	*N*-methylimidazole
NMP	*N*-methylpyrrolidone
PMHS	polymethylhydrosiloxane [$Me_3SiO(HSiMeO)_nSiMe_3$]
PPMA	poly(methyl methacrylate)
PPN	bis(triphenylphosphoranylidene)ammonium
PZ^+F^-	phosphazenium fluoride
TAS $TMSF_2$	Tris(dimethylamido)sulfonium difluorotrimethylsilicate [$(Et_2N)_3S^+Me_3SiF_2^-$]
TBAF	tetrabutylammonium fluoride
TfO	trifluoromethanesulfonate
THP	tetrahydropyran-2-yl

X. References

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