

SOME STUDIES IN
ORGANOSILICON CHEMISTRY

by

J. O'BRIEN

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October, 1968.

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Since October 1965, the Author has been engaged in research in the Department of Chemistry at the University of Manchester Institute of Science and Technology, under the supervision of Professor R. N. Haszeldine, Dr. M. J. Newlands and, since October 1967, Dr. K. A. Hooton.

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"There is a tide in the affairs of men,
Which, taken at the flood, leads on to fortune;
Omitted, all the voyage of their life
Is bound in shallows and in miseries.
On such a full sea are we now afloat;
And we must take the current as it serves,
Or lose our ventures".

W. Shakespeare
(Julius Caesar, Act IV, Sc. iii).

SUMMARY

Although silane-amine complexes have been known for some time, a recent report has shown that the introduction of a fluorinated alkyl chain into the silane is sufficient to give isolable complexes. The 1:1 trimethylamine and 1:2 β -picoline complexes of 1,1,2,2-tetrafluoroethylsilane ($\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$) are remarkable in that they are liquid at room temperature. This study was directed towards examining the effect on complex stability of the position and degree of fluorine substitution in the ethyl group of ethylsilanes.

Complex formation between the fluoroalkylsilanes and tertiary amines was investigated by a tensiometric method; vapour pressure - molar composition isotherms indicated the stoichiometries of the complexes. Thermodynamic data were obtained for the isolable complexes from vapour pressure-temperature measurements, and used as a measure of complex stability.

Attempts were made to explain the stability of the complexes in terms of polar and steric factors.

Nuclear magnetic resonance and infrared spectroscopy provided some confirmatory evidence of complex formation for the liquid complexes.

The reaction of 2,2-difluoroethyltrifluorosilane ($\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2$) was of particular interest, as reaction with tertiary amines caused decomposition of the silane, producing vinyl fluoride. Reaction mechanisms have been proposed to account for the unusual reaction products.

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1.1. Complexes of Compounds of the Group IVb Elements

The elements of Group IVb - carbon, silicon, germanium, tin and lead - have a ground state, outer electronic configuration of $ns^2.np^2$. The group valency of four is reached by promotion of an s-electron to the empty p-orbital and hybridisation to give four degenerate sp^3 hybrid orbitals. All the elements form compounds derived from the valence state of four. But although silicon and the heavier elements of Group IVb have the same outer electronic configuration as carbon, little of the chemistry of silicon can be inferred from that of carbon.

The group valency of four is the maximum that carbon can attain, as Werner pointed out. However, silicon and the other elements of Group IVb have empty d-orbitals which are of sufficiently low energy for them to participate in bond formation and for six co-ordinate octahedral species, sp^3d^2 hybridisation can be postulated. It has been suggested that many reactions of Group IVb compounds occur by mechanisms in which the co-ordination shell of the central atom is expanded from four to five or six by the use of one or two d-orbitals. These elements might, therefore, be expected to act as 'vacant orbital' acceptors to form acceptor-donor complexes of the Lewis acid-base type with strong electron donors.

Any discussion of the complexes formed would not be complete without considering the factors which are important in complex formation and the theories which have been developed in an attempt to explain the observed experimental results.

1.2. Theories of Complex Formation

The phenomenon of complex formation has played an interesting and important role in the development of chemistry and for many years the theoretical interpretation has been somewhat of a challenge to chemists.

In 1923, Lewis advanced a new concept on complex formation derived from the electronic theory of valence, which showed the similarity of an acceptor-donor relationship to that of a generalised acid-base relationship. He defined an acid as a

substance that can accept a pair of electrons from a donor substance; the base. It was this acceptor-donor principle that has prompted (1) the use of the terms Lewis acid and base.

During the following two decades the development and study of Lewis acids and bases was primarily of a quantitative nature, which kept in step with the theories of inductive and steric effects that were prevalent at the time. With the increase in available experimental data, it is perhaps surprising that so few serious attempts were made either to use the results obtained to formulate new theories, or even to compare the results qualitatively. Of those that were made, the most notable were by Sidgwick (2) in 1941 and by Ahrland, Chatt and Davies (3) in 1958; but even these were more of a general classification of the available data rather than true interpretations.

Ahrland, Chatt and Davies (3) recognised that metals and metal ions could be divided into two categories. Those metal ions which interacted most effectively with donor atoms of first row elements rather than donor atoms of succeeding rows were termed class 'a' acids, while those metals that interacted more effectively with the highly polarisable second, third, etc., row donor atoms were termed class 'b' acids. Acids whose electron clouds are easily distorted (2nd and 3rd row transition metal ions) interact most strongly with polarisable bases, while acids that are not readily polarised (1st row transition metal ions) interact most strongly with polar bases.

While this classification by Ahrland and co-workers was the first attempt to systematise the information on acceptor-donor adducts, unfortunately it can only be regarded as an empirical approach. This is because the criteria used for stability were not thermodynamic (free energy or enthalpy) and thus any inferences made could be subject to criticism.

In more recent years, however, there has been a growing awareness in chemistry that the problems involved in the Lewis acid-base reaction have yet to be answered. More specifically, there is a great need for a more quantitative means of comparing the stability of Lewis acid-base complexes and to find a scale for the strengths of these acids and bases. The current interests of such workers as Pearson and Drago are directed towards these ends.

Pearson (4) has recently extended the concepts of Ahrlund, Chatt and Davies to a wide range of acids and bases, and classified them according to their bonding characteristics. Acids and bases which are most readily polarised and form predominantly covalent bonds display class 'b' behaviour, or, to use Pearson's nomenclature, are 'soft' acids and bases. Acids and bases that are non-polarisable and are most effective in electrostatic bonding, display class 'a' behaviour and are referred to as 'hard' acids and bases. This classification has arisen from the observation that combination of 'like' acids and bases gives the most effective combination. Pearson recognised that because every acid and base has both 'hard' and 'soft' characteristics (i.e. both electrostatic and covalent character), division into these two categories is not absolute and intermediate cases occur. The examples of hard and soft acids and bases given in Table 1.1. demonstrate the connection between polarisability and the hard-soft character of a species.

TABLE 1.1.

	<u>Hard</u>	<u>Borderline</u>	<u>Soft</u>
Acids	H^+ , Li^+ , Na^+ , Be^{2+} , Al^{3+} , Ti^{4+} , $(Me_2Sn)^{2+}$, BF_3 , BCl_3 , $Al(Me)_3$	BMe_3 , NO^+ , Pb^{2+}	$MeHg^+$, I_2 , Br_2 , M^0 (Metal atoms), Cu^+ , Ag^+ , Hg^+
Bases	H_2O , OH^- , F^- , ROH , R_2O , NH_3 , RNH_2 , N_2H_4	$PhNH_2$, C_5H_5N , N_3^- , Cl^-	R_2S , RSH , R_3P , I^- , Br^- , CN^- , H^- , R^-

Polarisability is simply a convenient property to use in a classification. It may well be that other properties which are roughly proportional to polarisability are more responsible for the typical behaviour of the two classes of acids and bases.

For example, a low ionisation potential is usually linked with a large polarisability and a high ionisation potential to a low polarisability. Hence ionisation potential, or the related electronegativity, might be the important property. Unsaturation, with the possibility of acceptor π - bonding in the acid-base complex, and ease of reduction, favouring strong electron transfer to the acid, are also associated with high polarisability.

Edwards (5) has developed a fairly successful equation for predicting nucleophilic reactivity using proton basicity and oxidation-reduction potential as the two parameters on which reactivity depends. Later it was shown that a polarisability term could take the place of the oxidation-reduction term with about equal success (6).

The presence of both electrostatic and covalent character has prompted Hudson and Klopman (7) to consider the reactivity of a molecule toward a particular atom on a second molecule by attempting to estimate the perturbation produced by the interaction of the bonding orbitals. A simple perturbation treatment yields an equation for the interaction energy in which two main effects predominate,

- (i) an ionic effect due to Coulombic interaction,
- and (ii) a covalent interaction due to the formation of a bond.

The relative importance of these terms depends on the energy difference (ΔE) between the interacting orbitals. When $\Delta E \gg 0$, then the covalent interaction tends to zero and the Coulombic term determines the interaction, which should therefore take place between polar centres. But as ΔE decreases, the covalent term increases and as $\Delta E \rightarrow 0$, the interaction of the highest occupied orbital of the donor with the lowest unoccupied orbital on the acceptor becomes predominant. This state of affairs is analogous to Pearson's concept and both predict the same results. When $\Delta E \gg 0$ (i.e. the acceptor has a low electron affinity and the donor a high ionisation potential), the interaction is equivalent to a hard acid - hard base interaction.

But a large perturbation, produced by reagents of high polarisability, leads to extensive covalent interaction and is, therefore, equivalent to a soft acid - soft base interaction.

The most serious shortcomings of these ideas are their qualitative nature. It would be significant if the magnitude of the interactions between acids and bases could be put on a quantitative basis, even if the relationships were empirical in nature.

Drago and Wayland have correlated the magnitude of acceptor-donor interactions with the electronic properties of the acids and bases. From the earlier qualitative interpretations of these interactions, they proposed (8) a double scale enthalpy equation;

$$-\Delta H = E_a E_b + C_a C_b$$

where E_a and E_b are the susceptibilities of the acid and base to undergo electrostatic interaction, and C_a and C_b are the susceptibilities of the acid and base to form a covalent bond.

By selecting a reference acid and choosing to assign arbitrary values to E_a and C_a for this acid, Drago and Wayland were able to extend this approach to a large number of systems, and to evaluate the E and C parameters for some acceptors and donors. But, again, although the parameters assigned and obtained agree with qualitative chemical intuition regarding acid-base interactions and also with semi-quantitative estimates regarding the degree of covalency, there is still a degree of chemical intuition in this approach.

It can be seen from this equation, that acids having large values for E_a interact strongly with bases having large E_b values; and conversely, acids with large C_a values interact strongly with bases having large C_b values. This would appear again to augment the ideas behind Peasons's hard and soft acid and base concept (4). Indeed the basis of this model was used some years previously by Mulliken to describe the bonding in addition compounds.

Mulliken (9) has developed a theory of covalent bonding suitable for discussing soft acids and bases. He postulated

that for the reaction,



to occur, the wave function (ψ_n) of the complex could be represented by the equation,

$$\psi_n = a \psi_0 + b \psi_1 + \dots$$

where ψ_0 is the no-bond wave function for the complex AB and ψ_1 is the dative bond wave function for ($A^- - B^+$); a and b are constants.

The nature of the acceptor-donor interaction is governed primarily by the two constants. When $a^2 \gg b^2$, the contribution from the no-bond wave function is predominant and corresponds to the formation of weak molecular complexes. For the formation of a Lewis acid-base complex, the condition $b^2 \gg a^2$ must apply, and so the strength of the interaction is governed largely by the characteristics of the dative bond. It can be seen that by considering the most favourable conditions for the dative bond wave function, viz. ($A^- - B^+$), Mulliken's conclusions are the same as those deduced by Hudson and Klopman with their perturbation treatment (7).

In conclusion, one might say that the factors leading to strong complex formation, (i.e. $b^2 \gg a^2$) are a high electron affinity of the acceptor and a low ionisation potential of the donor (10). Close approach of the centres of gravity of the resultant charges on A^- and B^+ , also lowers the energy of ψ_1 , both through an increased Coulombic interaction and strong covalent bonding.

1.3. The Acceptor Strength of Lewis Acids

It is difficult to obtain a quantitative physical measure of the acceptor strength of a molecule without reference to specific ligands. Although a high electron affinity is a prime requirement for high acceptor strength, it is difficult to measure for all but the simplest molecules. For the Group IVb

elements, it might appear that the values of the 4th ionisation potential (equivalent to the electron affinity of the quadripositive metal ion) might give some indication as to the order of acceptor strengths. But instead of a progressive trend in the values, Table 1.2. shows there is surprisingly little difference

Table 1.2.

<u>Element</u>	<u>4th I.P.(eVs)</u>
Si	45.1
Ge	45.5
Sn	39.4
Pb	42.1

between silicon and germanium. This can be attributed to the interpolation between the two elements of the first transition series which gives rise to the scandinide contraction and a less effective shielding of the germanium nucleus.

The atomic radii of the Group IVb atoms, in Table 1.3., increase from Si to Pb, and so the steric requirements of the donor will be accommodated more readily by Sn and Pb than by Si and Ge.

Table 1.3.

<u>Element</u>	<u>Covalent radius (Å)</u>
C	0.77
Si	1.17
Ge	1.22
Sn	1.40
Pb	1.46

A comparison of the dissociation vapour pressures and heats of

formation for the trimethylamine complexes of silicon, germanium and tin tetrachlorides (11), in Table 1.4., gives some confirmation of this. Pyridine forms 1 : 2 octahedral complexes

Table 1.4.

<u>Complex</u>	<u>Dissociation vapour pressure</u>	<u>ΔH</u>
$\text{Me}_3\text{N} \cdot \text{SiCl}_4$	3.9mm./-56.2°	24.0 kcal.mole ⁻¹
$\text{Me}_3\text{N} \cdot \text{GeCl}_4$	6.4mm./ 0°	27.4 kcal.mole ⁻¹
$\text{Me}_3\text{N} \cdot \text{SnCl}_4$	negligibly small/0°	-

with silicon and germanium tetrachloride and tetrabromide. The considerable differences between the heats of formation, Table 1.5., of analogous Si and Ge complexes has been ascribed to

Table 1.5.

<u>Complex</u>	<u>ΔH</u>
$\text{SiCl}_4 \cdot 2\text{py}$	51.67 kcal.mole ⁻¹
$\text{GeCl}_4 \cdot 2\text{py}$	41.44 kcal.mole ⁻¹
$\text{SiBr}_4 \cdot 2\text{py}$	46.05 kcal.mole ⁻¹
$\text{GeBr}_4 \cdot 2\text{py}$	33.79 kcal.mole ⁻¹

differences in stereochemistry (12). The silicon halide complexes are cis and the germanium halide complexes trans. The cis isomers have non-zero dipole moments, leading to increased lattice energies and greater observed heats of formation.

Apart from the influence of the metal atom on the Lewis acidity of an acceptor, the substituent groups can radically affect the Lewis acidity of a given metal. The majority of studies carried out in order to observe the effect of substituent groups have been limited to the halogenosilanes:

The heats of formation of silicon and germanium tetrahalide complexes with isoquinoline (12) indicate in Table 1.6., an acceptor sequence,

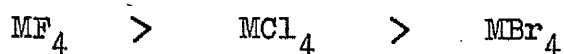


Table 1.6.

<u>Complex</u>	<u>ΔH</u> <u>kcal. mole⁻¹</u>	<u>Complex</u>	<u>ΔH</u> <u>kcal. mole⁻¹</u>
SiF ₄ . 2iq	27.80	GeF ₄ . 2iq	35.70
SiCl ₄ . 2iq	17.36	GeCl ₄ . 2iq	22.29
SiBr ₄ . 2iq	12.79	GeBr ₄ . 2iq	18.01

Such a trend can be satisfactorily explained by the effects of atomic size and steric hindrance of the halogen atom; inductive arguments and bond polarity support these results in that the more electronegative fluorine, by removing electron density from the metal atom, results in an increase in Lewis acidity. Campbell-Ferguson and Ebsworth (13) have however pointed out that straight forward comparisons of fluoro- and chlorosilane adducts with bromo- and iodosilane adducts are not likely to yield meaningful results because the former are usually covalent and the latter are likely to be ionic.

The separate effects of steric hindrance and bond polarity are illustrated upon replacing the halogen atoms with hydrogen atoms. A study of complexes formed by trimethylamine with the silanes H_nSiCl_{4-n} (n=0, 1, 2, 3,) (14), shows an increase in stability on passing from SiCl₄ to H₃SiCl (Table 1.7.).

Table 1.7.

<u>Complex</u>	<u>Temperature of Zero Dissociation</u>
$\text{SiCl}_4 \cdot \text{NMe}_3$	$\sim -78^\circ$
$\text{HSiCl}_3 \cdot \text{NMe}_3$	$\sim -70^\circ$ to $\sim -30^\circ$
$\text{H}_2\text{SiCl}_2 \cdot \text{NMe}_3$	$\sim -20^\circ$
$\text{H}_3\text{SiCl} \cdot \text{NMe}_3$	$\sim -0^\circ$
$\text{SiH}_4 \cdot \text{NMe}_3$	not formed

Thus a predominant steric influence explains the increasing stability upon replacing chlorine with hydrogen. However the inability of silane to complex does show that one electronegative substituent is necessary for silicon to assume the role of a Lewis acid.

By substituting hydrogen for fluorine, and so minimising any changes in steric effects, the significance of bond polarity has been demonstrated (14). A comparison of heats of formation and dissociation vapour pressures in Table 1.8., indicates that the loss of the more electronegative fluorine results in

Table 1.8.

<u>Complex</u>	<u>Dissociation Vapour Pressure</u>	<u>ΔH</u>
$\text{SiF}_4 \cdot \text{NMe}_3$	6.5mm./ 0°	$-27.4 \text{ kcal.mole}^{-1}$
$\text{HSiF}_3 \cdot \text{NMe}_3$	24mm./ 0°	$-25.1 \text{ kcal.mole}^{-1}$
$\text{MeSiF}_3 \cdot \text{NMe}_3$	11.7mm./ -70.5°	$-21.2 \text{ kcal.mole}^{-1}$

reduced stability. The sensitivity of the acceptor atom to substituent effects is also demonstrated by the reduction in Lewis acidity on substitution of methyl groups. For the trimethylamine adducts of HSiF_3 and MeSiF_3 the reduction of the heat of formation can best be explained by a steric effect. However, the pyridine adduct of methyltrichlorosilane is less

stable than that of SiCl_4 (15) and as the steric requirements of the Cl^- and CH_3 groups are similar this change is most readily ascribed to inductive effects. The group electronegativities of CH_3 (0.00) compared to hydrogen (0.49) (16) confirm that the presence of a methyl group will lower the Lewis acidity of an acceptor.

A more recent study (17) similarly concludes that the introduction of methyl groups in place of hydrogen or halogen weakens the acceptor power of silicon. Me_3SiI and Me_2SiI_2 give only 1:1 adducts with pyridine in contrast to the 1:2 adduct of H_3SiI and the 1:4 adduct of H_2SiI_2 . The low stability of the methylated silane adducts was said to be due to steric hindrance at silicon - though a decrease in the lattice energy of the adduct may possibly occur on methylation. A further explanation has been postulated, in that the introduction of organic groups leads to compounds which are susceptible to molecular association; e.g. Me_3SiCl has been reported (18) as a dimer in cyclohexane. For complexation to occur, an expenditure of energy would be required to dissociate the associated molecules.

Similar considerations apply to the other Group IVb elements, although the steric effect of substituent groups bonded to larger acceptor atoms are less important. There is still evidence however, of an inductive effect of the ligands, and a decrease in stability of methylchlorotin adducts with pyridine has been observed (19),



In many cases, steric factors and inductive arguments complement one another. Atomic size and bond polarity operate in the same sense in the trimethylamine adducts of a series of chlorofluorosilanes (Table 1.9.) although the former is probably the more important since the polarity of the silicon-fluorine bond is probably reduced by π -bonding (21).

Table 1.9.

<u>Complex</u>	<u>Dissociation Vapour Pressure</u>	<u>Reference</u>
$\text{SiF}_4 \cdot \text{NMe}_3$	6.5mm. /0°	20
$\text{ClSiF}_3 \cdot \text{NMe}_3$	23mm. /0°	11
$\text{Cl}_2\text{SiF}_2 \cdot \text{NMe}_3$	40-70mm./0°	11
$\text{Cl}_3\text{SiF} \cdot \text{NMe}_3$	260mm. /0°	11
$\text{SiCl}_4 \cdot \text{NMe}_3$	3.87mm./-56.2°	14

Since the involvement of d-orbitals of the Group IVb metals is invoked during complex formation, the availability of these d-orbitals will be an important factor in the 'ease' of complex formation. The presence of electronegative groups withdraws electron density from the metal atom, shrinking the d-orbitals and so makes the metal atom a better acceptor. For the smaller Group IVb elements, i.e. silicon, there is also the possibility of π -bond formation between the silicon and a substituent group. With the halogen atoms, the formation of a partial $p_\pi - d_\pi$ bond would increase the electron density on silicon and reduce its Lewis acidity. Dipole moment studies have sometimes been used to show that back-donation occurs in silicon-halogen compounds. The low dipole moments of the halosilanes (22), compared to their carbon analogues (Table 1.10.), may arise from $p_\pi - d_\pi$ bonding, although the interpretation of dipole moments of molecules in terms of molecular structure is always a somewhat uncertain process. The decrease in

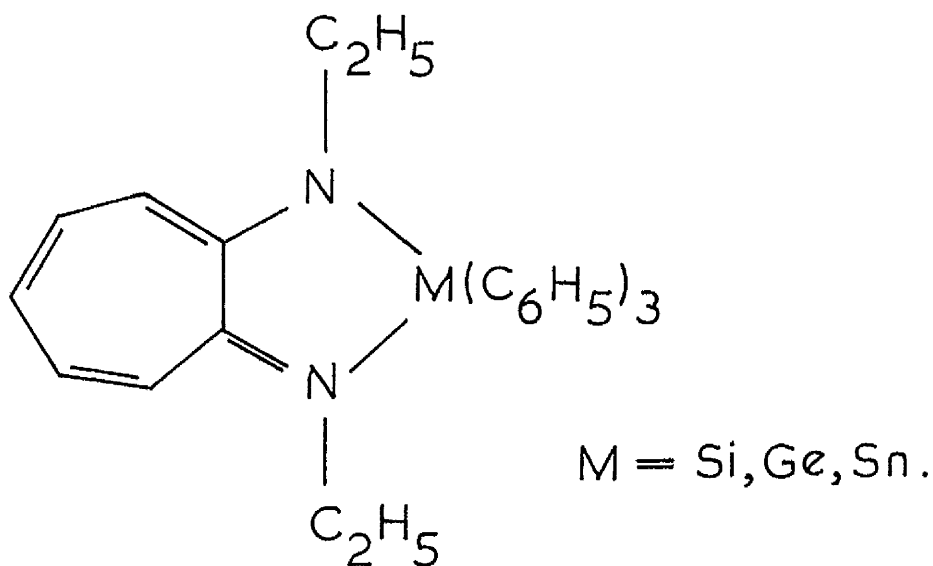
Table 1.10.

<u>Compound</u>	<u>Dipole Moment</u>
CH_3F	1.79D
CH_3Cl	1.87D
CH_3Br	1.80D
SiH_3F	1.27D
SiH_3Cl	1.30D
SiH_3Br	1.32D

interatomic distances in silicon-halogen bonds compared to the

sum of the covalent radii has also been attributed to $p\pi - d\pi$ bonding (23, 24). The results of an electron spin resonance study (25) of the radical ions, $(\text{CH}_3)_3\text{MC}_6\text{H}_5^\cdot$ ($\text{M} = \text{Si}, \text{Ge}$) show unambiguously that there is a certain π -electron density on the metal atom. But it should be noted that these results do not imply that the Si or Ge is part of an extended π -system; i.e. these results do not provide evidence for conjugation. A further e.s.r. study (26) on,

Figure 1.



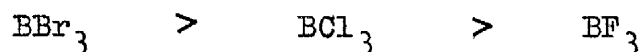
has found no evidence for conjugation in a $d\pi - p\pi$ system between the phenyl groups and the metal atom, whilst optical experiments (27) and the more recent work of Najy et al. (28) demonstrates the interaction of unfilled d-orbitals on Si, Ge and Sn with neighbouring π -orbitals in Me_3MPh .

$p\pi - d\pi$ interaction will probably be most favourable for fluorine as the sizes of the atoms and energies of the participating orbitals are most comparable, and probably becomes less effective down the halogen group. Indeed in the silicon tetrahalides, the observed bond lengths (Table 1.11.) are shorter than those calculated from the 'radius sum' of Pauling's atomic radii (29). This shortening, which is greatest for fluorine,

Table 1.11.

<u>Si-X bond length in</u>	<u>Observed</u>	<u>'Radius Sum'</u>
SiF ₄	1.54Å	1.89Å
SiCl ₄	2.01Å	2.16Å
SiBr ₄	2.15Å	2.31Å
SiI ₄	2.43Å	2.50Å

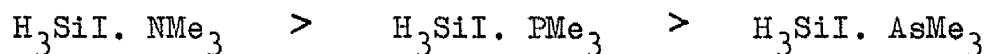
has been attributed to $p\pi - d\pi$ bonding and also to the polar character of the bonds concerned; π - bond formation would therefore predict SiF₄ to be the weakest acceptor. That SiF₄ is actually the strongest acceptor indicates the magnitude of this phenomenon relative to steric and electronegativity effects. It is of interest to note that extensive $p\pi - p\pi$ back-donation occurs in the boron trihalides and gives the reverse stability sequence (30, 31),



1.4. The Donor Strength of Lewis Bases

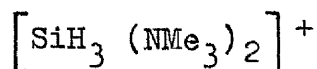
From Mulliken's postulates (9) on complex formation, it is apparent that the donor strength of a Lewis base is a balance between inductive and steric factors. But unfortunately there is a lack of comprehensive data for comparing donor strengths with Group IVb acceptors.

The stability of the 1:1 adducts formed by H₃SiI and the trimethyl derivatives of some Group Vb elements (32) show that nitrogen is the strongest donor in that group.



These results show that H_3SiI (and probably silicon acceptors in general) exhibits class 'a' character and is a hard acid. That tetrahydrofuran forms a 1:1 adduct with H_3SiI (33), although only at low temperatures, whereas the sulphur analogue does not, further indicates the nature of silicon acceptors. Group VIb ligands usually form weaker complexes than Group Vb ligands as is demonstrated by the lack of reaction between H_3SiI and Me_2O (33).

While a comparison of ionisation potentials would predict that trimethylamine ($I_b = 9.4$) would form more stable complexes than pyridine ($I_b = 9.7$), the steric requirements of pyridine are such that silicon tetrachloride co-ordinates two molecules of pyridine to form $\text{SiCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ (34), whilst the size of trimethylamine is such that $\text{SiCl}_4 \cdot \text{NMe}_3$ is the stable adduct formed (35). It is only when the steric requirements of the acceptor are low, that trimethylamine forms a 1:2 adducts; e.g. with silicon tetrafluoride both $\text{SiF}_4 \cdot \text{NMe}_3$ and $\text{SiF}_4 \cdot 2\text{NMe}_3$ are formed (11). The existence of 1:2 trimethylamine adducts with H_3SiBr and H_3SiI (17) is due to the formation of the cation



Inductive effects in the donor molecule have been studied by Brown in his work on the complexes of pyridine and the picolines with trimethylboron (36). The introduction of a methyl group should increase the availability of the lone pair of electrons on the nitrogen atom by a + I inductive effect. But the observed order of stability (Table 1.12.) is different from that predicted; i.e. $\alpha > \beta > \gamma > \text{py}$. The low stability of the α -picoline adduct is attributed to the steric effect of the methyl group in the α -position. The greater stability of the γ -picoline adduct relative to the β -picoline adduct has been explained by the inability of the methyl group in the β -position to increase the base strength of the amine by hyperconjugation; the γ -methyl group, however is able to do so.

Table 1.12.

<u>Complex</u>	<u>Dissociation Vapour Pressure</u>	<u>ΔH</u>
py. BMe ₃	7.46mm./60.4°	-17.0 kcal.mole ⁻¹
α -pic.BMe ₃	37.6mm. /26°	~ -10 kcal.mole ⁻¹
β -pic.BMe ₃	3.29mm./61.1°	-17.8 kcal.mole ⁻¹
γ -pic.BMe ₃	1.99mm./59.7°	-19.4 kcal.mole ⁻¹

The triethylamine adduct of Me₃B (37) has a considerably lower stability than the trimethylamine adduct (38). The inductive effects of the ethyl and methyl groups are of the same order, and this difference is due mainly to steric effects. That this is so is indicated by the heat of formation (Table 1.13.) of the quinuclidine adduct (39) in which the C₂ fragments have been 'tied back' in such a manner that steric hindrance at the central atom is minimal.

Table 1.13.

<u>Complex</u>	<u>ΔH</u>
Me ₃ B. NMe ₃	-17.62 kcal.mole ⁻¹
Me ₃ B. NEt ₃	-10 kcal.mole ⁻¹
Me ₃ B. Quin	-19.94 kcal.mole ⁻¹

Stoichiometry and Stereochemistry of Addition Complexes

1.5. Acceptor - Donor Ratio 1:1

The adducts formed which have the overall stoichiometry of 1:1, viz. X₄M. NR₃, may have one of three possible structures,

- (i) ionic,
- (ii) a five co-ordinate metal atom,
- or (iii) a six co-ordinate metal atom with a bridging halogen atom.

Examples are known for each class and the ionic species are the easiest to characterise. It is often difficult however, on the evidence available, to assign either structure (ii) or structure (iii) to a given adduct.

1.5.1. Ionic Species

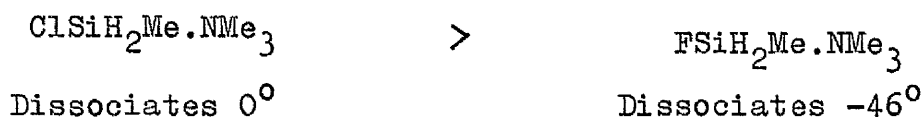
The majority of the data available are from adducts involving bromo- and iodosilanes, where a tetrahedral 'siliconium' cation is proposed. (40, 41, 42). Ebsworth and Campbell-Ferguson (13) have found that the 1:1 iodo-, bromo- and chlorosilane adducts with Me_3N appear to be strong electrolytes in acetonitrile, whereas solutions of the fluorosilane adduct do not conduct.

The infrared spectrum of $\text{H}_3\text{SiI} \cdot \text{NMe}_3$ is found to be identical with that of the 1:1 adduct formed from N, N-dimethylamino-silane ($\text{H}_3\text{Si} \cdot \text{NMe}_2$) and methyl iodide, suggesting that both compounds contain the ions $[\text{H}_3\text{SiNMe}_3]^+$ and I^- (32). A similar technique has been employed to suggest that the adduct $\text{Me}_3\text{SiI} \cdot \text{NMe}_3$ contains $[\text{Me}_3\text{SiNMe}_3]^+$ and iodide ions (13, 35), and conductivity measurements are compatible with this formulation (43).

As the silicon-bromine and silicon-iodine bonds are the most readily ionised (44), one might predict the infrared spectra for complexes of the empirical formula $[\text{H}_3\text{SiL}]^+ \text{X}^-$, ($\text{X} = \text{Br}, \text{I}$), to be identical. But although the 1:2 adducts with Me_3N do give identical spectra, there is a difference between the spectra of $\text{H}_3\text{SiBr} \cdot \text{NMe}_3$ and $\text{H}_3\text{SiI} \cdot \text{NMe}_3$ (13). Since the iodosilane adduct is known to be ionic from conductivity measurements, this could mean that the bromosilane adduct is not ionic, although the differences could also arise from ion-ion interactions.

While most work on 1:1 ionic complexes has involved trimethylamine as the donor, two pyridine complexes have also been prepared (13). It has been proposed on the basis of infrared data that the 1:1 adducts of pyridine with Me_3SiI and Me_2SiI_2 are ionic species containing tetrahedral 'siliconium' ions rather than covalent species containing five co-ordinate silicon.

It has been previously mentioned that the stabilities of fluorosilane complexes are generally greater than those of their chlorosilane analogues. However, when considering the stability of monohalomethylsilane complexes with trimethylamine the reverse is found to be the case (35).



This trend in stability would therefore appear to be related to the ionic character of these compounds; it is of interest to note that the chloro-complex, $\text{H}_3\text{SiCl.NMe}_3$ which has been reported to give a conducting solution in acetone (35), was originally postulated as a quaternary ammonium salt (i.e. $[\text{H}_3\text{SiNMe}_3]^+ \text{Cl}^-$) (45), although the possibility that conductivity arose from hydrolysis in solution should not perhaps be overruled. With the formation of a four co-ordinate 'siliconium' ion, the halogen atoms of larger radius are displaced into the outer sphere of co-ordination. The stability of the complex is then determined by the ease of formation of the ionic structure $[\text{R}_3\text{SiL}]^+ \text{X}^-$ and of ionisation of the silicon-halogen bond.

When reporting or discussing the existence of an ionic silane-amine adduct in the literature, several authors have referred to the cation as a 'siliconium' ion. However, it should be noted that the use of the term 'siliconium' is possibly dangerous in that it implies the positive charge to be localised entirely on the silicon atom. In view of the wide occurrence of quaternary ammonium salts, and lack of evidence for a silicon cation, and considering that in such a species the silicon is bonded to one or two nitrogen atoms, it would appear reasonable that the positive charge be localised instead either partly or wholly on the nitrogen atoms.

1.5.2. A Five Co-ordinate Metal Atom

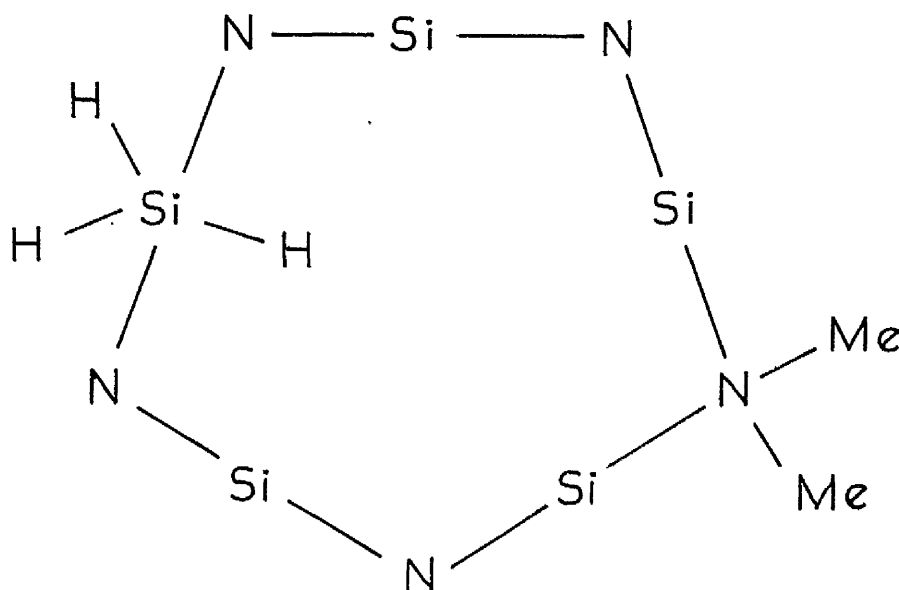
Compounds of the Group IVb elements in which the 'metal' is five co-ordinate are few in number, and it has only been in recent years that unambiguous verification of this co-ordination system has been established.

A number of five co-ordinate structures with tin as the central atom are well known in the crystalline state (46). The assignment of a five co-ordinate structure for the 1:1 complex of trimethyltin chloride and pyridine, based on its infrared spectrum (47), has been confirmed by an x-ray crystallographic analysis(19). This analysis shows the complex to consist of monomeric covalent units of $\text{Me}_3\text{SnCl.py}$, with a trigonal bipyramidal arrangement of ligands around the central atom, the three methyl groups lying in the equatorial plane.

Structural data on five co-ordinate germanium compounds are singularly lacking; the germanium co-ordination in GeF_2 has been described (48) as a distorted trigonal bipyramidal arrangement of four bridging fluorine ligands and one non-bonding electron pair, but is not a true example of five co-ordination.

For silicon, several recent examples of compounds with five co-ordination are known. An x-ray diffraction study on dimethylsilylamine $[\text{Me}_2\text{N}(\text{SiH}_3)]$ at -120° reveals that the unusual physical characteristics of this compound are due to the formation of a pentamer (49)

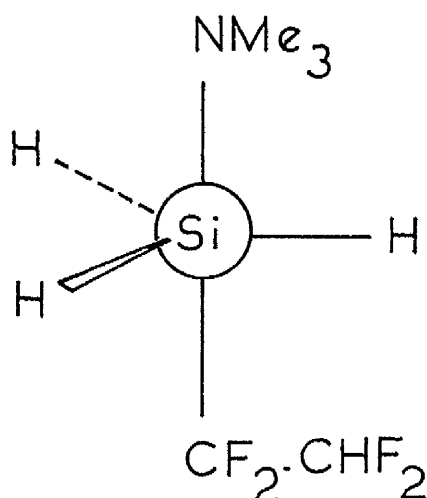
Figure 2.



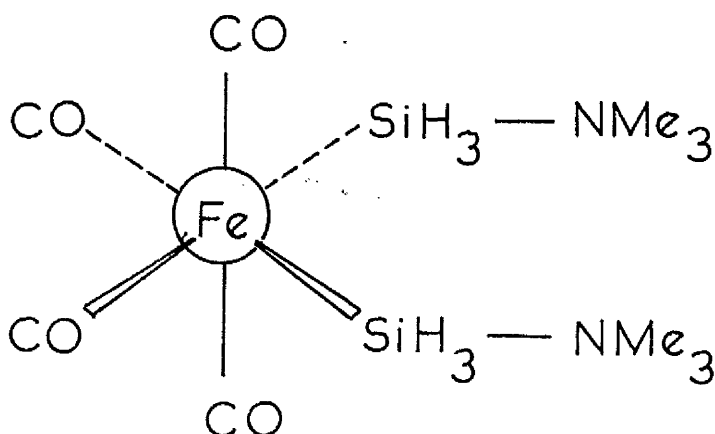
In the ten membered ring of alternate silicon and nitrogen atoms, the silicon atoms are five co-ordinate with the plane of the silyl group perpendicular to the plane of the ring.

Evidence of five co-ordinate silicon has been obtained for the stable liquid complex of 1, 1, 2, 2- tetrafluoroethylsilane and trimethylamine (50). The n.m.r. spectrum of this complex shows only a single resonance for the three silicon protons; this implies that the structure is trigonal bipyramidal with the three equivalent protons in the equatorial plane,

Figure 3.

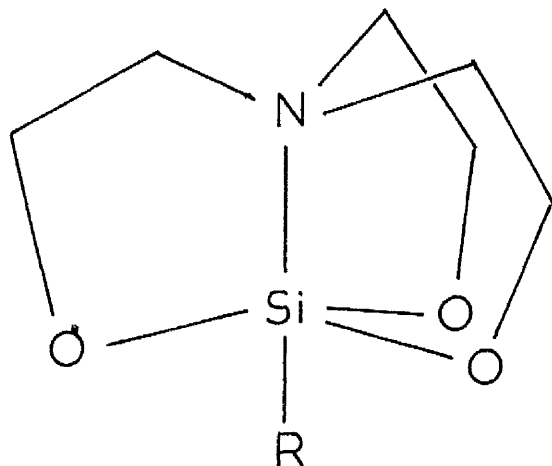


It might appear from these two examples that the presence of a silyl group is favourable for the formation of five co-ordinate silicon. Indeed, Aylett (51,52) has found that the silyl group in silyl-manganese pentacarbonyl forms a rather weak complex with 2, 2' - bipyridyl. But surprisingly disilyl-iron carbonyl, $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$, forms only a 1:2 adduct with excess Me_3N (53), which means that either both amine molecules are co-ordinated to one silyl group or there is one amine per silyl group. Silyl-transition metal bonds are easily cleaved by an excess of hydrogen chloride when the silyl group is co-ordinated to an amine, and the authors have found that upon reacting with excess HCl , $\text{H}_2\text{Fe}(\text{CO})_4$ is formed and not the product $(\text{SiH}_3) \cdot \text{HFe}(\text{CO})_4$ which would be expected if only one silyl group was complexed. It therefore appears that both silyl groups are co-ordinated with one amine molecule to give a five co-ordinate silicon atom.

Figure 4.

Although Stone and Seyferth (54) considered the halosilane-trimethylamine adducts ($\text{H}_3\text{SiX} \cdot \text{NMe}_3$) to be five co-ordinate, other authors have now formulated the complexes as quaternary ammonium compounds (13,44,45,55). The 1:1 adducts of HSiF_3 and SiF_4 with trimethylamine are probably not unimolecular in the solid state; it is more likely that they exist as halogen-bridged, six co-ordinate dimers or polymers (11).

Silicon almost certainly has a co-ordination number of five in the silatranes (Figure 5.) investigated by Voronkov and his co-workers. Compounds have been prepared where

Figure 5.

$\text{R} = \text{Me}, \text{Et}, \text{i-Pr}, \text{Ph}, \text{EtO}$ and PhO (56,57). The dipole moments have been measured and the infrared and n.m.r. spectra studied.

Frye had prepared the hydrogen derivative several years previously (58), and a more recent x-ray diffraction study (59) on the phenyl silatrane shows that the stereochemistry about the silicon is a distorted trigonal bipyramid.

The co-ordination of silicon to five donor atoms has also been suggested in a number of compounds where organosilanes are co-ordinated to ligands which can function as chelating agents, although the evidence is mostly tentative. 2, 2', 2'' - nitrilophenol (60) (Figure 6.) and catechol (61) (Figure 7.) have been used as chelating agents.

Figure 6.

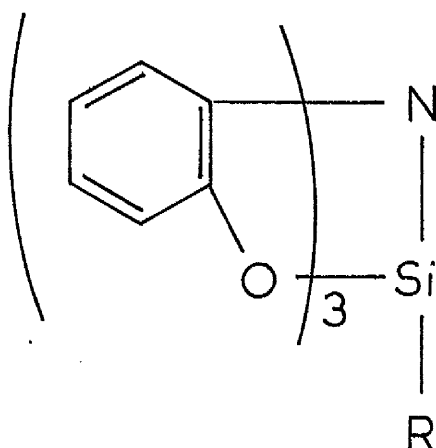
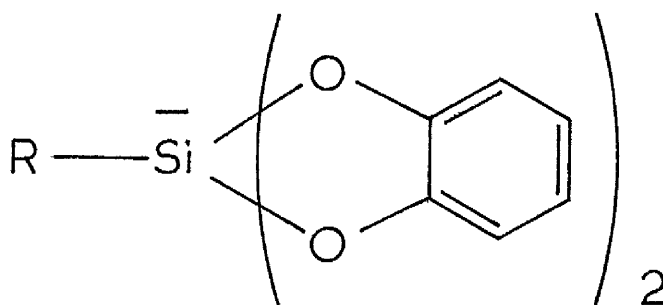


Figure 7.



Trimethylchlorosilane (62) and triphenyliodo-silane (40)

apparently form five co-ordinate siliconium ions when complexed with 2, 2' -bipyridyl. These conclusions are drawn from the observations that the adducts appear to ionise completely in dilute solution, giving conducting solutions. Corey and West (40) do however point out that their proposals are not definite, as such conductivity measurements in solution are always subject to difficulties in interpretation.

1.5.3. A Six Co-ordinate Metal Atom with a Bridging

Halogen Atom On the basis of conductivity measurements Emeleus and Miller (45) considered the adduct $\text{H}_3\text{SiCl} \cdot \text{NMe}_3$ to be a quaternary ammonium salt. But in view of the trend in stability (Table 1.14.), observed for the 1:1 adducts of Me_3N with the series of chlorosilanes, $\text{H}_n\text{SiCl}_{4-n}$ (14), the formulation of these adducts as ionic compounds seems questionable, for a displacement of chlorine as an ion would remove most of the steric

Table 1.14.

<u>Complex</u>	<u>Temperature of Zero Dissociation</u>
$\text{H}_3\text{SiCl} \cdot \text{NMe}_3$	$\sim 0^\circ$
$\text{H}_2\text{SiCl}_2 \cdot \text{NMe}_3$	$\sim -20^\circ$
$\text{HSiCl}_3 \cdot \text{NMe}_3$	$\sim -70^\circ \text{ to } -30^\circ$
$\text{SiCl}_4 \cdot \text{NMe}_3$	$\sim -78^\circ$

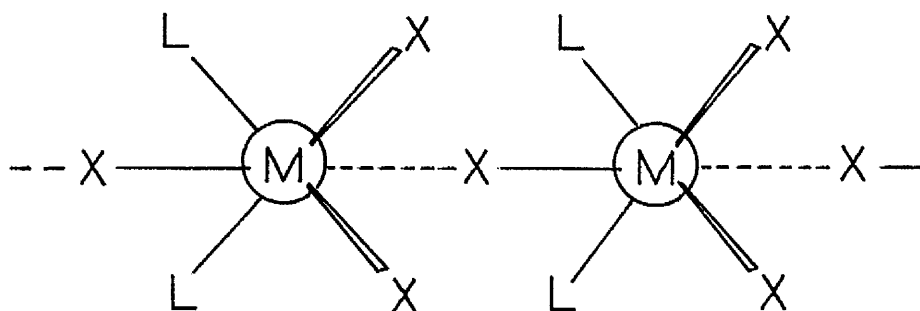
hindrance permitting the electronegativity effect to establish a stability order different from that observed. An alternative structure is a six co-ordinate metal atom with a bridging chlorine atom, although the possibility of a five co-ordinate silicon atom cannot be entirely discounted in view of the recent studies of that stereochemistry (49,50,59,63).

Trimethylamine forms a series of 1:1 adducts with fluoro- and chlorosilanes. Wilkins and his co-workers (11,20) have found that SiF_4 , SiF_3Cl , SiF_2Cl_2 , SiFCl_3 and MeSiF_3 form 1:1 adducts with Me_3N . Equimolar adducts are also reported to be formed with trimethylamine by SiH_3F (64), SiH_2F_2 (17), SiHF_3 (65) and by the monomethylhalosilanes, MeSiH_2F and MeSiH_2Cl (35).

The widespread occurrence of these 1:1 amine-silane complexes and the regular trends in their dissociation pressures has led to the suggestion (11) that they might have a common structure type within which lattice energies and enthalpies of formation do not vary greatly. A molecular bridge structure is an attractive postulate, as the central atom then attains its maximum covalency of six through halogen bridging. Such a structure requires the presence of at least one halogen atom, and this could possibly explain the lack of reaction between SiH_4 and Me_3N (14), although this is more probably due to the absence of an electronegative substituent on silicon.

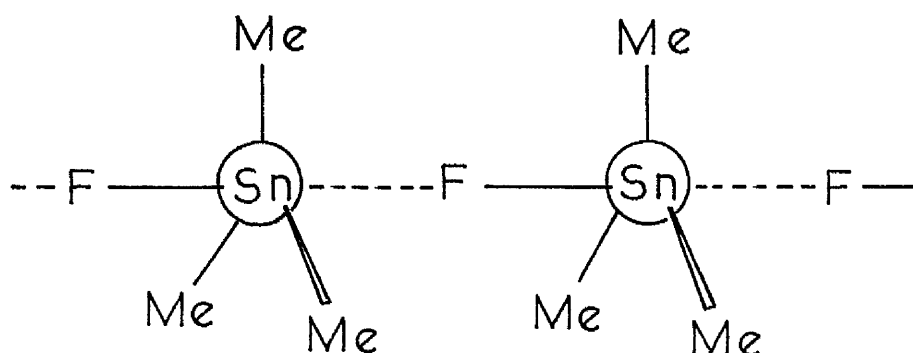
A polymeric complex would result if one halogen atom from each molecule were involved in the bridging, as shown in Figure 8. Unfortunately there is no absolute evidence for this

Figure 8.



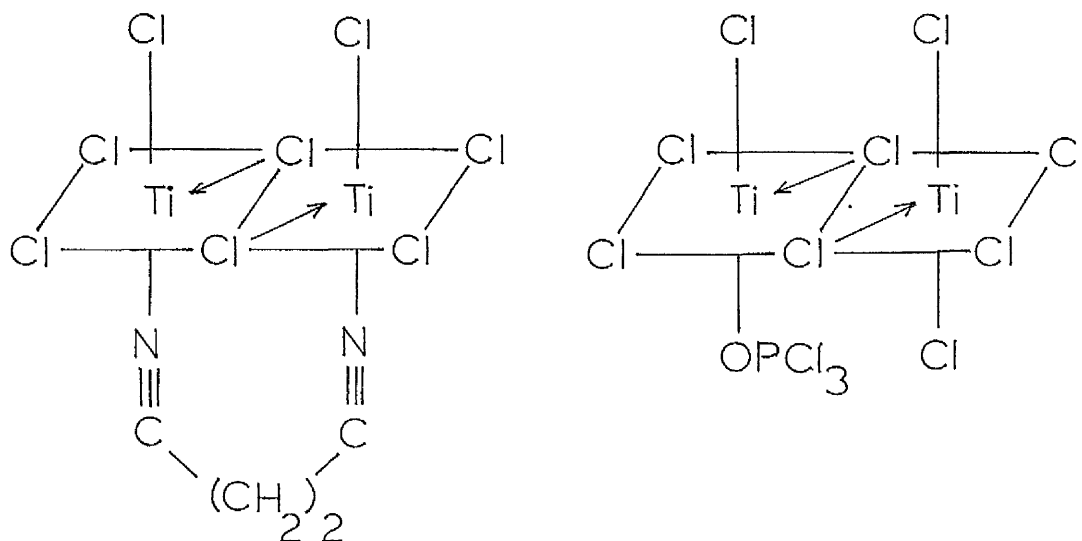
bridged structure for a Group IVb element. Perhaps it is of interest to note that an x-ray diffraction study shows association through fluorine in trimethyltin fluoride (66,67).

Figure 9.



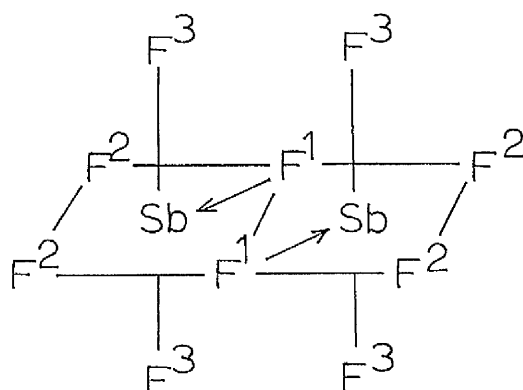
Halogen bridging could also result in a dimeric structure. Such a structure has been proposed for the complex $[\text{TiCl}_4]_2 \cdot \text{N} \equiv \text{C}(\text{CH}_2)_2 \cdot \text{C} \equiv \text{N}$ (68), where the two metal atoms are held together by two bridging chlorine atoms. X-ray diffraction studies on the complex $\text{TiCl}_4 \cdot \text{POCl}_3$ (69), which show that the molecule is dimeric with two chlorine bridges, would appear to support this structure.

Figure 10.



Muetterties has reported (70) the isolation of the 1:1 adducts from silicon or titanium tetrafluorides and Me_3N or pyridine. None of these solid complexes has a sharp melting point and all are relatively intractable, being sparingly soluble in polar, non-protonic solvents. These physical properties certainly indicate that these complexes are polymeric rather than molecular, five co-ordinate complexes. Six co-ordination would be preserved in a polymeric complex through halogen bridging.

A comparison has been made between these 1:1 complexes and antimony fluoride. Antimony pentafluoride has an octahedral co-ordination in the liquid state (71) with fluorine bridges and may be considered to be analogous to these 1:1 complexes. The octahedral co-ordination of antimony pentafluoride is suggested by its ^{19}F n.m.r. spectrum which shows three types of fluorine environments.

Figure 11.

1.6. Acceptor-Donor Ratio 1:2

1.6.1. Ionic Species Earlier reports (72) that bromo- and iodosilane both form 1:2 adducts with pyridine, have been confirmed recently by Campbell-Ferguson and Ebsworth (17), who have also prepared the analogous adducts with MeSiH_2Br and MeSiH_2I . A solution of $\text{H}_3\text{SiI} \cdot 2\text{py}$ in acetonitrile gave a conductivity of 102 mhos.cm.^2 , approximately the value expected for a strong 1:1 electrolyte. A further indication of the ionic character of these adducts is obtained from their infrared spectra. The spectra of the bromine containing adducts are very similar to those containing iodine, and this similarity makes it probable that these adducts contain the same cation, $[\text{SiH}_3 \cdot 2\text{py}]^+$ and $[\text{MeSiH}_2 \cdot 2\text{py}]^+$. N.m.r. spectra of the iodine adducts indicate that the hydrogen atoms are either in equivalent positions or exchange rapidly, and so if a five co-ordinate cation is postulated, it is likely that the hydrogens are in the equatorial plane of a trigonal bipyramidal configuration, with the two pyridine molecules in the axial positions.

Despite previous reports (32) to the contrary, both $\text{H}_3\text{SiBr} \cdot 2\text{NMe}_3$ and $\text{H}_3\text{SiI} \cdot 2\text{NMe}_3$ give conducting solutions in acetonitrile (72). As with the pyridine adducts, the infrared spectra (13) are almost identical and indicate the presence of a common five co-ordinate $[\text{SiH}_3 \cdot 2\text{NMe}_3]^+$ cation.

Aylett (52) has found that silyl-manganese carbonyl and silyl-cobalt carbonyl form 1:2 adducts with Me_3N and pyridine. It is therefore surprising to find that disilyl-iron carbonyl forms only the 1:2 adduct with Me_3N (53) and not a 1:4 adduct which might have been predicted. On the basis of the position of the $\nu_{\text{C=O}}$ bands in the infrared spectra given in Table 1.15., it would appear that these compounds contain the carbonyl metallate anion and can thus be formulated as $[\text{SiH}_3.2\text{B}]^+ [\text{M}(\text{CO})_n]^-$.

Table 1.15.

<u>Complex</u>	<u>Frequency cm^{-1}</u>
$\text{SiH}_3.\text{Mn}(\text{CO})_5$	2106, 2021
$\text{SiH}_3.\text{Mn}(\text{CO})_5 2\text{py}$	1860
$\text{SiH}_3.\text{Mn}(\text{CO})_5 2\text{NMe}_3$	1860
$\text{Mn}(\text{CO})_5^-$	1898, 1864
$\text{SiH}_3.\text{Co}(\text{CO})_4$	2106, 2051, 2026
$\text{SiH}_3.\text{Co}(\text{CO})_4 2\text{py}$	1882
$\text{SiH}_3.\text{Co}(\text{CO})_4 2\text{NMe}_3$	1870
$\text{Co}(\text{CO})_4^-$	1883, 1861

1.6.2. Six Co-ordinate Molecular Species

Although there are many reports of 1:2 adducts between the tetrahalides and hydrohalides of silicon and tertiary amines, the nature of these adducts has long been in doubt owing principally to the low solubility of the fluoro- and chlorosilane adducts. Consequently nearly all the available data are limited to the infrared spectra.

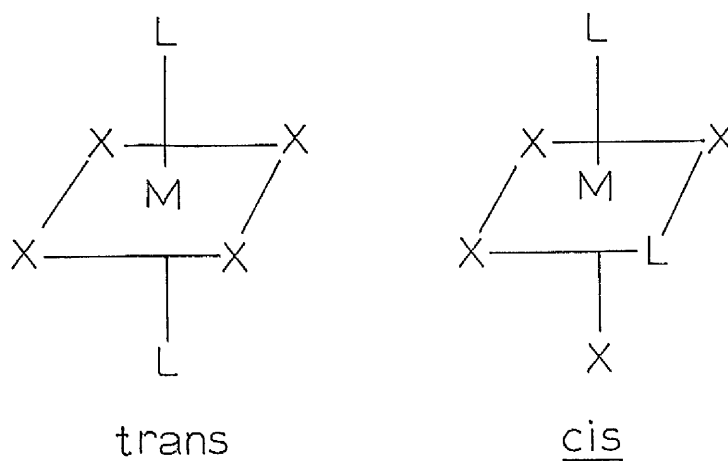
The 1:2 adducts of SiF_4 (17, 70, 73), SiCl_4 (15, 17, 73, 74, 75, 76, 77, 78) and SiBr_4 (41, 73, 74) with pyridine are usually described as molecular (41, 73). Of the hydride analogues only $\text{HSiF}_3.2\text{py}$, $\text{HSiCl}_3.2\text{py}$ and $\text{H}_2\text{SiCl}_2.2\text{py}$ have been isolated (17); the authors report that the pyridine complexes obtained with H_2SiF_2 , H_3SiF and H_3SiCl disproportionate.

A series of interhalosilane compounds has been recently reported with pyridine (79); Cl_3SiBr , ClSiBr_3 , Cl_2SiI_2 and Cl_3SiI all form 1:2 adducts, but there is a lack of structural information.

Wilkins and his co-workers (11,20) found that SiF_4 , ClSiF_3 and Cl_2SiF_2 form 1:2 adducts with Me_3N . Although an earlier attempt (80) to obtain the infrared spectrum of the SiF_4 adduct is probably suspect owing to hydrolysis, the presence of a doublet at 905 and 935 cm^{-1} in the infrared spectrum of $\text{SiF}_4 \cdot 2\text{NH}_3$ (81) strongly implies a cis-octahedral structure, as only the asymmetric Si-N stretching mode would be infrared active in a trans-octahedral structure.

If these 1:2 adducts are molecular, then an octahedral distribution of ligands about the acceptor atom is expected. For complexes of this type, i.e. MX_4L_2 , where L is a non-chelating ligand, there is therefore the possibility of cis-trans isomerism. Beattie (82) states that when X is much

Figure 12.



larger than L, the main repulsions will be between X and X. Initially therefore it may appear that a trans-adduct is favoured if only X - X repulsions are considered. But in view of the number of cis-adducts which have been obtained, it is obvious that other factors need to be considered. If the cis-adduct is distorted so that the MX_4 skeleton becomes more like the original tetrahalide, then on the basis of X - X repulsions only, a cis-adduct becomes a stereochemical probability. This can be illustrated by considering the complex $\text{SnCl}_4 \cdot 2\text{MeCN}$ (41) in which the relatively unhindered nitrogen atoms of the acetonitrile molecules could co-ordinate to two of the 'open'

faces of the SnCl_4 tetrahedron, causing distortion and effectively forming a cis-complex. But if a larger or more sterically hindered ligand is used, as in $\text{SnCl}_4 \cdot 2\text{NMe}_3$, then L-X repulsions assume the greater importance and a change over to a trans-complex occurs (83).

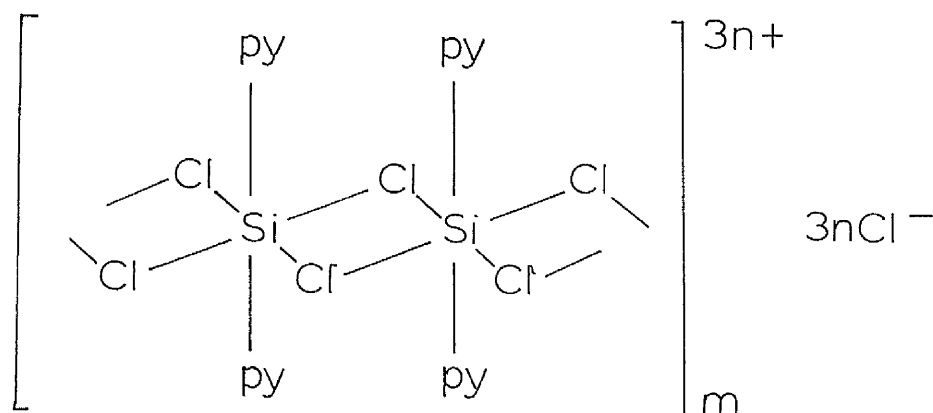
From a consideration of the 1:2 adducts of SnCl_4 prepared by Beattie and co-workers (41, 83), Wilkins (84) concluded that the stereochemistry is determined by the ligand rather than the halogen atom; if the donor atom is part of a polarisable π -system (e.g. MeCN , EtCN , Me_2CO , POCl_3) then a cis-complex is formed with SnCl_4 . Otherwise a trans-complex tends to be formed (e.g. $(\text{CH}_2)_4\text{O}$, Me_3N , Et_2O). This generalisation implied that overlap of the π -bonding orbital of the ligand with an empty d-orbital on the central atom plays a significant part in bond formation and that stronger bonding of the ligands can be obtained through the use of two different d-orbitals as in the case of the cis-complex.

Pyridine however appears to be marginal in conforming to this generalisation, as it forms both cis and trans isomers with Group IVb tetrahalides. An x-ray diffraction study (85) has confirmed the assignment of a trans-configuration to $\text{GeCl}_4 \cdot 2\text{py}$ (86). A cis-configuration has been assigned to $\text{SiCl}_4 \cdot 2\text{py}$ and $\text{SiBr}_4 \cdot 2\text{py}$ (87) because of their high heats of formation (88), as has already been discussed. In view of the apparent simplicity of the infrared spectrum of $\text{SiF}_4 \cdot 2\text{py}$ (89), it is probable that it can be assigned a trans-octahedral structure.

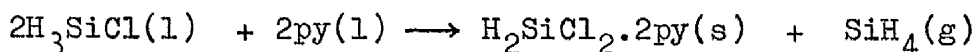
Ebsworth and Campbell-Ferguson (13) have criticised this argument on the basis of the solubilities of the adducts. $\text{SiCl}_4 \cdot 2\text{py}$ and $\text{SiBr}_4 \cdot 2\text{py}$ are insoluble in all common solvents whereas trans- $\text{GeCl}_4 \cdot 2\text{py}$ is soluble in both benzene and chloroform (78). They suggest that if these adducts are in fact cis-isomers, then being less symmetrical they would be expected to be more soluble as an increased solvation energy would probably compensate for any increases in the lattice energy. As an alternative, it is proposed that these adducts contain polymeric cations, with bridging halogen atoms.

For example,

Figure 13.



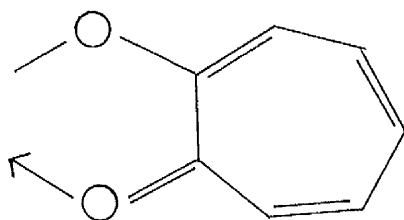
The non-formation of $\text{H}_3\text{SiCl} \cdot 2\text{py}$ (17) could then be explained if it is supposed that a similar bridging mechanism stabilises the formation of $\text{H}_2\text{SiCl}_2 \cdot 2\text{py}$ with the liberation of SiH_4 .



1.7. Complexes with Acceptor - Donor Ratios other than 1:1 or 1:2

The maximum co-ordination number for silicon and germanium is probably six. But for their heavier analogues in Group IVb, components are formed in which the co-ordination number is eight. Muetterties (90, 91) has prepared tetratropolonate-tin and -lead, and confirmed eight co-ordination by infrared and n.m.r. spectroscopy. T_3SnPh and T_3SnCl are thought to be seven co-ordinate, where T =

Figure 14



An eight co-ordinate tin atom also appears to exist in tetrakis-(8-quinolinato) tin and tetraoxinate tin (92).

Complexes with high acceptor-donor ratios for silicon can be categorised into three types.

1.7.1. Ionic Species

Silicon tetraiodide forms a 1:4 complex with pyridine (17, 41, 73, 93, 94). This adduct gives a conducting solution in acetonitrile and is formulated as a six co-ordinate silicon cation, $[\text{SiI}_2 \cdot 4\text{py}]^{2+} \cdot 2\text{I}^-$, although early workers (73, 95) suggested a structure involving $[\text{Si}4\text{py}]^{4+}$ cations. The assignment of the infrared spectrum of $[\text{SiI}_2 \cdot 4\text{py}]^{2+} \cdot 2\text{I}^-$ in terms of a cis-octahedral structure has been criticised (13) and the alternative trans-structure has been suggested in view of the simplicity of the spectrum.

Since SiBr_4 forms only a 1:2 adduct with pyridine (73), it is perhaps surprising that H_2SiBr_2 and HSiBr_3 form pyridine adducts with a 1:4 stoichiometry (17). More predictably though, H_2SiI_2 , HSiI_3 and HSiMeI_2 form 1:4 adducts with pyridine. $\text{H}_2\text{SiI}_2 \cdot 4\text{py}$ has a molar conductivity of $300 \text{ mhos} \cdot \text{cm}^2$, a value consistent with a strong 1:2 electrolyte; and in view of the infrared spectra of $\text{H}_2\text{SiBr}_2 \cdot 4\text{py}$ and $\text{H}_2\text{SiI}_2 \cdot 4\text{py}$, it is reasonable to conclude that the $[\text{SiH}_2 \cdot 4\text{py}]^{2+}$ cation is common to both adducts (13).

A 1:3 adduct between SiCl_4 and 2, 2'-bipyridyl is reported (62) and has been proposed to contain the six co-ordinate cation $[\text{Si}(\text{bipy})_3]^{4+}$. The 1:6 adduct formed by Et_3N with SnBr_4 is probably ionic (96), containing $[(\text{Et}_3\text{N})_6\text{Sn}]^{4+}$, since with AgNO_3 a stoichiometric amount of bromide is precipitated, yielding $[(\text{Et}_3\text{N})_4\text{Sn}] (\text{NO}_3)_4$.

1.7.2. Non-Reproducible Data

There are several reports in the literature in which previously published procedures and observations have not been duplicated and in most cases these anomalies arise because of hydrolysis of halosilanes or the use of impure reagents. The material described as $(\text{SiF}_4)_2 \cdot 3\text{py}$ (89) seems likely, from a comparison of its x-ray powder pattern, to have consisted of mainly pyridinium hexafluorosilicate, probably formed by hydrolysis during prolonged pumping. Similarly, the 1:4 adduct

of SiCl_4 and pyridine (97) seems likely to have been a product of hydrolysis (15, 77). Trost also claimed to have prepared $\text{SiCl}_4 \cdot 4n\text{-Bu}_3\text{N}$ and $\text{SiCl}_4 \cdot 4\text{Et}_3\text{N}$ (97, 98); but other workers have not been able to reproduce these results using rigorously dried reagents under similar conditions (76). Beattie and Leigh (15) have also criticised the report of $\text{SiI}_4 \cdot 4(\text{isoquinoline})$ (89), suggesting that hydrolysis of the solutions used for conductivity measurements occurred. It has been shown that there is no reaction between SiI_4 and quinoline, α -picoline, acridine or collidine (34), despite earlier reports (73) to the contrary that these donors formed 1:4 adducts.

1.7.3. Ligand Association

High acceptor-donor ratios have been reported for certain amide complexes of silicon tetrachloride; e.g. $\text{SiCl}_4 \cdot 10\text{HCONH}_2$, $\text{SiCl}_4 \cdot 5\text{HCONMe}_2$ (76,99), and it is conceivable that ligand association may account for these high ratios. It is known that amides have a strong tendency to associate and this tendency may not entirely disappear on complex formation. The extra ligand molecules may also be present as solvent of crystallisation. Co-ordination in amide complexes has been shown to be through the nitrogen atom (100, 101) and also through the oxygen of the carbonyl group (100, 102, 103). It has been suggested that co-ordination to the halogen may also occur, especially in the presence of excess ligand and for the heavier halogens (76, 104).

1.8. Complexes Formed by Halo-substituted Alkylsilanes

The reduced Lewis acidity of the silicon atom produced by replacing hydrogen or halogen atoms with methyl groups has been discussed earlier, and in a study of the 1:2 complexes of some methylchlorosilanes, Cook (105) has found that the dissociation vapour pressures of these adducts are consistent with inductive and steric arguments.

Table 1.16.

Silane \ Base	<u>β - picoline</u>	<u>γ - picoline</u>
HSiCl ₃	13.2mm./55°	1.2mm./57°
HSiMeCl ₂	60.8mm./11.4°	19.6mm./11.6°
HSiMe ₂ Cl	Unstable at 0°	Unstable at 0°

The introduction of an ethyl group would be expected to cause a further decrease in the Lewis acidity of the silicon atom. However, it was also shown that if the ethyl chain is fluorinated, then the enhanced electron withdrawing power of the organic group is sufficient to give isolable complexes. The 1:1 trimethylamine and 1:2 β -picoline complexes of the 1, 1, 2, 2-tetrafluoroethylsilanes ($X_3SiCF_2CHF_2$; $X = H, Cl, F$) have been prepared. The two complexes of 1, 1, 2, 2-tetrafluoroethylsilane are remarkable in that they are liquid at room temperature. The unusual stereochemistry of the trimethylamine adduct has already been discussed.

This work using halo-substituted alkylsilanes was the first of its kind to be reported and prompted this present study. The present study was directed towards examining the effect on complex stability of the position and degree of fluorine substitution in the ethyl group of ethylsilanes; thermodynamic heats of formation being used as a measure of complex stability.

1.9. The Use of Spectroscopy for Structure Assignment

1.9.1. Infrared Spectroscopy

The examination of the stereochemistry of complexes of the type $MX_4 \cdot 2L$ is most conveniently carried out using infrared and Raman spectroscopy. The symmetry of the MX_4 residue in $MX_4 \cdot 2L$ is lower for a cis-adduct (C_{2v}) than for a trans-adduct (D_{4h}), leading to the prediction that the infrared spectrum of the cis-adduct (three fundamentals) should be more complex than that of the trans-adduct (one fundamental) in the region of the M-X stretching vibrations (83). The spectra of adducts that contain chelate ligands, and are therefore expected to

yield the cis-isomer, appear to support these conclusions; e.g. the adducts of 1,10-phenanthroline (phen), 2, 2'-bipyridyl (bipy) and N, N, N', N'-tetramethylethylenediamine (TMEN).

It has been shown (41) that for the 1:2 adducts of silicon tetrahalides and tertiary aromatic amines, the Si-Cl stretching vibrations lie in the region $482 - 382 \text{ cm}^{-1}$, while for the corresponding bromides the region of $425 - 350 \text{ cm}^{-1}$. For assignments of the Si-F bond, which occur at higher frequencies, the position is often difficult as the stretching absorptions often coincide with those of the ligand.

Some examples of complexes for which the stereochemistry has been assigned by vibrational spectroscopy are given in Table 1.17.

Table 1.17.

<u>Complex</u>	<u>Assignment</u>	<u>Reference</u>
SiCl ₄ · phen	cis	41
SiBr ₄ · phen	cis	41
SiCl ₄ · bipy	cis	41
SiBr ₄ · bipy	cis	41
GeCl ₄ · phen	cis	86
SnCl ₄ · phen	cis	86
GeCl ₄ · bipy	cis	86
SiCl ₄ · TMEN	cis	106
SnF ₄ · bipy	cis	84
SnF ₄ · TMEN	cis	84
SiF ₄ · 2NH ₃	cis	81
SiF ₄ · NH ₂ NH ₂	cis	81
SnF ₄ · 2py	trans	84
GeCl ₄ · 2py	trans	78, 86
SiF ₄ · 2Ph ₃ PO	trans	87
SiF ₄ · 2py	trans	87
SiCl ₄ · 2py	cis	41
SiBr ₄ · 2py	cis	41
SnCl ₄ · bipy	cis	86
SnCl ₄ · 2MeCN	cis	86
SnCl ₄ · 2EtCN	cis	86
SnCl ₄ · 2Me ₂ CO	cis	83
SnCl ₄ · 2POCl ₃	cis	107
SnCl ₄ · 2(CH ₂) ₄ O	trans	83
SnCl ₄ · 2(CH ₂) ₄ S	trans	83
SnCl ₄ · 2Et ₂ O	trans	83
SnCl ₄ · 2Et ₂ S	trans	83
SnCl ₄ · 2NMe ₃	trans	83

Generally the picture emerging from the table is that small ligands tend to give cis-adducts, while ligands which are sterically hindered tend to give trans-adducts. This apparent preference for the cis conformation may be partly rationalised by the possible formation of π - bonds between the ligand and the metal atom. The cis-isomer involves the use of two metal d-orbitals whereas only one such d-orbital is required for the trans-form.

Ligand vibrations have also been used, though less satisfactorily, to assign stereochemistries. For example, the splitting of the frequency associated with the S-O bond in the dimethylsulphoxide complexes of SnCl_4 (108) and SnF_4 (109), and for the phosphoryl absorption in $\text{SnCl}_4 \cdot 2\text{POCl}_3$ (110) all suggest a cis-configuration for these molecules. Similarly the lack of splitting in the complex $\text{SnCl}_4 \cdot 2\text{EtOAc}$ (11) (a single sharp carbonyl band), $\text{SiF}_4 \cdot 2\text{Me}_2\text{SO}$ and $\text{GeF}_4 \cdot 2\text{Me}_2\text{SO}$ (both with a single sulphinyll) (109) has been taken to indicate a trans - complex. The spectrum of the phosphine oxide in the P-O stretching region of $\text{SnF}_4 \cdot 2\text{Ph}_3\text{PO}$ has two bands, with only one in the free ligand; this evidence is taken to confirm the cis-structure of the complex already predicted from the multiplicity of the Sn-F absorption, even under ideal conditions. The coupling between the two ligands via the metal atom of a complex will depend on the force constant of the metal-ligand bond and on the mass of the central atom.

The main danger in the use of metal-halogen absorptions to assign stereochemistries, is the possibility of metal-ligand vibrations being mistaken for metal-halogen vibrations, as these two regions are often coincident. The absorptions at 403 and 367 cm^{-1} , in the spectrum of $\text{SiI}_4 \cdot 4\text{py}$ have both been assigned to silicon-iodine stretching frequencies and as a consequence a cis-stereochemistry was proposed for the octahedral cation $[\text{SiI}_2 \cdot 4\text{py}]^{2+}$ (41). The spectrum of $\text{H}_2\text{SiI}_2 \cdot 4\text{py}$ contains a strong absorption at 361 cm^{-1} , (13); since the analogous cation $[\text{SiH}_2 \cdot 4\text{py}]^{2+}$ postulated for this adduct contains no iodine bound to silicon, it seems possible that bands near 360 cm^{-1} may be due to vibrations involving primarily the silicon atom and pyridine molecules. If so, only

one Si-I stretching frequency can then be identified in the spectrum of $\text{SiI}_4 \cdot 4\text{py}$. This, combined with the simplicity of the spectrum in the CsBr region, makes it appear more likely that the configuration of the octahedral $[\text{SiI}_2 \cdot 4\text{py}]^{2+}$ is trans rather than cis (13).

The assignment of the bands to Si-N stretching frequencies is likewise very difficult, and considerable confusion has resulted in the literature, not only for silicon, but for many other elements also. If, as Beattie and co-workers (41) believe, the Si-N force constant may be lower than 10^5 dyne. cm^{-1} , then it is unlikely that a vibration will be observed where nitrogen is contained in a large residue.

1.9.2. Raman Spectroscopy

Raman spectroscopy has been employed for the assignment of stereochemistries and most of the studies merely confirm structures already proposed from infrared spectra measurements; e.g. some adducts of SnCl_4 (112). It should be noted however that Raman work on the addition compounds of SnCl_4 (113) does not agree with the cis infrared assignments (86) for the acetonitrile and propionitrile adducts. Based on symmetry arguments, three and one bands are expected for the cis and trans isomers respectively, although it has been pointed out (112) that intensity effects may be misleading in attempting to distinguish between the two.

1.9.3. Nuclear Magnetic Resonance Spectroscopy.

N.m.r. spectroscopy has been applied to the study of the stereochemistry of adducts of tin tetrafluoride (70). The ^{19}F spectrum of SnF_4 with certain ligands, from ca. $+ 15^\circ$ down to the freezing point of the ligand, consists of two peaks of equal intensity, each split into triplets. This behaviour is to be expected for a 1:2 cis-adduct where there are two pairs of fluorines in different environments. But on warming the solutions, the peaks broaden and finally coalesce into a single resonance. This is characteristic of an exchange process of the ligands, with an order of magnitude of exchange rate of 10^3 sec^{-1} at $0^\circ \pm 30^\circ$. Recooling of the solutions of the complexes yielded the original ^{19}F splitting pattern.

Thus the cis structure appears to be thermodynamically favoured for these SnF_4 complexes, suggesting that repulsions between fluorine atoms and ligand molecules are structure determining.

The ^{19}F spectra of the SiF_4 and GeF_4 1:2 adducts with pyridine, Me_3N and Me_2SO consisted of a single fluorine resonance from the freezing points of the solutions up to $+30^\circ$. This could indicate a preferential trans-formation; however it is not conclusive because the absence of any fine splitting could also be due to fast ligand exchange.

Proton magnetic resonance spectroscopy has been used in two recent examples to obtain information about structural possibilities. Basically only a single Si-H resonance occurs in the spectra of $\text{H}_3\text{SiI} \cdot 2\text{py}$ (13) and $\text{H}_3\text{SiCF}_2\text{CHF}_2 \cdot \text{Me}_3\text{N}$ (50), while for $\text{MeSiH}_2\text{I} \cdot 2\text{py}$ a 1:3 :3:1 quartet due to the SiH_2 group was observed together with a 1:2:1 triplet due to the CH_3 group. All indicate that the hydrogens bonded to silicon are either in equivalent positions (i.e. all the silicon protons probably lie in the equatorial plane of a trigonal bipyramidal structure) or are exchanging rapidly.

1.9.4. X-ray Crystallography

This method of structural analysis should offer the best means of unequivocally determining the structures of chemical addition compounds in the solid state. Unfortunately most of the Group IVb complexes are very readily hydrolysed and exist as insoluble powders, making crystal growth very difficult. Consequently this technique has been unable to realise its full potential.

The only x-ray data available for 1:2 adducts are those from the determinations on cis- $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ (114), cis- $\text{SnCl}_4 \cdot 2\text{POCl}_3$ (107) and trans- $\text{GeCl}_4 \cdot 2\text{py}$ (78). More recently, x-ray structure determinations have confirmed the existence of five co-ordinate silicon species in the low temperature pentamer of dimethylsilylamine (49) and in phenylsilatrane (59).

1.9.5. Mössbauer Spectroscopy

A recent survey of the Mössbauer spectra of six co-ordinate tin IV compounds (115) has found that no measurable quadrupole interaction (ΔE) is observed when all six donor atoms have non-bonding π -electrons, even though all six bonded atoms may be different. Thus the 1:1 adducts of

SnX_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with 2, 2' -bipyridyl have a ΔE value of zero. But when some of the bonded groups have no p_π - electrons, then substantial quadrupole splitting occurs. The introduction of the methyl group has such an effect and the quadrupole splitting values of some tin IV compounds are given in Table 1.18.

Table 1.18.

<u>Compounds</u>	<u>Reference</u>	<u>ΔE mm.sec⁻¹</u>	<u>Me groups</u>	<u>Other Assignments</u>
$\text{Me}_2\text{Sn}(\text{Oxin})_2$	116	1.98	cis	cis; dip.mom(119)
$\text{Me}_2\text{SnCl}_2 \cdot \text{bipy}$	116	4.09	trans	trans; i.r.(120)
$\text{Me}_2\text{SnCl}_2 \cdot \text{phen}$	117	4.03	trans	-
$(\text{py} \cdot \text{H})_2(\text{Me}_2\text{SnCl}_4)$	118	4.32	trans	trans; i.e. (19)

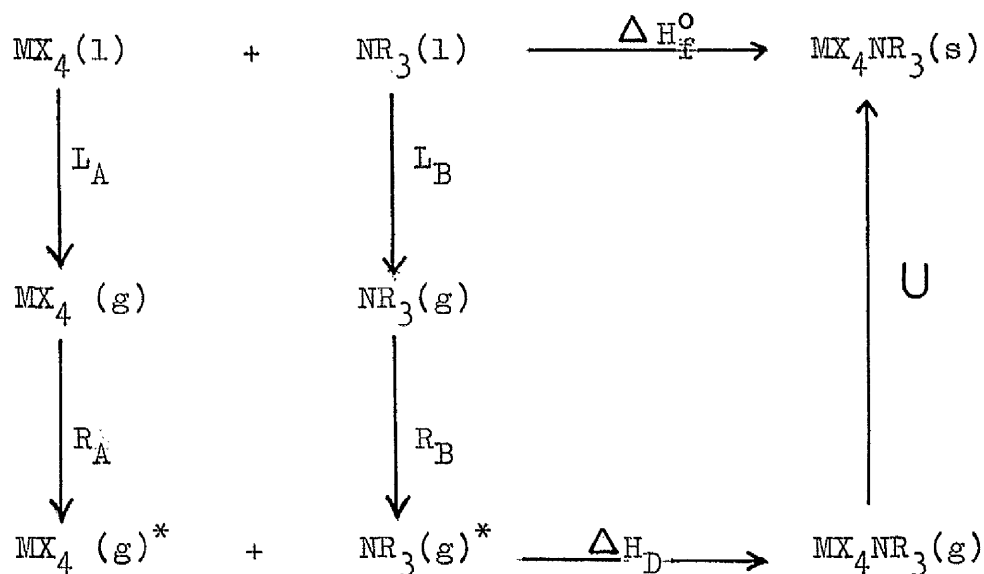
From a study of the ΔE values for these and other tin compounds, it has been found (118) that $\Delta E_{\text{trans}} \approx 2 E_{\text{cis}}$ and also that $\Delta E_{\text{trans}} \sim 4 \text{cm} \cdot \text{sec}^{-1}$ and $\Delta E_{\text{cis}} \sim 2 \text{cm} \cdot \text{sec}^{-1}$. On the basis of this study, the problem of cis - trans isomerism has been resolved for these compounds and the results are in agreement with previously assigned stereochemistries.

1.10. The Thermodynamics of Complex Formation

In any discussion on acceptor-donor complexes it is important to understand what is meant by the term 'stability', for a great deal of confusion can arise when the term is applied to a chemical compound. One must specify whether it is thermodynamic or kinetic stability which is meant, or stability towards heat or hydrolysis, or with respect to irreversible decomposition of the compound. With few exceptions, the complexes of the Group IVb halides are solid compounds. Therefore it is both practicable and convenient to refer to the stability of these adducts as 'the presence, at a particular temperature of a solid for which the partial pressures of both its constituents in the vapour phase, in equilibrium with the solid, are lower than the vapour pressures of the pure constituents'. (82)

Brown and Pearsall (121) consider that of two addition compounds of closely similar structure and molecular weight, the less stable exhibits the higher saturation vapour pressure and this observation has been used many times as a criterion of stability for Group IVb adducts. But for covalent molecular complexes the most obvious index of stability is the stability of the metal-ligand co-ordinate bond, and the most satisfactory measure of this bond strength might appear to be the enthalpy change, ΔH_D , for the gas phase dissociation of the complex into the component acceptor and donor molecules. All the evidence for silicon complexes however, indicates that they do not exist in the gas phase but dissociate extensively, so making ΔH_D immeasurable. Instead, the enthalpy change that is usually measured, $\Delta H'$, is that derived from the Van't Hoff isochore where the vapour pressure of the solid complex is measured as a function of temperature. A necessary requirement is that the complex is fully dissociated in the gas phase (122); although if one component is a relatively non-volatile liquid at the experimental temperatures, a modified form of the Van't Hoff isochore can be used (123).

The significance of such an enthalpy is best illustrated with reference to a Born-Haber cycle. Below are the energy changes involved in the formation of $MX_4.NR_3$ from the components in their standard states.



where L_A = latent heat of vapourisation of MX_4
 L_B = latent heat of vapourisation of NR_3
 R_A = rehybridisation energy of MX_4
 R_B = rehybridisation of NR_3
 ΔH_D = bond dissociation energy of M-N bond
 U = lattice energy
 and ΔH_f° = heat of formation of $MX_4NR_3(s)$ from MX_4
 and NR_3 in their standard states.

Thus it can be seen that the enthalpy change $\Delta H'$, that is measured from vapour pressure experiments is the sum of the bond dissociation energy and the lattice energy of the complex; i.e.

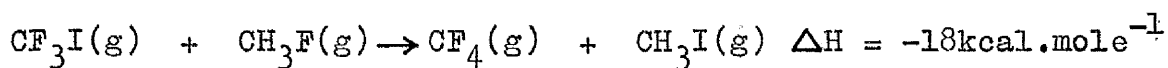
$$\Delta H' = \Delta H_D + U$$

So although lattice energies might be expected to be similar for related compounds, conclusions regarding the stability of co-ordination compounds based on vapour pressure measurements of solids are open to question and can only be of qualitative interest in the absence of adequate structural evidence.

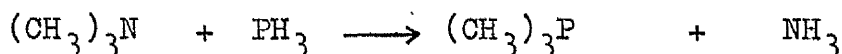
It is perhaps worthwhile noting that Pearson and Songstad (124) have shown how the thermodynamic stabilities of many kinds of organic molecules can be rationalised by the hard and soft-acid and base concept proposed by Pearson (4) and discussed earlier. The method used was to carry out a theoretical dissociation of the organic species into a Lewis acid fragment such as a carbonium ion or acylium ion, and a Lewis base fragment such as a carbanion, hydride or halide ion. The stability of the molecule was then considered in terms of the acid-base interaction,



From the principles of the HSAB concept, one would predict CF_3^+ to be harder than CH_3^+ , and therefore to bind preferentially to the hardest halide, viz. fluoride. This statement is justified by the exothermic reaction involving CF_3I and CH_3F ,



Further, the prediction that displacements such as,



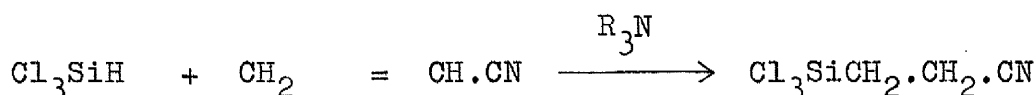
will occur is justified by the heat of reaction, $-24.7\text{kcal.mole}^{-1}$, thus demonstrating that a hard-hard, soft-soft interaction, viz. N - H or P - CH₃, is more stable than a mixed hard-soft interaction, viz. N - CH₃ or H - P.

Drago and Wayland (125) have developed a double scale enthalpy equation, which has been discussed earlier, for correlating the enthalpies of Lewis acid-base interactions with parameters which correspond to Pearson's hard and soft character. An investigation using complexes of Me₃SnCl in solution (126) has shown that there is a good correlation between the parameters and ΔH° , and this would therefore appear to give some substance to Pearson's arguments. Indeed from a study of complex formation of metals in solution, Ahrlund (127) has concluded that the formation of complexes depends on the 'a' (hard) and 'b' (soft) character of the acceptor and ligand, and also that the entropy and enthalpy contributions toward the free energy of complex formation are influenced in different ways depending on whether the bonds formed are predominantly electrostatic or covalent. Ahrlund presumes that while ΔH° provides a good measure of the covalency, ΔS° is a function of the electrostatic interaction though prone to complications by factors such as solvation. He therefore concludes that the free energy of formation is the resultant of the interactions due to covalent and electrostatic contributions.

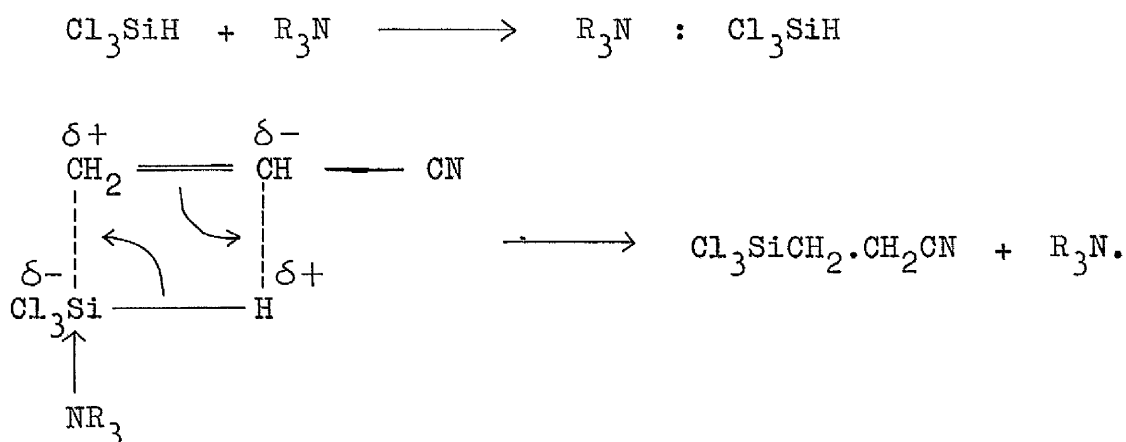
DISCUSSION

2.1. Introduction

The study of the hydrosilation reaction has been expanded in recent years because of its value in attaching to silicon, organic radicals which contain reactive, functional groups. Hydrosilation can be promoted thermally, by irradiation with ultraviolet light or γ -rays, or by the presence of peroxides, metal salts or tertiary bases. One commercial application of the reaction is the base-catalysed addition of silanes to olefinic hydrocarbons, and in particular the addition of trichlorosilane to acrylonitrile using a tertiary amine catalyst:



The efficiency of different amine catalysts has been studied by several workers (128, 129, 130) who have proposed a number of mechanisms to explain the role of the base in these reactions. One of these proposes the formation of a donor-acceptor complex, in which the function of the amine is to reverse the polarisation of the Si-H bond, or at least increase the electron density on the silicon atom. The mechanism can be envisaged as going through a four-centred cyclic transition state:



It is the scant knowledge of the nature of these silane-amine reaction intermediates, together with a general interest in complexes on the Lewis acid-base type, that has prompted the present work. The purpose of the research programme was to examine the Lewis acidity of a series of fluoroalkylsilanes towards selected amines, and the effect on complex stability of the position and degree of fluorine substitution in the alkyl group of the fluoroalkylsilanes.

The preparation and examination of the silane-amine complexes was initiated by Iles (131) and Cook (105), with the isolation of the 1:1 trimethylamine and 1:2 β -picoline complexes of 1,1,2,2-tetrafluoroethylsilanes ($X_3SiCF_2.CHF_2$; $X = H, Cl, F$). These compounds were prepared and characterised in vacuo and essentially the same techniques have been employed in this research, as described in the experimental section.

The necessity of using carefully dried amines is paramount and some considerable time was spent at the start of this work perfecting techniques for the preparation of rigorously anhydrous amines. Normal distillation techniques, including several redistillations and storage of the amine over freshly calcined molecular sieves or barium oxide, were found to be inadequate. The hygroscopic nature of pyridine and its methyl substituted analogues was found to be so extreme, that even on using freshly distilled samples of pyridine and γ -picoline, hydrogen chloride was liberated on contact with 2-fluoroethyl-trichlorosilane.

The seriousness of this problem can be seen by considering the following examples. The presence of only 20 p.p.m. of water by weight ($\sim 0.002\%$) in a sample of pyridine means a water molarity of $\sim 0.001M$. In carrying out titrations of silicon halides with pyridine, conductance curves have been obtained (85) which show remarkable resemblances to those found for the titration of pyridine with hydrogen halides, while, at $10^{-4}M$, only 2 p.p.m. of water makes the mole ratio of compound to water 1:1.

Consequently it was found necessary to use the "mutual drying" technique employed by Cook (105), whereby final traces of moisture are removed by condensing the amine in vacuo onto trichlorosilane. In all subsequent reactions this technique was found to yield satisfactory results.

The majority of investigations on silicon complexes have been confined to stoichiometric determinations, while only rarely have thermodynamic data been obtained. Hence one of the objectives of this research programme was to determine the thermodynamic functions of the isolable complexes with the hope of providing a quantitative means for comparing trends in

stability of the complexes with variation of the silanes and amines.

The fluoroalkylsilanes used in this study were:

2-fluoroethyltrichlorosilane	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{F}$
2,2-difluoroethyltrichlorosilane	$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$
2,2-difluoroethyltrifluorosilane	$\text{F}_3\text{SiCH}_2\text{CHF}_2$
1,2,2-trifluoroethyltrichlorosilane	$\text{Cl}_3\text{SiCHFCH}_2\text{CHF}_2$
1,2,2-trifluoroethyltrifluorosilane	$\text{F}_3\text{SiCHFCH}_2\text{CHF}_2$
1,2,2-trifluoroethylsilane	$\text{H}_3\text{SiCHFCH}_2\text{CHF}_2$
1,1,2,2-tetrafluoroethyltrichlorosilane	$\text{Cl}_3\text{SiCF}_2\text{CH}_2\text{CHF}_2$
1,1,2,2-tetrafluoroethyltrifluorosilane	$\text{F}_3\text{SiCF}_2\text{CH}_2\text{CHF}_2$
1,1,2,2-tetrafluoroethylsilane	$\text{H}_3\text{SiCF}_2\text{CH}_2\text{CHF}_2$
and trifluorosilane	F_3SiH

It was intended to gain information about the effect on the Lewis acidity of the silicon atom of introducing successive fluorine atoms into the ethyl chain, and about the comparative inductive and steric effects of hydrogen, chlorine and fluorine. Previous workers, with the exception of Cook (105), have limited their choice of silanes to halosilanes or halomethylsilanes; it was hoped that the present silanes would increase the complexes' solubility by a polarity factor.

It will be noted that only the trichloro- and trifluoro-derivatives of 2,2-difluoroethylsilane were chosen; 2,2-difluoroethylsilane, and 2-fluoroethyltrifluorosilane, decompose to the fluoro-olefin and corresponding silane during their preparation (132).

The amines chosen for study were:

trimethylamine
pyridine
 α -picoline
 β -picoline
 γ -picoline
2,2'-bipyridyl
and diazabicyclo-octane ("Dabco").

Pyridine and the picolines should demonstrate the effects of base strength and steric factors on complex stability, and it was hoped to make comparisons with the analogous complexes of trimethylboron (133). Trimethylamine exhibits a marked preference for the formation of 1:1 complexes; if this stoichiometry can be attained with silanes which contain no silicon-halogen bonds, and hence eliminate the possibility of halogen bridging, then further five co-ordinate silicon species might be isolated. The inclusion of 2,2'-bipyridyl and "Dabco" was to introduce a second donor site in the same molecule and to investigate the possibility of the ligand donating to two separate silicon atoms to form polymeric species.

2.2. Methods of Characterisation

The volatility of the silanes and amines meant that complex formation was studied most conveniently by a tensiometric method, using vapour pressure-molar composition isotherms to show directly the stoichiometry of a complex. Several workers have taken a mixture of the two reactants, and removed the excess component by distillation to discover the complex's stoichiometry (11, 14, 18). While this method has normally yielded satisfactory results, errors can be incurred during the removal of the excess component if the complex has a high vapour pressure. By working in vacuo, completely anhydrous conditions can be maintained. The use of greaseless taps throughout this work was found to be most satisfactory.

Vapour pressures were measured to 0.02mm. with the cathotometer and so the error was within the limits set by the principle of this method; i.e. the different volatilities of the two components. When using pyridine (v.p. = 10.2 mm. at 20°), for example, and the least volatile silane, 2-fluoroethyl-trichlorosilane (v.p. = 25.6mm. at 20°), the difference in vapour pressures was sufficiently large to make any error between successive readings negligible. The sharp increase in vapour pressure that occurred when the stoichiometric reaction was complete, was therefore readily detected and with acceptable accuracy.

The accuracy and significance of the tensiometric studies to obtain thermodynamic data will be discussed later.

2.3. Reactions of 2-Fluoroethyltrichlorosilane

2-Fluoroethyltrichlorosilane ($\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{F}$) was treated with trimethylamine, pyridine, α -picoline, β -picoline, and γ -picoline, and vapour pressure-molar composition measurements were made to study each reaction. No reaction was observed with trimethylamine and α -picoline; but the pyridine, β -picoline, and γ -picoline reactions did produce a small amount of white solid, but which could not be characterised. After a mole ratio of ca.0.2 (silane/amine) had been attained, the reaction pressures increased upon the additions of further silane until the saturation vapour pressure of the silane was reached.

The initial pressure in the trimethylamine reaction was 174.5 mm., and instead of the expected increase in pressure due to the addition of the silane, a small decrease was in fact observed, which on the addition of further silane tended to 165.5mm. No visible signs of complex (liquid or solid) were however observed.

The five reactions were repeated at -23° , but did not produce any results different from those obtained at room temperature. Reactions at lower temperatures were not attempted as this would have caused the solidification of the amine reagents.

2.4. Reactions of 2,2-Difluoroethyltrichlorosilane

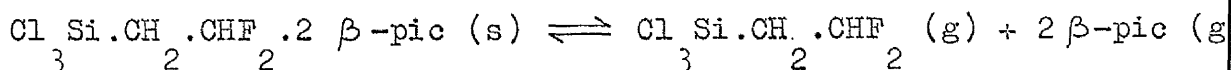
2,2-Difluoroethyltrichlorosilane ($\text{Cl}_3\text{SiCH}_2\text{CHF}_2$) was treated with trimethylamine, pyridine, α -picoline, β -picoline, and γ -picoline, and where complex formation occurred, the stoichiometry was determined from vapour pressure-molar composition measurements. Table 2.1. summarises the results.

Table 2.1.

<u>Amine</u>	<u>Stoichiometry</u>	<u>Comment</u>
Me ₃ N	-	No reaction at -23°
py	?	Not characterised at -23°
α-pic	-	No reaction at -23°
β-pic	1:2	isolable at -23°
γ-pic	1:2	isolable at -23°

Although at a temperature of -23°, the vapour pressures of both the amine (ca., 1mm. at -23°) and 2,2-difluoroethyltri-chlorosilane (ca., 16mm. at -23°) are considerably reduced, they are still sufficient to allow accurate stoichiometric determinations. Indeed both the β-picoline and γ-picoline systems clearly showed that reaction had occurred with the formation of a 1:2 (silane/amine) complex at -23°.

The isolation of the β-picoline and γ-picoline adducts permitted the calculation of thermodynamic quantities; e.g. ΔH, ΔG, ΔS. Because of the unstable nature of these adducts at room temperature, it was necessary to measure the dissociation vapour pressures at lower temperatures, and the range from -10° to +15° was selected for study. The evaluation of these thermodynamic quantities is based on the calculation of the equilibrium constant, K_p, from the dissociation vapour pressures. The derivation of K_p (see section 2.13.), for a 1:2 complex, e.g.,



assumes that each component behaves ideally, that there is complete dissociation in the gas phase, and also requires that one-third of the total pressure be exerted by the dissociated silane and that two-thirds of the total pressure be exerted by the dissociated amine. However a comparison of the vapour pressures of the complex and two amines at the experimental temperatures (Table 2.2.), shows clearly that the final condition for the amine is not satisfied; i.e. not all the uncomplexed amine

exists in the vapour phase, but partly in the liquid phase as

Table 2.2.

<u>Temp.</u>	<u>Saturation</u> <u>Vapour Pressure</u>		<u>Dissociation Vapour Pressure</u>	
	β -pic	γ -pic	$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$: <u>2 β-pic</u>	$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$: <u>2 γ-pic</u>
-10°	1.34mm.	1.41mm.	3.04mm.	2.76mm.
$+5^\circ$	2.28mm.	2.39mm.	6.29mm.	4.81mm.

well. Consequently, K_p does not equal $4P^3/27$ under these conditions.

The saturation vapour pressure of $\text{Cl}_3\text{Si.CH}_2.\text{CHF}_2$ at -10° is 16.4mm., and at $+5^\circ$ is 24.3mm. These do indicate that the silane is totally in the vapour phase and therefore the pressure exerted by the dissociated silane provides a means of measuring the equilibrium constant, for K_p becomes equal to p_{silane} (measured in atmospheres). It is assumed in the derivation that the dissociated silane neither dissolves in the undissociated complex nor forms a solution in the dissociated liquid phase amine. The measured heats of dissociation are given in Table 2.3.

Table 2.3.

	<u>ΔH meas'd</u> <u>kcal.mole⁻¹</u>	<u>Latent heat of</u> <u>vapn. of amine</u> <u>kcal.mole⁻¹</u>	<u>ΔH calc'd</u> <u>kcal.mole⁻¹</u>
$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$:2 β -pic	2.74	9.34	21.42
$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$:2 γ -pic	3.57	9.37	22.31

However this measured enthalpy change gives only the energy associated with the silane on complexation. To obtain the enthalpy change incurred when one mole of silane complexes with two moles of amine, it is necessary to allow for the latent heat of vaporisation of the amine (134), as reaction occurs in the gas phase (See section 1.10.) and the compensated heats of formation are given in Table 2.3.

The heats of dissociation show that γ -picoline forms the more stable adduct, and this gives the same order of stability as was found for the complexes of trimethylboron (133) and trichlorosilane (105).

2.5. Reactions of 2,2-Difluoroethyltrifluorosilane

The reactions of 2,2-difluoroethyltrifluorosilane ($\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2$) were investigated using trimethylamine, pyridine, α -picoline, β -picoline, and γ -picoline as Lewis bases. Preliminary investigations showed that this silane decomposed, with the liberation of vinyl fluoride as well as undergoing complexation. In this discussion, it is intended to consider these reactions in three sections, these sections being determined by what is thought to be the degree and mechanism of reaction:

- (i) the reactions of pyridine, β -picoline, and γ -picoline
- (ii) the reaction of α -picoline,
- and (iii) the reaction of trimethylamine.

(i) Reactions of Pyridine, β -Picoline, and γ -Picoline

Preliminary investigations showed that on treating $\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2$ with aliquots of pyridine, β -picoline, and γ -picoline the formation of a white solid was accompanied by the liberation of a low boiling gas which was shown to be vinyl fluoride by infrared spectroscopy and molecular weight determination. The liberation of vinyl fluoride was instantaneous and was complete after about 30 minutes.

The reactions were repeated quantitatively to determine the amount of vinyl fluoride formed. Reactions were carried out in a calibrated reaction vessel and pressure changes measured with a cathotometer. Allowance was made for the vapour pressure of the amine, and the volume of gas corrected to S.T.P. The amounts of vinyl fluoride liberated are given

in Table 2.4., expressed as a percentage of the amount of silane used. It was noticed that reaction was somewhat less than 100%; on repeating the experiments, the data were reproducible to within 0.5%. It was found that on removing the vinyl

Table 2.4.

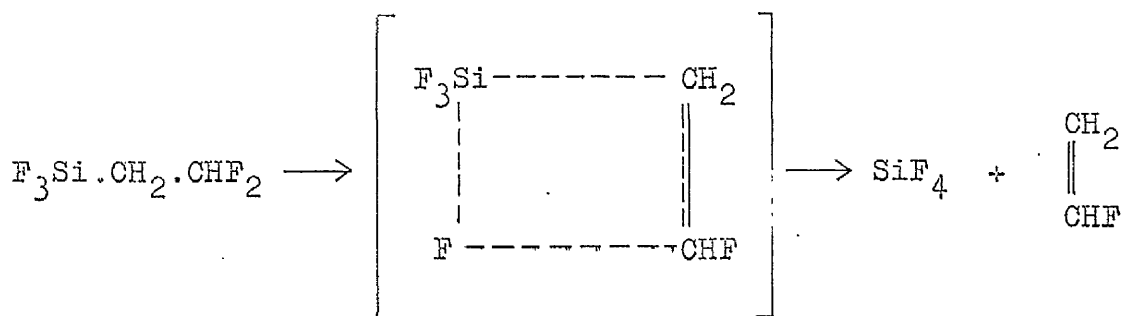
<u>Amine</u>	<u>% CH₂ = CHF</u> <u>liberated</u>	<u>% CH₂ = CHF on</u> <u>warming to 65°</u>	<u>pK_a</u> <u>amine</u>
py	92.5	7.3	5.20
β-pic	94.0	5.6	5.66
γ-pic	95.9	4.0	6.05

fluoride, the residual olefin could be obtained by warming the reaction mixture to ca. 65°.

It is perhaps worthwhile noting at this point that there appears to be some correlation between the amine base strength (pK_a) and the extent of initial decomposition. Too much significance should not perhaps be attached to this point, as the difference between the three decomposition figures is not large.

The decomposition of 2,2-difluoroethyltrifluorosilane is not a new phenomenon; indeed studies of the kinetics of the pyrolysis of fluoroalkylsilanes in which fluorine is present in the α, β, or γ positions in the fluoroalkyl chain have confirmed three distinct types of mechanism for the decomposition of the α (135), β (132,135,136,137) and γ (135) substituted compounds.

For fluoroalkylsilanes where a β-fluorine, but no α-, or γ-fluorine is present (viz., 2,2-difluoroethyltrifluorosilane (136) or 2-fluoroethyltrifluorosilane (132), it is proposed that the mechanism of β-elimination proceeds via a 4-centred transition state, the process (Fig. 2.1.) being unimolecular. The studies on F₃Si.CH₂.CHF₂ were carried out

Fig. 2.1.

between 151° and 221° , and it would appear that decomposition is appreciable only at these elevated temperatures as the process is negligible at room temperature (132); indeed none was observed in this work on storing the silane for periods of up to 6 weeks. It would appear therefore that the decomposition of $\text{F}_3\text{Si} \cdot \text{CH}_2 \cdot \text{CHF}_2$ encountered in this work is to some extent "catalysed" by the presence of a base. Indeed, some analogy might be drawn with the process whereby fluoroalkylsilanes are hydrolysed by dilute hydroxide solutions to yield the corresponding fluoro-olefin and either silica or siloxane polymer.

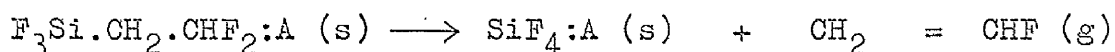
The stoichiometric studies indicate that reaction between $\text{F}_3\text{Si} \cdot \text{CH}_2 \cdot \text{CHF}_2$ and pyridine, β -picoline, and γ -picoline, involves one mole of silane and two moles of amine. As the silane is stable at room temperature, it is reasonable to assume that it is the co-ordination of one or both moles of amine that precipitates the decomposition. The initial co-ordination of both moles of amine is highly improbable as this would produce a six co-ordinate silicon which would have to increase its co-ordination to seven to proceed via the 4-centred transition state; seven co-ordinate silicon is, as yet, unknown.

It is more reasonable to assume the co-ordination of only one mole of amine, thus involving a six co-ordinate silicon atom in the transition state. The decomposition could then proceed via the postulated mechanism to produce vinyl fluoride and SiF_4 : A (where A denotes the amine); the latter could then co-ordinate the second mole of amine to achieve the maximum covalency of six.

Kinetic studies (135) on the decomposition of $\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2$ and $\text{Me}_3\text{Si}.\text{CH}_2.\text{CHF}_2$ have shown that replacement of fluorine by a methyl group causes a marked decrease in the rate of decomposition. This has been attributed to electron release by the methyl group to the silicon atom, making silicon less electropositive and less susceptible to attack by the β -fluorine. The co-ordination of the amine to the silane is effectively an electron donation process and would therefore not be expected to "catalyse" the decomposition; but in view of the different co-ordinations in the transition states, is difficult to rule out electronic effects entirely. The decomposition can however be rationalised more satisfactorily if steric effects are considered. The decomposition is effected by the electrostatic attraction between the silicon and the terminal β -fluorine. The orientation of the fluoroethyl group is such that there is one position, assuming free rotation about the carbon linkages, at which the

β —fluorine is adjacent to the silicon and decomposition can proceed with the formation of the 4-centred transition state. The presence of the co-ordinated amine might be expected to force the fluoroalkyl group into this position and hence facilitate the decomposition.

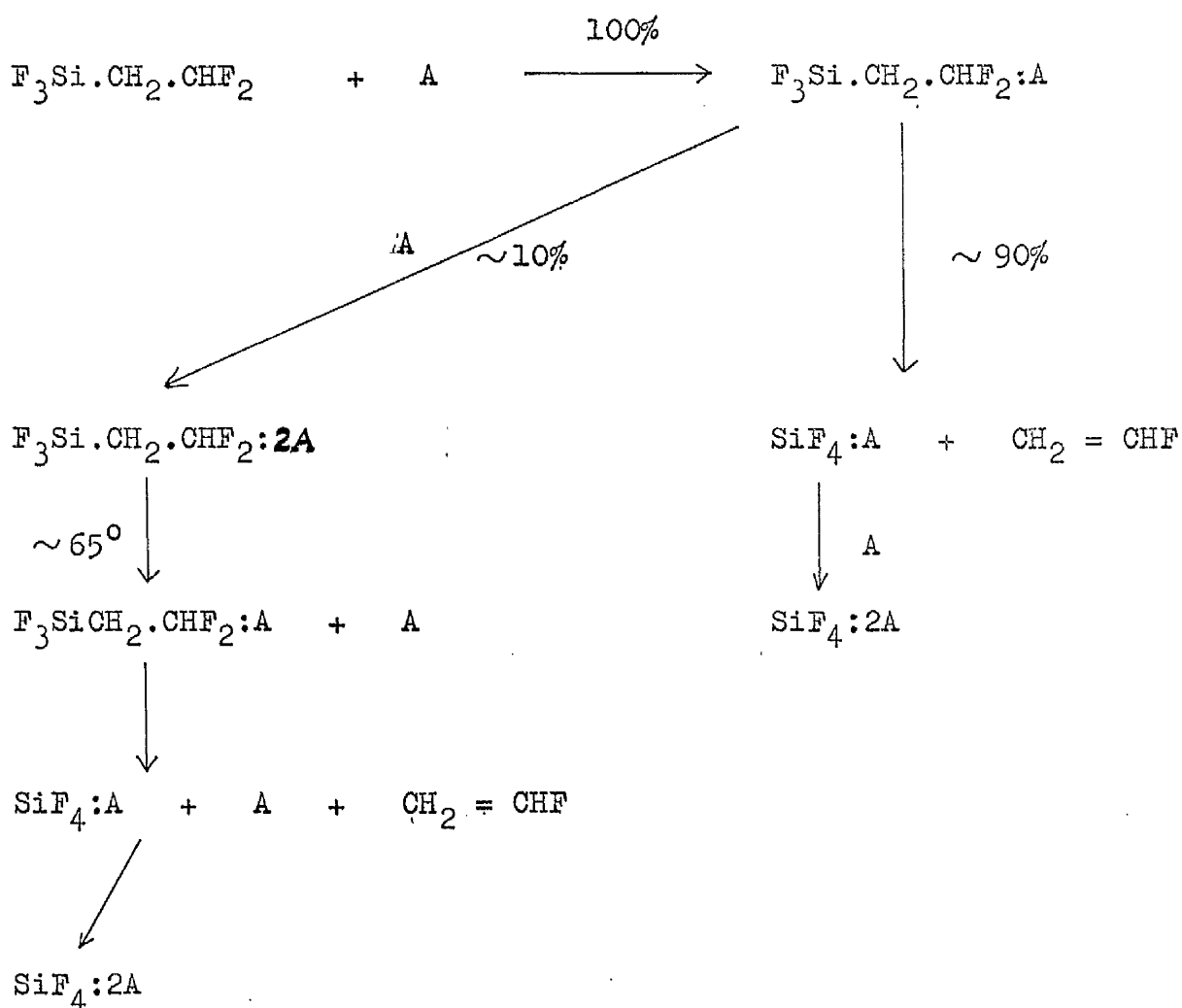
In view of this, decomposition might be expected to be quantitative; however, this was not found to be so. The stoichiometric studies showed that although some vinyl fluoride was formed immediately, the decomposition proceeded for about 30 minutes. During this decomposition step in the reaction,



both $\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2:\text{A}$ and $\text{SiF}_4:\text{A}$ would be expected to compete for the second mole of amine. The formation of $\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2:2\text{A}$ in this way would prevent further decomposition for two reasons. First, further decomposition would require the formation of a seven co-ordinate silicon in the transition state. And secondly, the steric grouping around silicon would prevent the approach of silicon and the terminal β -fluorine atoms. This yields the

reaction scheme shown in Figure 2.2.

Fig. 2.2.



A = pyridine,
 β -picoline,
 or γ -picoline.

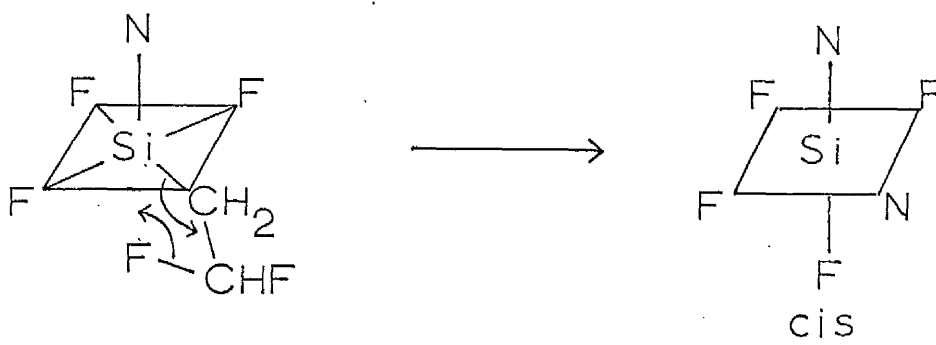
With the formation of a six co-ordinate silicon in the transition state, it is apparent that the relative positions of the two amine molecules are of some interest, as they give rise to cis-trans isomerism. The different arrangements in the transition state are shown in Figure 2.3., together with the isomers that result on co-ordination of the second molecule, if co-ordination of the second amine molecule occurred before the transition state returned to a five co-ordinate trigonal

Figure 2.3.

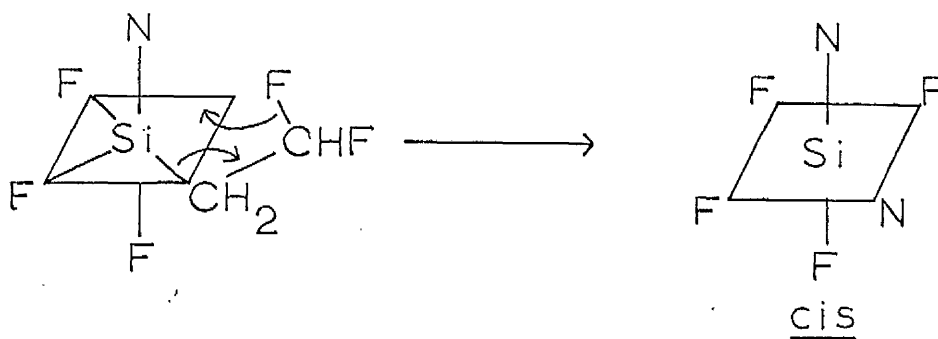
The isomers of $\text{F}_3\text{SiCH}_2\text{CHF}_2$:A in the transition state, together with the resultant isomers.

(N = pyridine, β -, or γ -picoline)

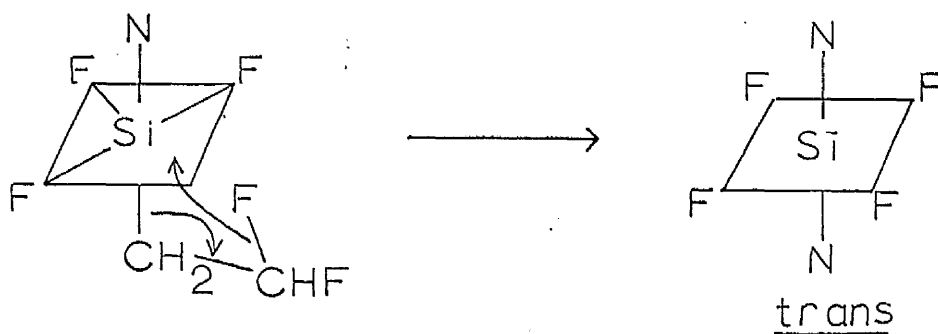
(a)



(b)



(c)



bipyramidal structure. This problem would best be resolved by n.m.r. spectroscopy, but the insolubility of the 1:2 pyridine, β -picoline, and γ -picoline complexes of SiF_4 meant that structural investigations were limited to their infrared spectra. The infrared spectra were obtained for these adducts, but an absolute assignment of bands is made difficult by the coincidence of Si-F stretching vibrations with those of the ligand. The principal bands of the recorded spectrum of $\text{SiF}_4:2\text{py}$ are in good agreement with those reported in the literature (13, 89, 106), and a trans configuration has been proposed for the complex. This assignment is based on the simplicity of the spectrum, and a single Si-F band at 803cm^{-1} .

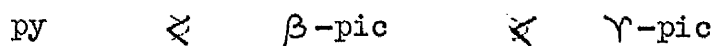
Likewise, it is difficult to make categorical assignments to the bands in the spectra of $\text{SiF}_4:2\beta$ -picoline and $\text{SiF}_4:2\gamma$ -picoline. But the bands at 829cm^{-1} in the former and at 820cm^{-1} in the latter might be considered to be Si-F stretching vibrations. Other bands in this region are associated with the amine. Indeed, there is little apparent reason why the structure of the β -picoline and γ -picoline adducts should differ in stereochemistry from the pyridine analogue.

Tensiometric studies were carried out on the solid adducts obtained after heating to 65° in vacuo. The dissociation of the complexes was found to be reversible and no vinyl fluoride was detected at the end of the measurements. From these studies the heats of dissociation were calculated and are tabulated below.

Table 2.5.

<u>Complex</u>	<u>ΔH kcal.mole⁻¹</u>
$\text{SiF}_4:2\text{py}$	28.73
$\text{SiF}_4:2\beta\text{-pic}$	32.80
$\text{SiF}_4:2\gamma\text{-pic}$	36.42

The value obtained for $\text{SiF}_4:2\text{py}$ is in good agreement with a previous report (12) of $29.01\text{ kcal.mole}^{-1}$. The order of heats of dissociation demonstrates the order of Lewis basicity predicted by pK_a and hyperconjugation theories; i.e.,



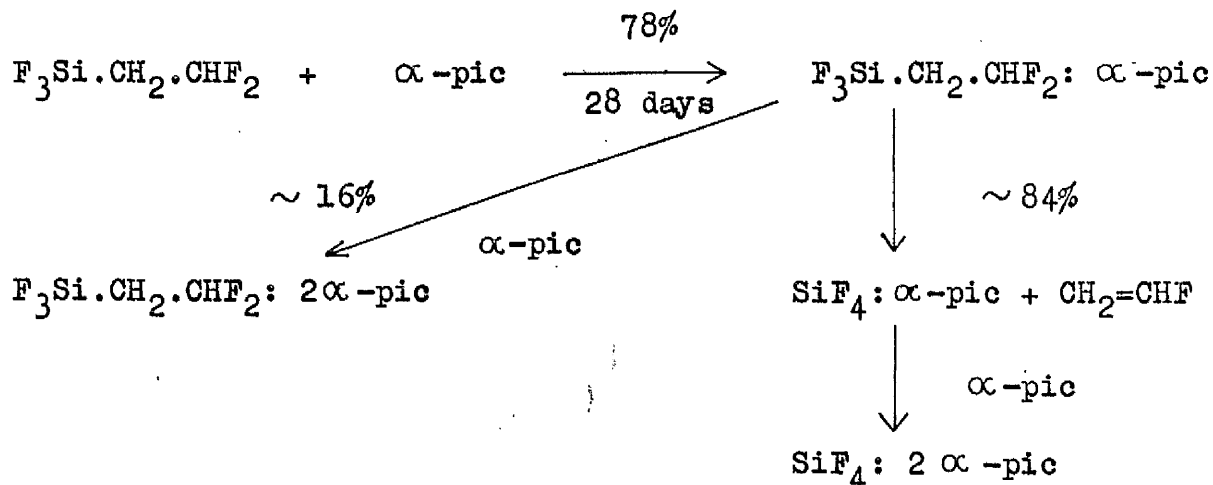
(ii) The Reaction of α -Picoline

A preliminary study of the reaction between 2,2-difluoroethyltrifluorosilane and α -picoline showed that reaction was slow, and that only a small amount ($<10\%$) of vinyl fluoride was liberated after 48 hours.

A separate experiment was carried out in a sealed tube using 0.315 mmole. of $\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2$ and 0.630 mmole. of α -picoline (mole ratio = 0.5). After 28 days in the dark, an analysis of the products showed that 0.069 mmole of silane remained (equivalent to 22%) and that 0.207 mmole. of vinyl fluoride had been produced (equivalent to 84% of the reacted silane.)

It is reasonable to assume that reaction has occurred by a mechanism similar to that discussed for the pyridine, β -picoline and γ -picoline reactions, and therefore it can be assumed that 78% of the silane had reacted after 28 days. Of this 78% of complexed silane, the amount of vinyl fluoride liberated indicates that 84% had decomposed. This produces a reaction scheme as described by Figure 2.4.

Fig. 2.4.



The slow initial reaction can be attributed to the large steric effect of the methyl group in the 2-position. Once the intermediate, $\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2 : \alpha\text{-pic}$, has been formed, only 84% decomposition occurred. This would appear to be in agreement with the proposal in Section 2.5.(i) that there is a correlation between the degree of decomposition and base strength. α -picoline, due to the position of the methyl group, cannot act as effectively as the more sterically favoured pyridine, β -picoline and γ -picoline.

(iii) The Reaction of Trimethylamine

An initial reaction using equimolar amounts of 2,2-difluoroethyltrifluorosilane and trimethylamine led to the formation of a small amount of white solid. Considerable amounts of silane and amine were still present, however, as shown by infrared spectroscopy. After 2 days, the infrared spectrum of the vapour phase showed that no trimethylamine remained, but that small amounts of the silane and vinyl fluoride were present.

As reaction appeared to be slow, two sealed tube reactions were carried out using equimolar mixtures of 2,2-difluoroethyltrifluorosilane and trimethylamine. The vapour phases were analysed after 3 days and 8 days, and the results are tabulated in Table 2.6. (Products are expressed as % of the silane taken).

Table 2.6.

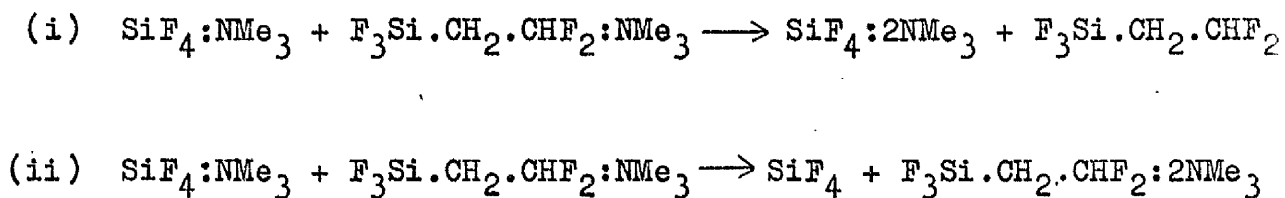
<u>Product</u>	<u>3 Days</u>	<u>8 Days</u>
$\text{CH}_2 = \text{CHF}$	21%	43%
$\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2$	19%	39%

The formation of a white solid and liberation of vinyl fluoride indicate that reaction has occurred. From the initial study, it is evident that the trimethylamine reacts totally and prior to the liberation of the bulk of the vinyl fluoride. The most likely reaction that can have occurred during the initial process is the formation of the adduct, $\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2 : \text{NMe}_3$. A 1:1 adduct is formulated rather than a 1:2 adduct

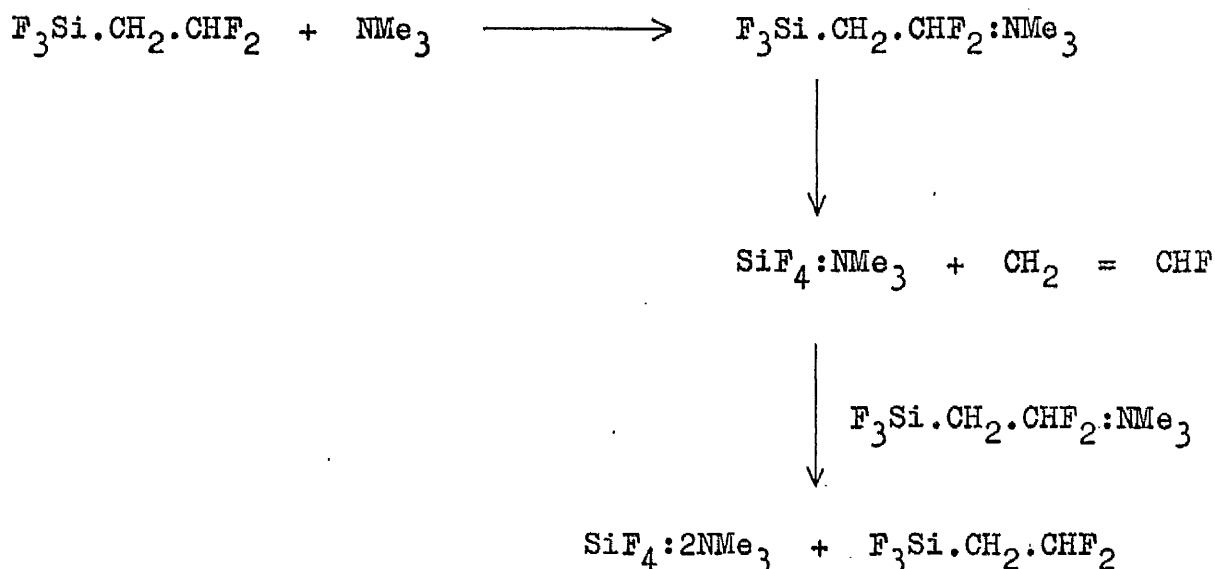
in view of the preference trimethylamine has for this co-ordination in similar systems; e.g., $X_3SiCF_2CHF_2$ (105).

The formation of vinyl fluoride means that decomposition of the silane has occurred. It has been proposed that the co-ordination of one mole of amine (e.g., pyridine, β -picoline, and γ -picoline in Section 2.5.(i)) causes decomposition via a 4-centred transition state. Since trimethylamine is a stronger base ($pK_a = 10.72$) than the other amines considered (pK_a from 5.20 to 6.05), there is no reason to suppose that the 1:1 adduct decomposes to $SiF_4:NMe_3$ and vinyl fluoride by an alternative mechanism. However, despite the high pK_a value for trimethylamine, the large steric considerations of trimethylamine will probably account for the slow rate of decomposition.

However, this does not account for the presence of a considerable amount of $F_3Si.CH_2.CHF_2$ in the reaction products. SiF_4 is capable of co-ordinating two moles of trimethylamine to form $SiF_4.2NMe_3$ (80). Once decomposition of the $F_3Si.CH_2.CHF_2:NMe_3$ intermediate has started, $SiF_4:NMe_3$ will be present and there is the possibility of the following ligand transfer reactions occurring:



The presence of $F_3Si.CH_2.CHF_2$ and not SiF_4 in the reaction products indicates that the former transfer is predominant. This transfer is also the more thermodynamically favoured. Although no data are available for $F_3Si.CH_2.CHF_2$, there are some for the stronger Lewis acid, $F_3Si.CHF.CHF_2$; the heats of dissociation for the β -picoline and γ -picoline adducts of $F_3Si.CHF.CHF_2$ (32.68 and 34.46 kcal.mole⁻¹) indicate that those of SiF_4 are the stronger (32.80 and 35.86 kcal.mole⁻¹). By inference therefore, SiF_4 is a stronger acceptor than $F_3Si.CH_2.CHF_2$ and would be expected to remove trimethylamine from the intermediate complex, or its dissociated form as it will undoubtedly have a dissociation vapour pressure. The proposed overall mechanism is shown in Figure 2.5.

Fig.2.5.

By this mechanism, equimolar amounts of vinyl fluoride and silane would be expected when the reaction has gone to completion. But during the reaction, the amount of vinyl fluoride would be expected to be the larger as its formation preceeds the production of $\text{F}_3\text{SiCH}_2\text{CHF}_2$; the reaction figures for 3 days and 8 days do indeed appear to confirm this.

It will be noted that in the proposed mechanism, the first intermediate involves a five co-ordinate silicon species, and two further reactions were carried out, only at lower temperatures, with the intention of isolating this species by reducing the rate of decomposition of the complex. The results are given in Table 2.7.

Table 2.7.

<u>Product</u>	<u>28 Days at -10°</u>	<u>28 Days at -23°</u>
$\text{CH}_2 = \text{CHF}$	43%	23%
$\text{F}_3\text{SiCH}_2\text{CHF}_2$	35%	13%

The fact that vinyl fluoride has been formed indicated that the required intermediate had decomposed to some extent; but the analysis figures do illustrate certain points in the

postulated mechanism, assuming an identical mechanism at the lower temperature.

The fact that approximately the same amount of vinyl fluoride is produced after 28 days at -23° as after only 8 days at room temperature, would seem to indicate that the decomposition of the silane is temperature dependent, as might be expected from the kinetic studies on the decomposition of $\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2$ (136).

A further feature of these low temperature reactions is that there is a significant difference between the amounts of silane and vinyl fluoride produced (almost 50% at -23°), whereas at room temperature the amounts produced differ only slightly. This would be expected if the step involving ligand transfer from $\text{F}_3\text{Si}.\text{CH}_2.\text{CHF}_2:\text{NMe}_3$ to $\text{SiF}_4:\text{NMe}_3$ occurred in the gas phase where both complexes are presumably dissociated species; the dissociation vapour pressure is known to be temperature dependent.

2.6. Reactions of 1,2,2-Trifluoroethyltrichlorosilane

1,2,2-Trifluoroethyltrichlorosilane ($\text{Cl}_3\text{Si}.\text{CHF}.\text{CHF}_2$) was treated with trimethylamine, pyridine, α -picoline, β -picoline and γ -picoline. Two further reactions were also attempted using 2,2'-bipyridyl and diazabicyclo-octane ("Dabco"), which will be considered later. The results of the reactions are summarised in Table 2.8.

Table 2.8.

<u>Amine</u>	<u>Stoichiometry</u>	<u>Comment</u>
Me ₃ N	no adduct	at -23°
pyridine	not characterised	"
α-picoline	no adduct	"
β-picoline	1:2	} Stable at room temperature
γ-picoline	1:2	

It will be seen that although there was some evidence of reaction with pyridine at -23°, only the 1:2 adducts of α-β-picoline and γ-picoline were stable enough to be characterised at room temperature.

Tensiometric studies were completed on these two isolable adducts, and the heats of dissociation in Table 2.9. show that the γ-picoline adduct was the more stable.

Table 2.9.

<u>Complex</u>	<u>ΔH kcal.mole⁻¹</u>
Cl ₃ Si.CHF.CHF ₂ :2 β-pic	28.23
Cl ₃ Si.CHF.CHF ₂ :2 γ-pic	31.87

The vapour pressures measured in the tensiometric studies indicate that both the silane and amine were totally in the vapour phase; i.e., the saturation vapour pressure of Cl₃Si.CHF.CHF₂ > 1/3 measured pressure, and the amines' saturation vapour pressures > 2/3 measured pressure. Therefore no corrections were necessary for the measured pressures, and K_p was equal to $4p^3/27$.

The infrared spectra of both the isolable complexes were recorded. Great difficulty was experienced in the preparation of the mulls, the solids being very hard. The spectra that were obtained indicated that some hydrolysis had occurred during the recording time. Broad bands were found between

3.5 and 4.2 μ , and 9.0 and 10.2 μ , the former being coincident with NH^+ stretching vibrations in the amine hydrochloride and the latter with Si-O-Si stretching vibrations.

Two additional reactions were undertaken, with two solid amines, 2,2'-bipyridyl and "Dabco". As both ligands contain two donor sites, the possibility arises that they need not co-ordinate to the same acceptor. If this were so, the resultant structure could be a dimer, or a long chain polymer with bridging amine molecules.

The stoichiometric studies used the standard techniques employed elsewhere in this work. Both studies indicate that some reaction occurred, but the reaction pressures do not indicate the stoichiometry of any product. The problem in using a solid reagent is that reaction need only occur at the surface layer of the sample and the top layer of the product thus formed would prevent further reaction. Therefore more meaningful results might be obtained if these two reactions were repeated in solution.

2.7. Reactions of 1,2,2-Trifluoroethyltrifluorosilane

1,2,2-Trifluoroethyltrifluorosilane ($\text{F}_3\text{Si}.\text{CHF}.\text{CHF}_2$) was treated with β -picoline and γ -picoline. Both reactions yielded a 1:2 adduct isolable at room temperature. Tensiometric studies were carried out on the two complexes and the heats of dissociation are given in Table 2.10.

Table 2.10.

<u>Adduct</u>	<u>$\Delta H \text{ kcal.mole}^{-1}$</u>	<u>Dissociation Vapour Pressure</u>
$\text{F}_3\text{SiCHFCHF}_2:$ 2 β -pic	32.68	4.91mm./25°
$\text{F}_3\text{SiCHFCHF}_2:$ 2 γ -pic	34.46	3.99mm./25°

The heats of dissociation and the dissociation vapour pressures show that γ -picoline forms the more stable adduct. There is an increase in the stability of both adducts compared to the corresponding adducts of $\text{Cl}_3\text{Si}.\text{CHF}.\text{CHF}_2$. This increase is to be expected in view of the more favourable inductive and steric effects of the Si-F bond relative to the Si-Cl bond.

The insolubility of the two complexes prevented the recording of their n.m.r. spectra. The infrared spectra were however obtained. The formation of a 1:2 adduct should give an octahedral silicon environment, with either a cis or a trans configuration. The bands at 810cm^{-1} . in the β -picoline adduct and at 826cm^{-1} . in the γ -picoline adduct could be assigned to $\nu_{\text{Si-F}}$, other bands in this region being due to the amine molecules. The presence of a single Si-F absorption would be consistent with the trans isomer, but such an assignment is only tentative in the absence of more definite structural data.

2.8. Reactions of 1,2,2-Trifluoroethylsilane

When investigating some reactions of 1,1,2,2-tetrafluoroethylsilane, Cook (105) found that β -picoline formed a stable 1:2 adduct and trimethylamine a stable 1:1 adduct. The fact that these adducts were liquids was their most remarkable feature, and enabled the use of n.m.r. spectroscopy for structural analysis. By using 1,2,2-trifluoroethylsilane ($\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2$), it was hoped that further structural data could be obtained.

The reactions of 1,2,2-trifluoroethylsilane with trimethylamine, β -picoline and γ -picoline were investigated and the results are summarised in Table 2.11. Little or no reaction was found with the two picolines at room temperature. By lowering the temperature to -23° , the volume of liquid in the reaction vessel appeared to increase as the reaction proceeded; indeed the reaction pressures indicated that some reaction had occurred. But the adduct was not sufficiently stable to be characterised.

Table 2.11.

<u>Amine</u>	<u>Stoichiometry</u>	<u>Comment</u>
Me ₃ N	1:1	Stable at -23°
β-picoline	not characterised	at -23°
γ-picoline	not characterised	at -23°

With trimethylamine, some reaction was observed at room temperature but the pressure measurements showed that the complex had too high a dissociation vapour pressure at room temperature. At -23°, however, the liquid complex was found to have a 1:1 stoichiometry.

A tensiometric study was completed on the trimethylamine adduct and the measurements showed that from -40° to +5°, both the dissociated components were in the vapour phase. The equilibrium constant, K_p , was therefore equal to $P^2/4$ for the dissociation of a 1:1 complex. The dissociation vapour pressure and calculated heat of dissociation are recorded in Table 2.12. The data reflect the lower stability of the H₃Si.CHF.CHF₂ adduct when compared to that of H₃Si.CF₂.CHF₂

Table 2.12.

<u>Complex</u>	<u>ΔH kcal.mole⁻¹.</u>	<u>Dissociation Vapour Pressure</u>
H ₃ Si.CHF.CHF ₂ :NMe ₃	-11.8	120mm./0°
H ₃ Si.CF ₂ .CHF ₂ :NMe ₃	-15.3	37mm./2°

and can be attributed to the inductive effect of the α-CF₂ group in H₃SiCF₂CHF₂ which increased the Lewis acidity of the silane.

These results were perhaps to be expected; but what is worth noting in the reactions of H₃Si.CHF.CHF₂ is that trimethylamine has formed a stable adduct whereas β-picoline and γ-picoline have not. The reactions of Cl₃Si.CH₂.CHF₂ and

$\text{Cl}_3\text{Si}.\text{CHF}.\text{CHF}_2$, reported in this work, have resulted in the formation of 1:2 β -picoline and γ -picoline adducts but not in the formation of an isolable trimethylamine complex, and this has been attributed to the difference in steric factors. The presence of three methyl groups bonded to nitrogen means that steric interaction between the amine and silane will be considerable. In the picolines, where nitrogen is sp^2 hybridised, there are only two bonds, and both are orientated behind the nitrogen atom by the requirements of the ring structure. But evidently with $\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2$, steric factors alone do not determine complex stability. Although replacement of the SiCl_3 group by the smaller SiH_3 group will reduce the electro-positive character of the silicon, steric influences have been reduced to a minimum. It is possible therefore that with this reduction in steric interaction, complex stability becomes more a function of base strength. A comparison of pK_a values shows that the order is in agreement with that found.

<u>Amine</u>	<u>pK_a</u>
Me_3N	10.72
β -picoline	6.05
γ -picoline	5.66

The very high dissociation vapour pressure (120mm./ 0°) of $\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2:\text{NMe}_3$ meant that an infrared spectrum was impracticable by conventional methods.

As the complex, $\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2:\text{NMe}_3$, was a liquid at -23° , it could be examined directly by n.m.r. spectroscopy without the added complication of a solvent in which dissociation or decomposition might occur.

The line pattern of the ^1H spectrum was very similar to that of $\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2$ apart from the extra Me_3N singlet. There was a small change in chemical shift to lower field for the silyl resonances. Table 2.13. compares the coupling constants and chemical shifts of $\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2$ and $\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2:\text{NMe}_3$.

Table 2.13.

<u>Chemical Shift(ppm)</u>	<u>H₃Si.CHF.CHF₂</u>	<u>H₃Si.CHF.CHF₂:NMe₃</u>
¹ H(from bz)		
-CHF ₂	+1.02	+1.00
-CHF-	+2.37	+2.30
-SiH ₃	+3.18	+3.31
¹⁹ F(from TFA)		
-CHF ₂	+48.8	+ 46.0
-CHF-	+160.4	+ 154.2
<u>Coupling Constants</u>		
c.p.s.		
J _{βF - βH}	56.5	55.3
J _{βF - αH}	18.9	16.9

The ¹⁹F spectrum contained the expected two resonances, but due to inadequate resolution, the fine splitting of both resonances was not observed. There was, however, a similarity between the line patterns of the complexed and free silanes. The apparent doublet of triplets for the α-CHF group (Fig.3.8.) in H₃Si.CHF.CHF₂:NMe₃ is similar to the overall appearance for the same resonance in H₃Si.CHF.CHF₂ (Fig.3.5.), while the inadequate resolution of the β-CHF₂ group caused the bands in H₃Si.CHF.CHF₂:NMe₃ to coalesce (Fig.3.9.) and give only an outline similarity to that of H₃Si.CHF.CHF₂ (Fig.3.6.). There was also a slight reduction in J_{βF-βH} and J_{βF-αH} on complexation.

However the major differences between the spectra of the complex and the silane were the changes in the fluorine chemical shifts; α-CHF was shifted to lower field by 6.2 p.p.m. and the β-CHF₂ was shifted 2.6 p.p.m. on complex formation. The truly remarkable feature of these data are that the fluorine resonances have been shifted to lower field, whereas a shift to higher field, as found in H₃Si.CF₂.CHF₂:NMe₃ (105), would have been expected since the donation of

electrons from donor to acceptor should increase the electron density and nuclear shielding around the fluorine nuclei. This variance of results is difficult to rationalise.

In view of the similarity of $\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2$ and $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ it would be tempting to assign the same five co-ordinate structure to $\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2.\text{NMe}_3$ as was assigned to $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2.\text{NMe}_3$ (105). This analogy is probably correct, although no explanation can be offered for the anomalous ^{19}F chemical shifts.

The ^1H and ^{19}F spectra of $\text{H}_3\text{Si}.\text{CHF}.\text{CHF}_2.\text{NMe}_3$ were recorded at -20° , 0° and $+20^\circ$, but apart from a small loss of resolution at the lower temperatures, no changes in the spectra were detected. This would appear to suggest that if ligand or proton exchange is occurring, the rate of exchange is still greater than $1/3$ sec. at -20° .

2.9. Reactions of 1,1,2,2-Tetrafluoroethyltrichlorosilane

Some reactions of 1,1,2,2-tetrafluoroethyltrichlorosilane ($\text{Cl}_3\text{Si}.\text{CF}_2.\text{CHF}_2$) have been reported previously (105). The purpose of this study was to obtain thermodynamic data for the 1:2 β -picoline and γ -picoline adducts. Tensiometric studies were completed and the results are shown in Table 2.14.

Table 2.14.

<u>Complex</u>	<u>Vapour Pressure</u> <u>mm./25°</u>	<u>ΔH</u> <u>kcal.mole⁻¹</u>
$\text{Cl}_3\text{SiCF}_2\text{CHF}_2.2\beta\text{-pic}$	2.12	30.71
$\text{Cl}_3\text{SiCF}_2.\text{CHF}_2.2\gamma\text{-pic}$	2.57	34.28

It is perhaps worthwhile noting the volatilities of the two complexes. The γ -picoline complex has the higher vapour pressure at 25° , whereas for the other silanes studied in this work, the β -picoline complex has the higher vapour pressure.

The heats of dissociation however, show that the γ -picoline complex is the more stable. It would appear therefore that these two adducts of $\text{Cl}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ are at variance with the empirical rule (121) that of two addition compounds of closely similar structure and molecular weight, the less stable exhibits the higher saturation vapour pressure.

2.10. Reactions of 1,1,2,2-Tetrafluoroethyltrifluorosilane

1,1,2,2-Tetrafluoroethyltrifluorosilane ($\text{F}_3\text{Si}.\text{CF}_2.\text{CHF}_2$) was treated with α -picoline, γ -picoline and pyridine and the results are summarised in Table 2.15.

Table 2.15.

<u>Amine</u>	<u>Stoichiometry</u>	<u>Comment</u>
pyridine	1:2	white solid
α -picoline	not characterised	white solid
β -picoline	1:2 (105)	white solid
γ -picoline	1:2	white solid
Me_3N	1:1 (105)	white solid

The ability of this silane to function as a relatively strong Lewis acid is shown by the reaction with α -picoline. Although the white solid formed was not characterised, the significance of this result is that partial reaction occurred, for no complexation at all was detected with $\text{Cl}_3\text{Si}.\text{CH}_2.\text{CH}_2\text{F}$, $\text{Cl}_3\text{Si}.\text{CH}_2\text{CHF}_2$, $\text{Cl}_3\text{Si}.\text{CHF}.\text{CHF}_2$ and $\text{F}_3\text{Si}.\text{CHF}.\text{CHF}_2$. The characterisation of the pyridine adduct is further evidence of the strong Lewis acidity of this silane. This strength can be attributed to the highly electropositive nature of the silicon produced by the fluorine ligands and the fluoroalkyl group, and the relatively low steric interaction of the SiF_3 group.

Tensiometric studies on the pyridine, β -picoline, and γ -picoline adducts yielded the data recorded in Table 2.16.

Table 2.16.

<u>Complex</u>	<u>ΔH</u> <u>kcal.mole⁻¹</u>	<u>Vapour Pressure</u> <u>mm./25°</u>
F ₃ SiCF ₂ CHF ₂ .2py	31.87	2.53
F ₃ SiCF ₂ CHF ₂ .2 β -pic	38.49	1.37
F ₃ SiCF ₂ CHF ₂ .2 γ -pic	39.60	1.17

These data, together with the partial reaction of α -picoline, provide the most complete evidence for the order of Lewis basicity of the amines; i.e.,



As was previously observed for the β -picoline adduct (105) great difficulty was experienced in the recording of the infrared spectra of the pyridine and γ -picoline adducts. The solids were very hard and it proved difficult to obtain efficient mulls. Poor resolution resulted in both spectra. There was no band at 1016cm⁻¹. due to ν_{SiF} in F₃Si.CF₂.CHF₂, but there were bands of medium intensity at 980cm⁻¹. in both spectra that could not be associated with any ligand vibrations. The appearance of these bands at 980cm⁻¹. might be due to $\nu_{\text{Si-F}}$ being shifted to lower frequencies. The band at 996cm⁻¹. in the β -picoline adduct has been similarly assigned (105).

The insolubility of these complexes prevented any n.m.r. spectra being obtained.

2.11. Reactions of 1,1,2,2-Tetrafluoroethylsilane

1,1,2,2-Tetrafluoroethylsilane ($\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$) was treated with pyridine, α -picoline and γ -picoline, and the results of these additions are summarised in Table 2.17.

Table 2.17.

<u>Amine</u>	<u>Stoichiometry</u>	<u>Comment</u>
pyridine	no adduct	} Colourless liquids stable at $+20^\circ$
α -pic	no adduct	
β -pic(105)	1:2	
γ -pic	1:2	
$\text{Me}_3\text{N}(105)$	1:1	

A previous study had found that the equilibration time for the γ -picoline system was so long that no reaction product could be characterised (105). Although the equilibration time took about 45 to 60 minutes, the 1:2 adduct with γ -picoline was accurately characterised on repeating the addition. Pyridine and α -picoline did not produce any discernible reaction with $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$; this was perhaps not unexpected as only $\text{F}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ has reacted with α -picoline.

Tensiometric studies were completed on the β -picoline and γ -picoline adducts. However a similar situation exists here as was found for the adducts of $\text{Cl}_3\text{Si}.\text{CH}_2.\text{CHF}_2$ (Section 2.4.). The dissociation vapour pressures show (Table 2.18.) that the amine was not totally in the vapour phase; i.e., saturation vapour pressure of the amine $< 2/3$ measured dissociation vapour pressure. The results were therefore treated as described in Section 2.4.

Table 2.18.

<u>Temp.</u>	<u>Saturation Vapour Pressure mm.</u>		<u>Dissociation Vapour Pressure mm.</u>	
	<u>β-pic</u>	<u>γ-pic</u>	<u>$\text{H}_3\text{SiCF}_2\text{CHF}_2$ 2 β-pic</u>	<u>$\text{H}_3\text{SiCF}_2\text{CHF}_2$ 2 γ-pic</u>
28.2°	9.00	7.96	21.72	29.90
55.0°	33.12	30.55	103.13	112.20

The resultant Van't Hoff isochores yielded the heats of dissociation given in Table 2.19.

Table 2.19.

<u>Amine</u>	<u>ΔH silane kcal.mole⁻¹.</u>	<u>Latent heat of vapn. of amine</u>	<u>$\Delta H_{\text{complex}}$ kcal.mole⁻¹.</u>
β -picoline	9.43	9.34	28.11
γ -picoline	9.66	9.37	28.40

The γ -picoline adduct appears to be the more stable from a comparison of the heats of dissociation and dissociation vapour pressures.

Because the complex, $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2:2\gamma\text{-picoline}$ is a liquid at room temperature, its infrared spectrum could be obtained without the complexities of mulling agents. Although the Si-H bond is hydrolysable, it is not as susceptible to atmospheric moisture as the Si-Cl or Si-F bonds, and so the problem of hydrolysis is less important. The most interesting feature of the infrared spectrum was the shift of $\nu_{\text{Si-H}}$ from 2222cm^{-1} in $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ to 2172cm^{-1} in the complexed silane. Similar shifts have been observed for the β -picoline (2165cm^{-1}) and trimethylamine (2155cm^{-1}) adducts (105). The introduction of +I electron donating groups onto silicon results in a shift to lower frequency; e.g., Cl_3SiH , $\nu_{\text{Si-H}} = 2257\text{cm}^{-1}$; Me_3SiH , $\nu_{\text{Si-H}} = 2217\text{cm}^{-1}$. It is reasonable to assume

therefore, that the donation of electron density from the nitrogen in γ -picoline to the empty 3d-orbitals on silicon has occurred; i.e., complexation has occurred. Apart from this particular band, no significant change was observed in the rest of the spectrum.

The liquid nature of the γ -picoline complex permitted the n.m.r. spectrum to be recorded. The ratio of proton resonances was found to be:-

$$\begin{array}{ccccccc} \alpha\text{-H ring} & = & \beta\text{-H ring} & = & \text{SiH}_3 & = & \text{ring CH}_3 \\ 10 & & 10 & & 6.7 & & 13.8 \end{array}$$

For a 1:2 complex, a ratio of 10:10:7.5:15 is expected. The slight discrepancies might be explained to some extent by the high vapour pressure of the complex; the dissociated silane will be predominantly in the vapour phase over the sample, while the dissociated amine remains in solution. The ^1H spectrum was similar to that of the free silane, apart from the presence of the γ -picoline resonances. Both the SiH_3 and CHF_2 resonances were shifted slightly to high field.

The line pattern in the ^{19}F spectrum for the $\alpha\text{-CF}_2$ group was a quartet of doublets, and a doublet of quartets for the $\beta\text{-CHF}_2$ group. Each band appeared to have further multiplet structure, due to $\alpha\text{F}-\beta\text{F}$ coupling, but this multiplicity could not be resolved. Essentially however, the patterns were very similar to those found for the parent silane. The $\alpha\text{-CF}_2$ was shifted to high field by 6.4 p.p.m. on complexation and the $\beta\text{-CHF}_2$ moved only 0.8 p.p.m. to high field. The larger shift to high field of the $\alpha\text{-CF}_2$ group is probably the result of an increase in electron density at the silicon, this increment being transmitted along the fluoroalkyl chain. The change for the $\beta\text{-CHF}_2$ group should be smaller, the group being further removed from the silicon atom. Because of the poor resolution of the ^{19}F spectrum, $J_{\alpha\text{F}-\beta\text{F}}$ could not be evaluated. A reduction from 1.6 c.p.s. to 0.7 c.p.s. in the β -analogue has been attributed to the increased shielding of the fluorine nuclei on complexation (105).

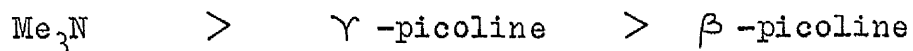
Table 2.22.

The ^{19}F n.m.r. Spectra of $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ and its
Complexes

<u>Chemical Shifts</u> (p.p.m. from TFA)	<u>$\text{H}_3\text{SiCF}_2\text{CHF}_2$</u>	<u>$\text{H}_3\text{SiR}_f.\text{NMe}_3$</u>	<u>$\text{H}_3\text{SiR}_f.$ 2 β-pic</u>	<u>$\text{H}_3\text{SiR}_f.$ 2 γ-pic</u>
α - CF_2	+44.0	+50.6	+49.2	+50.4
β - CHF_2	+55.7	+56.0	+55.3	+55.4
Coupling consts. (c.p.s.)				
$J_{\beta \text{ F-H}}$	56.0	55.6	55.2	55.4
$J_{\beta \text{ F-SiH}}$	3.1	2.9	2.9	2.8
$J_{\beta \text{ F-}\alpha \text{ F}}$	1.6	0.7	0.9	-
$J_{\alpha \text{ F-H}}$	5.0	6.5	6.4	6.7
$J_{\alpha \text{ F-SiH}}$	10.6	11.1	11.0	11.3
$J_{^{29}\text{SiH}}$	222.5	246	-	-

It is interesting to compare the α - CF_2 resonances in the trimethylamine, β -picoline, and γ -picoline complexes of $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$, as trimethylamine has induced the largest shift and β -picoline the smallest from free silane. In a study on some BMe_3 complexes (138), the most stable complexes had their B-Me resonances at highest field which is consistent with the electron donation process from donor to acceptor. If such a correlation were applied to the complexes of $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$, the

order of donor strength is:

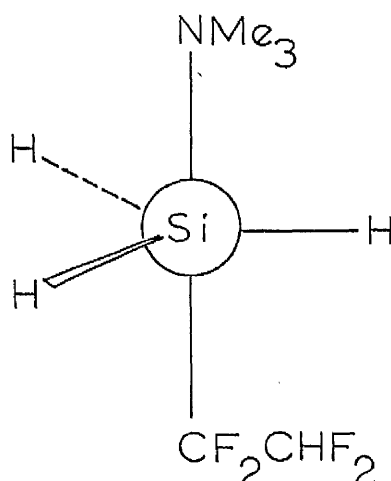


This is perhaps surprising as β -picoline and γ -picoline are the more sterically favoured donors and form the more stable adducts with silanes containing $\text{F}_3\text{Si-}$ and $\text{Cl}_3\text{Si-}$ fragments. However, trimethylamine formed the only isolable complex with $\text{H}_3\text{Si.CHF.CHF}_2$ and this would seem to suggest that co-ordination to the SiH_3 group is determined more by the base strength of the amine and less by steric considerations.

No $^{29}\text{Si-H}$ coupling was observed in the n.m.r. spectrum of the γ -picoline complex. Likewise none was observed for the β -picoline analogue, although $^{29}\text{Si-H}$ coupling was observed in the spectra of $\text{H}_3\text{Si.CF}_2.\text{CHF}_2$ and $\text{H}_3\text{Si.CF}_2\text{CHF}_2:\text{NMe}_3$.

The similarity of the SiH_3 resonances (a triplet of triplets) in the spectra of $\text{H}_3\text{Si.CF}_2.\text{CHF}_2$ and $\text{H}_3\text{Si.CF}_2.\text{CHF}_2:2\gamma\text{-pic}$ has already been noted. This might imply that the three silicon protons are either equivalent in the complex or that there is rapid exchange between the proton sites. In an attempt to resolve this, the spectra were recorded at lower temperatures. At -30° , line broadening and poor resolution occurred due to solidification of the sample. The proton spectra at -20° , -10° , 0° and $+10^\circ$ showed no changes in the resonances from those observed at room temperature. It therefore appears that either the protons are equivalent or the exchange process is still proceeding at -20° . The problem associated with the former is to find a structure consistent with three magnetically equivalent protons.

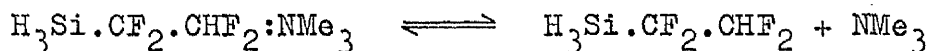
On the basis of the ^1H and ^{19}F parameters obtained from the n.m.r. spectrum, the 1:1 complex of $\text{H}_3\text{Si.CF}_2\text{CHF}_2$ and trimethylamine has been formulated as a five co-ordinate molecular silicon compound (105).

Fig. 2.6.

The single Si-H resonance and splitting of this resonance by the α - and β - CF_2 groups indicate that all the Si-H bonds are in identical chemical environments and that any inter- or intramolecular hydrogen exchange must be slow with respect to the smallest coupling constant which involves Si-H ($J_{\text{SiH}-\beta\text{F}} = 3.0$ c.p.s.) at the experimental temperature; i.e. $t_{1/2}$ for exchange $> 1/3.0\text{sec.}$ While the trigonal bipyramidal structure, with all hydrogens bonded to silicon in equatorial positions, is in accord with these observations, it is not possible to exclude rigorously the possibility of proton exchange.

A series of n.m.r. studies have been carried out on the complex, $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2:\text{NMe}_3$, to investigate this possibility. The ^1H and ^{19}F spectra were recorded at $-20^\circ, 0^\circ$ and $+20^\circ$. However, no changes in the chemical shifts and coupling constants found for the complex at $+35^\circ$ (105), were observed at these lower temperatures. This indicates that if proton exchange is occurring at $+35^\circ$, then it is still operating at -20° . The presence of only one type of SiH_3 signal and the fact that these protons are involved in a coupling process, means that $t_{1/2}$ is greater than $1/3$ sec.; i.e., this means that the species has a distinct chemical existence. But this does not preclude a slow exchange, where there would probably be a low concentration of any intermediate species. The equivalence of the Si-H

protons might also be achieved by a rapid ligand exchange process; viz.,



An attempt was made to resolve this problem of proton equivalence by using the deuterium analogue, 1,1,2,2-tetra-fluoroethylsilane- d_3 ($\text{D}_3\text{Si}.\text{CF}_2.\text{CHF}_2$). The ^1H spectrum of $\text{D}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ consisted of a triplet of triplets at 2.03 p.p.m. to high field of benzene ($J_{\text{CH}-\beta\text{F}} = 55.2$ c.p.s.; $J_{\text{CH}-\alpha\text{F}} = 4.8$ c.p.s.). The ^{19}F spectrum showed a doublet for the β - CF_2 group ($J_{\beta\text{F}-\text{CH}} = 55.2$ c.p.s.); the structure of each resonance in the doublet indicated that the bands were not singlets, but a multiplet structure that could not be resolved. The α - CF_2 resonance (Fig. 2.7.) was a nine band multiplet and the splitting between each band was ~ 1.8 c.p.s.

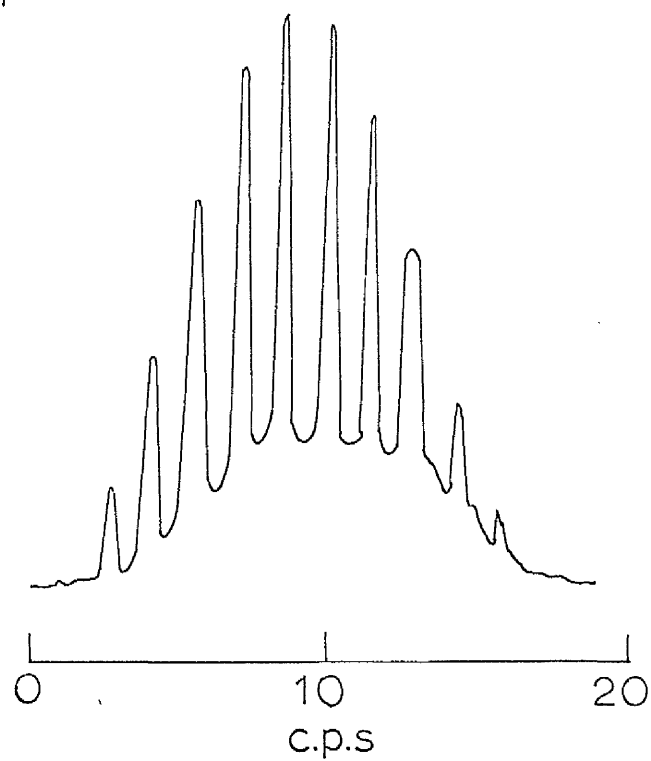
It would appear that this multiplet structure is caused by coupling with deuterium, since for the $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ analogue, the α - CF_2 resonance appears as a regular quartet of doublets of triplets (Fig. 2.8.). Deuterium has a spin number $I = 1$, and, when coupled to a further species, will produce splitting of that resonance in accordance with the formula $2nI + 1$, where n is the number of deuterium atoms. So when there is a single deuterium atom, a 1:1:1 triplet is produced, while $n = 2$ produces a 1:2:3:2:1 quintet and $n = 3$ produces a 1:3:6:7:6:3:1 heptet. An attempt was made to explain this nine band multiplet by computing different values of $J_{\alpha\text{F}-\text{D}}$. A value of $J_{\alpha\text{F}-\text{D}} = 2.4$ c.p.s., together with $J_{\alpha\text{F}-\text{CH}} = 4.8$ c.p.s., and $J_{\alpha\text{F}-\beta\text{F}} = 1.6$ c.p.s., produced the line pattern most consistent with the observed spectra; the line pattern has nine maxima in a symmetrical distribution of lines.

A sample of $\text{D}_3\text{Si}.\text{CF}_2.\text{CHF}_2:\text{NMe}_3$ was prepared and the n.m.r. spectrum determined. The ^1H spectrum showed that the triplet of triplets due to the CHF_2 resonance had shifted to low field by 0.59 p.p.m. This is difficult to explain in view of the increased electron density at silicon on complexation; a shift of 0.05 p.p.m. to high field was found for the

Figure 2.7.

^{19}F n.m.r. spectrum of $\text{D}_3\text{SiCF}_2\text{CHF}_2$

$\alpha\text{-CF}_2$ group



$\beta\text{-CHF}_2$ group

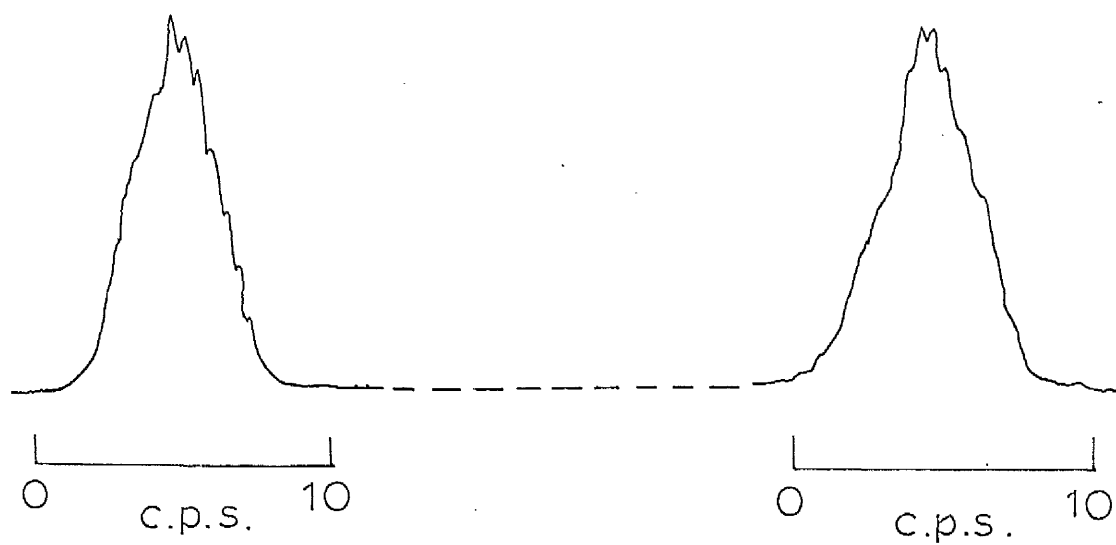
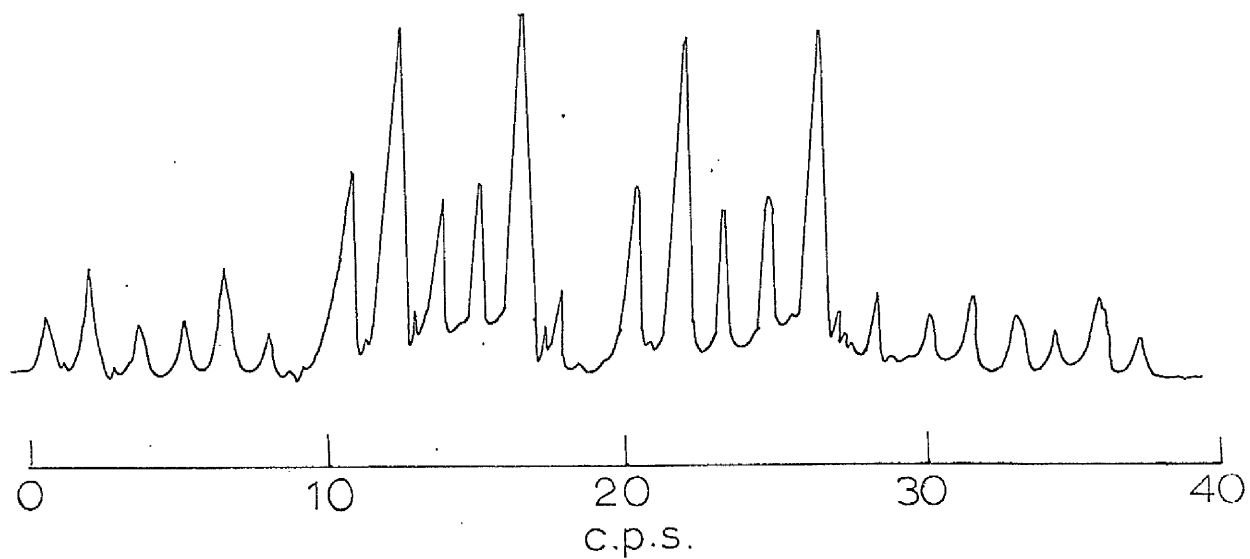


Figure 2.8.

^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCF}_2\text{CHF}_2$

$\alpha\text{-CF}_2$ group



$\beta\text{-CHF}_2$ group

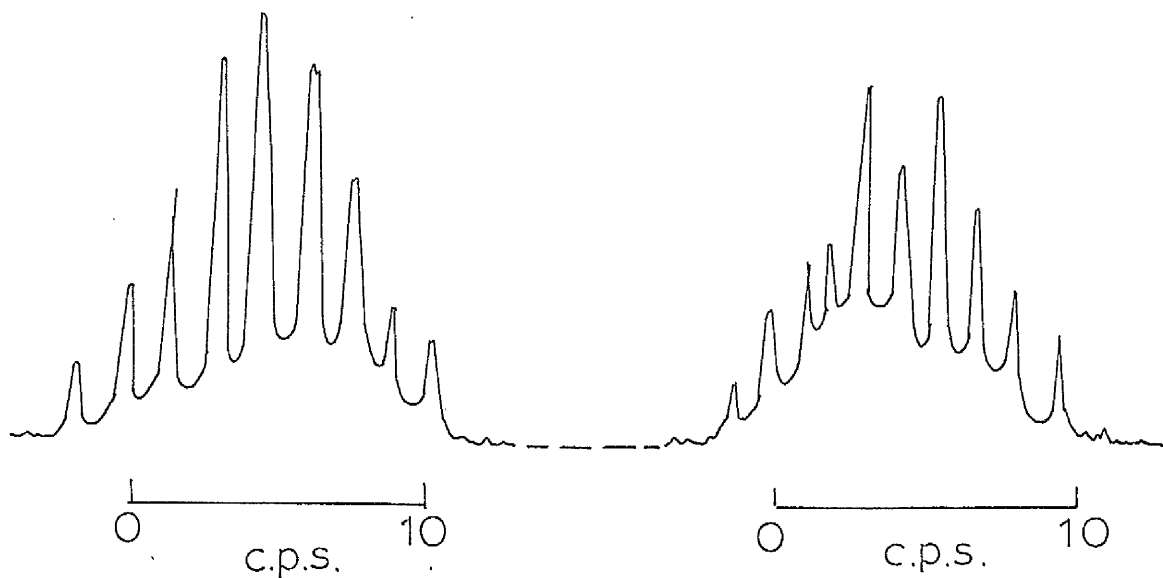
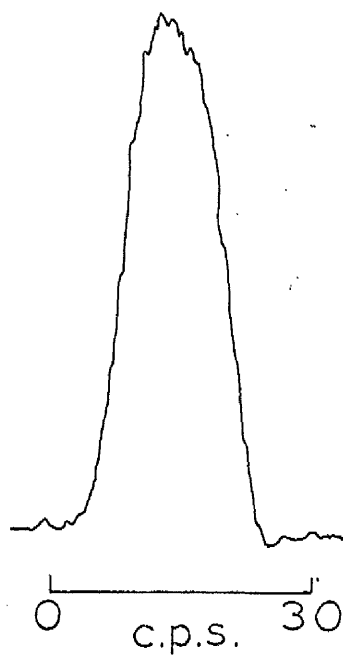


Figure 2.9.

^{19}F n.m.r. spectrum of $\text{D}_3\text{SiCF}_2\text{CHF}_2\cdot\text{NMe}_3$

$\alpha\text{-CF}_2$ group



$\beta\text{-CHF}_2$ group

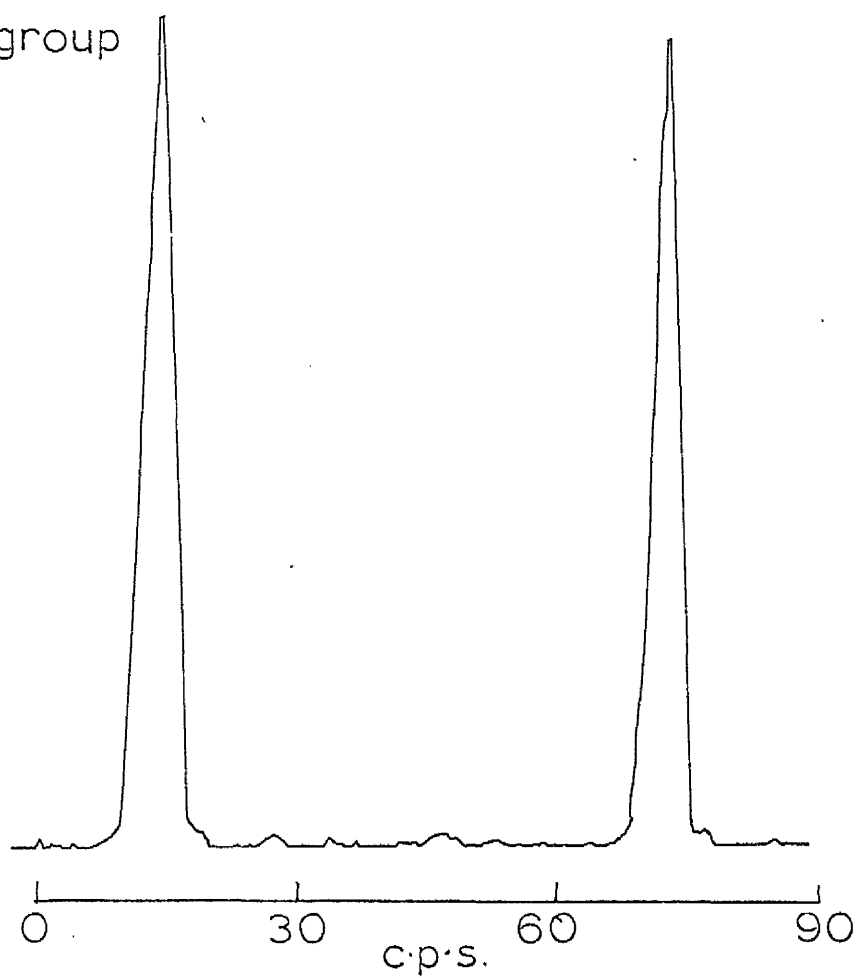
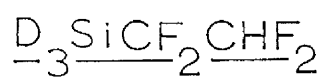
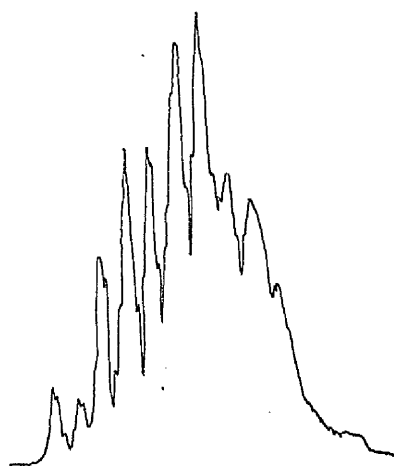


Figure 2.10.

^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCF}_2\text{CHF}_2\text{NMe}_3 + 20\%$

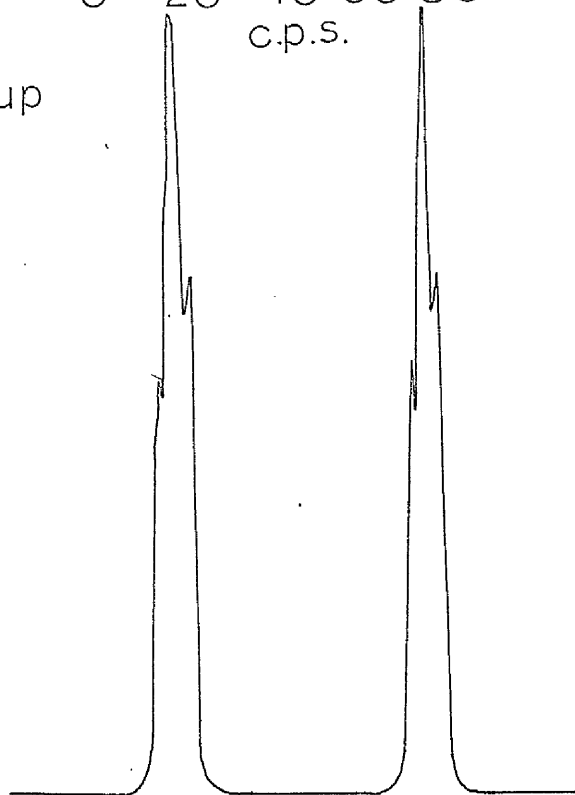


$\alpha\text{-CF}_2\text{-group}$



0 20 40 60 80
c.p.s.

$\beta\text{-CHF}_2\text{ group}$

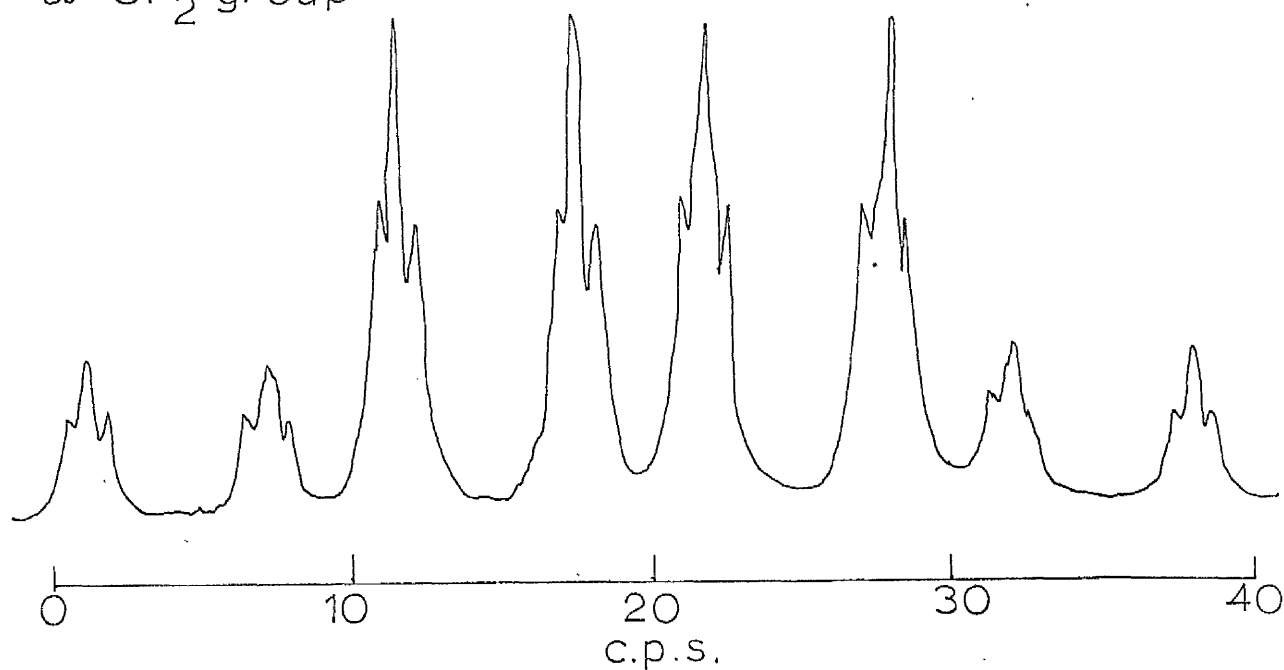


0 20 40 60 80
c.p.s.

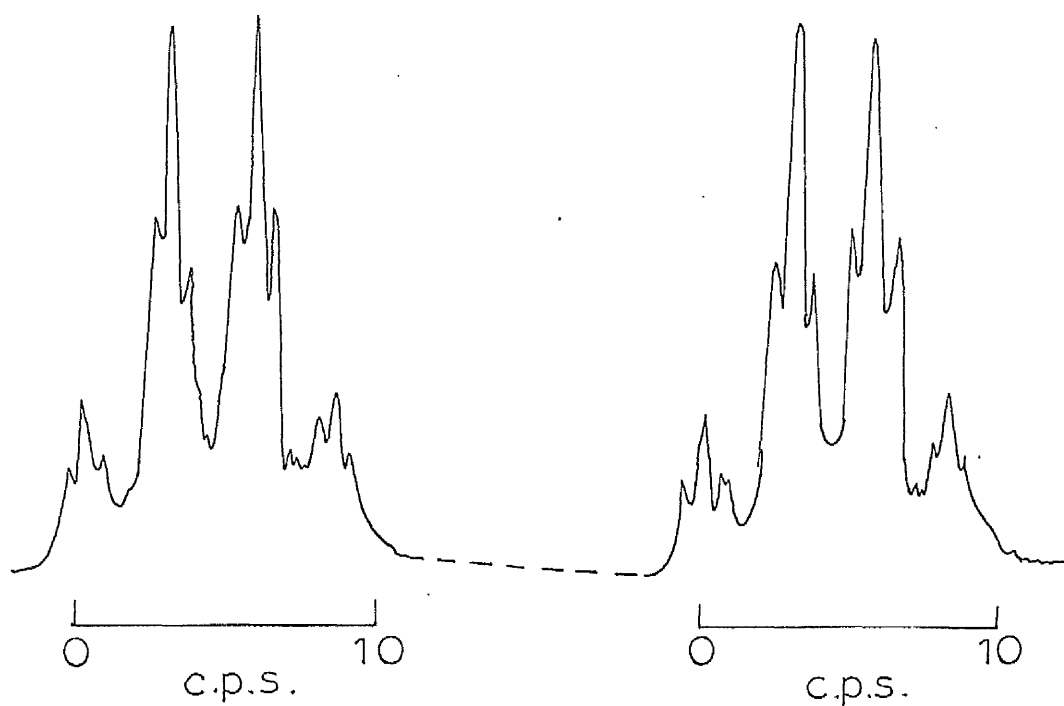
Figure 2.11.

^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCF}_2\text{CHF}_2\cdot\text{NMe}_3$

$\alpha\text{-CF}_2$ group



$\beta\text{-CHF}_2$ group

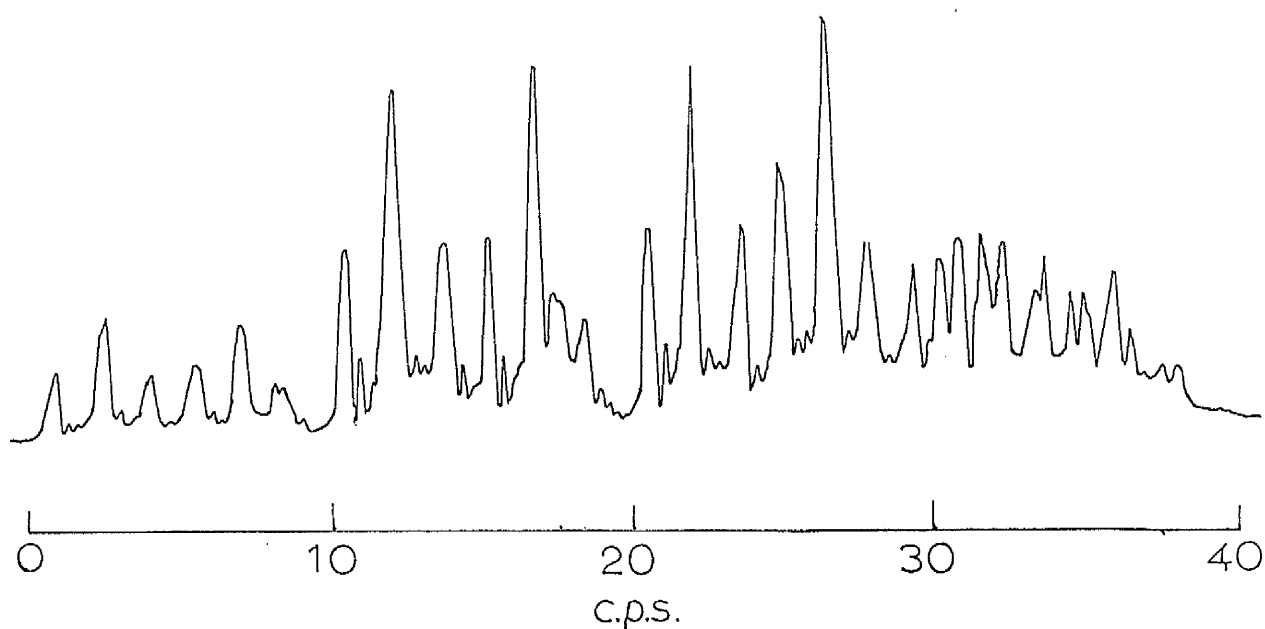


^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCF}_2\text{CHF}_2$ + 20%

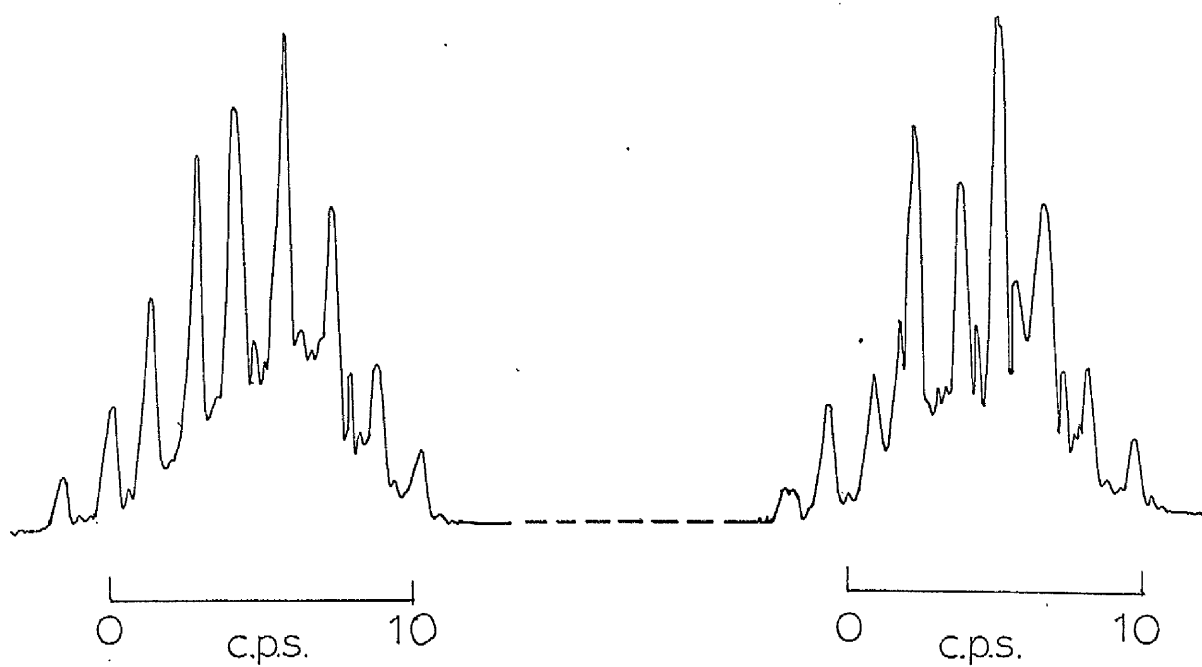
$\text{D}_3\text{SiCF}_2\text{CHF}_2$

Figure 2.12

$\alpha\text{-CF}_2$ group



$\beta\text{-CHF}_2$ group



$\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ analogue. However the ^{19}F spectrum (Fig.2.9.), is more compatible since the $\alpha\text{-CF}_2$ and $\beta\text{-CHF}_2$ resonances have been shifted to high field by 3.8 p.p.m. and 1.0 p.p.m. respectively; these shifts can be accounted for by the increased shielding of the fluorine nuclei which results from an increase in electron density in the silane on complexation. The structures of the resonances however have not altered on complexation, as the multiplet structure of each band still remains.

If proton exchange were occurring in the $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2:\text{NMe}_3$ complex, then the presence of $\text{D}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ might be expected to result in hydrogen-deuterium exchange. A 5:1 molar mixture of $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2:\text{NMe}_3$ and $\text{D}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ was prepared and the spectra recorded. The deuterated silane was condensed onto the complex at -196° , and the sample allowed to warm only when the spectra were to be recorded at -20° , 0° and $+20^\circ$. But apart from a slight loss of resolution at the lower temperatures, the three spectra were identical. The remarkable feature of the ^1H spectrum of the mixture was that the bands were identical to those for $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2:\text{NMe}_3$ and that there was a total absence of any bands due to the $\beta\text{-CHF}_2$ group in $\text{D}_3\text{Si}.\text{CF}_2.\text{CHF}_2$. If a hydrogen-deuterium exchange process was occurring between the silanes, then the formation of a partially deuterated silane species would be expected. The composition of this species would be governed by the hydrogen-deuterium ratio in the sample; statistically, the most common species would be $\text{DH}_2\text{Si}.\text{CF}_2.\text{CHF}_2$, although the exchange process would also produce a small concentration of $\text{D}_2\text{HSi}.\text{CF}_2.\text{CHF}_2$, and even $\text{D}_3\text{Si}.\text{CF}_2.\text{CHF}_2$. If coupling were to occur between the geminal deuterium and hydrogen in $\text{DH}_2\text{Si}.\text{CF}_2.\text{CHF}_2$, then each band in the triplet of triplets due to SiH_2 would be further split into a 1:1:1 triplet by the deuterium. No further splitting was observed but this is not necessarily indicative of no exchange occurring, as the value of $J_{\text{H-D}}$ would be expected to be small; e.g., < 0.5 c.p.s.

The ^{19}F spectrum consisted of two signals due to the $\alpha\text{-CF}_2$ (50.2 p.p.m.) and $\beta\text{-CHF}_2$ (55.4 p.p.m.) groups; a comparison with the chemical shifts in Table 2.23. shows that these are considerably nearer to the values of $\text{H}_3\text{Si.CF}_2.\text{CHF}_2\text{:NMe}_3$ than $\text{D}_3\text{Si.CF}_2.\text{CHF}_2\text{:NMe}_3$. However the remarkable feature

Table 2.23.

<u>Chemical Shifts</u> <u>(p.p.m. from TFA)</u>	<u>$\text{H}_3\text{SiCF}_2\text{CHF}_2$</u>	<u>$\text{H}_3\text{SiR}_f.\text{NMe}_3$</u>	<u>$\text{D}_3\text{SiCF}_2\text{CHF}_2$</u>
$\alpha\text{-CF}_2$	+44.0	+50.6	+42.6
$\beta\text{-CF}_2\text{H}$	+55.7	+56.0	+53.8
	<u>$\text{D}_3\text{SiR}_f.\text{NMe}_3$</u>	<u>$\text{H}_3\text{SiR}_f.\text{NMe}_3$</u> + <u>$\text{D}_3\text{SiR}_f$</u>	<u>$\text{H}_3\text{SiCF}_2\text{CHF}_2$</u> + <u>$\text{D}_3\text{SiCF}_2\text{CHF}_2$</u>
$\alpha\text{-CF}_2$	+46.4	+50.2	+43.0
$\beta\text{-CF}_2\text{H}$	+54.8	+55.4	+54.4

of these resonances is their structure; the doublet due to $\beta\text{-CHF}_2$ (Fig. 2.10.) strongly resembles the structure of the $\text{D}_3\text{Si.CF}_2.\text{CHF}_2\text{:NMe}_3$ doublet and not the distinctive doublet of quartets of triplets of $\text{H}_3\text{Si.CF}_2.\text{CHF}_2\text{:NMe}_3$ (Fig. 2.11.). Similarly the $\alpha\text{-CF}_2$ resonance (Fig. 2.10.) has an unresolved multiplet structure; a multiplet structure was found for $\text{D}_3\text{Si.CF}_2.\text{CHF}_2\text{:NMe}_3$ whereas the same band for $\text{H}_3\text{Si.CF}_2.\text{CHF}_2\text{:NMe}_3$ was a quartet of doublets of triplets. So although the chemical shifts are closely similar to those found for $\text{H}_3\text{Si.CF}_2.\text{CHF}_2\text{:NMe}_3$, the patterns of the bands resemble those found for $\text{D}_3\text{Si.CF}_2.\text{CHF}_2\text{:NMe}_3$ and $\text{D}_3\text{Si.CF}_2.\text{CHF}_2$.

It would seem therefore from the ^{19}F spectrum of the ($\text{H}_3\text{Si.CF}_2.\text{CHF}_2\text{:NMe}_3 + \text{D}_3\text{Si.CF}_2.\text{CHF}_2$) mixture, that deuterium is present in all the silane species in the sample; i.e., a hydrogen-deuterium exchange has occurred, which is probably at variance with the results of the ^1H spectrum. It is impossible to state the exact form of the scrambled species, but it is likely to be determined statistically by the H/D ratio in the sample and present an averaged value.

In order to determine if such an exchange is amine catalysed, a 5:1 molar mixture of $\text{H}_3\text{Si.CF}_2.\text{CHF}_2/\text{D}_3\text{Si.CF}_2.\text{CHF}_2$ was prepared at -196° , to examine the possibility of a hydrogen-deuterium exchange process between the pure silanes. The ^{19}F spectrum (Fig.2.12.) showed two signals due to the $\alpha\text{-CF}_2$ (+43.0 p.p.m.) and $\beta\text{-CHF}_2$ (+54.4 p.p.m.) groups, both being intermediate to the corresponding values for the free silane. The $\beta\text{-CHF}_2$ resonance consisted of a doublet ($J_{\beta\text{F-CH}} = 55.8$ c.p.s.), the pattern of each band being a multiplet structure similar in appearance to the bands observed in $\text{H}_3\text{Si.CF}_2.\text{CHF}_2$ (Fig.2.8.)(105).

It was noted that the $\alpha\text{-CF}_2$ resonance (Fig.2.12.) strongly resembled the quartet of doublets of triplets found for $\text{H}_3\text{Si.CF}_2.\text{CHF}_2$. But a number of extraneous bands were also observed, slightly to high field in the main pattern of lines. Seven of these bands were observed, and the pattern of intensities strongly resembles that found for the nine band multiplet in $\text{D}_3\text{Si.CF}_2.\text{CHF}_2$; the splitting between these bands was also ca. 1.8 c.p.s.

It would appear therefore that hydrogen-deuterium scrambling does not occur between $\text{H}_3\text{Si.CF}_2.\text{CHF}_2$ and $\text{D}_3\text{Si.CF}_2.\text{CHF}_2$ but might possibly be occurring on co-ordination of trimethylamine.

The analysis of the structure of $\text{H}_3\text{Si.CF}_2.\text{CHF}_2:\text{NMe}_3$ attempted here is comparatively superficial and not enough is known at present to expound further. The structure proposed in Fig. 2.6. agrees with chemical intuition, and it is difficult to propose a more attractive structure. But the results of some of the systems investigated here, demonstrate the possibility of a hydrogen or ligand exchange process, which could then cause some doubt about the validity of such a structure. But to understand and resolve this problem, and in particular the probable hydrogen-deuterium exchange process, it is necessary to study simpler species before attempting to analyse silane-amine systems of the present complexity.

2.12. Reactions of Trifluorosilane

Trifluorosilane was treated with β -picoline and γ -picoline, and the white solid complexes that resulted were found to have 1:2 stoichiometries.

The dissociation vapour pressures of $\text{HSiF}_3 \cdot 2 \beta\text{-picoline}$ and $\text{HSiF}_3 \cdot 2 \gamma\text{-picoline}$ were measured from 20° to 60° and Van't Hoff isochores used to evaluate the heats of dissociation. The results are presented in Table 2.24. The remarkable feature of these data is the exceptionally low vapour pressure of $\text{HSiF}_3 \cdot 2 \gamma\text{-picoline}$.

Table 2.24.

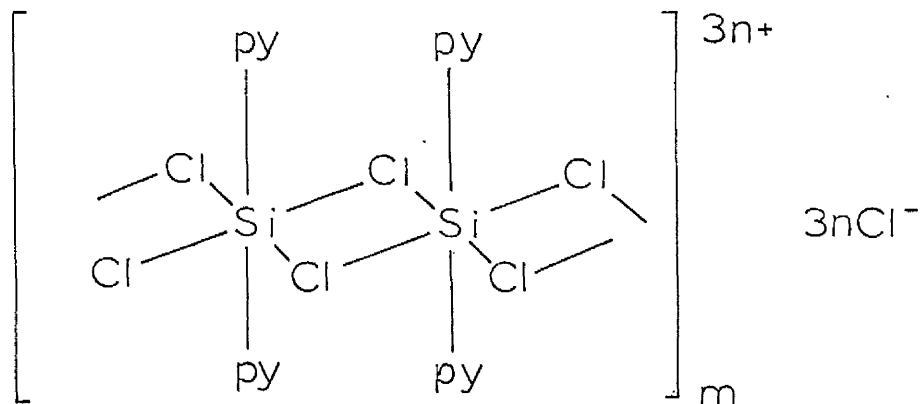
<u>Complex</u>	<u>ΔH kcal.mole⁻¹</u>	<u>Dissociation Vapour Pressure(mm).</u>
$\text{HSiF}_3 \cdot 2 \beta\text{-pic}$	51.25	5.93
$\text{HSiF}_3 \cdot 2 \gamma\text{-pic}$	56.11	0.78

The purpose of the preparation and study of these two adducts was to determine the effect of the fluoroalkyl chain on the Lewis acidity of the fluoroalkylsilanes. However, the heats of dissociation are very high compared to the values obtained for the fluoroalkylsilanes; e.g., for $\text{F}_3\text{Si} \cdot \text{CF}_2 \cdot \text{CHF}_2 : 2 \beta\text{-pic}$, $\Delta H = 38.69 \text{ kcal.mole}^{-1}$ and for $\text{F}_3\text{Si} \cdot \text{CF}_2 \cdot \text{CHF}_2 : 2 \gamma\text{pic}$, $\Delta H = 39.60 \text{ kcal.mole}^{-1}$. Although the size of tetrafluoroethyl group is large, the high +I effect of the group would be expected to compensate at least partially for this.

The occurrence of heats of dissociation of this magnitude for this type of complex has been encountered before and ascribed to differences in stereochemistry. cis- $\text{SiCl}_4 \cdot 2\text{py}$ ($\Delta H = 51.67 \text{ kcal.mole}^{-1}$) and trans- $\text{GeCl}_4 \cdot 2\text{py}$ ($\Delta H = 41.44 \text{ kcal.mole}^{-1}$) illustrate this point, as germanium compounds are normally stronger Lewis acids than their silicon analogues. The cis-isomer has a non-zero dipole moment, leading to increased lattice energies and greater heats of dissociation. By analogy therefore, $\text{F}_3\text{Si} \cdot \text{CF}_2 \cdot \text{CHF}_2$ appears to form trans

complexes while the complexes of F_3SiH appear to be the cis isomers.

A polymeric structure has been considered (13) to explain the insolubility of halo-silane complexes; e.g., the removal of one halide ion from each silicon atom would result in a bridged structure if the resultant cations were linked together



via a second halogen atom. However, the variation of the dissociation vapour pressure of the trifluorosilane-picoline adducts with temperature is not consistent with the idea of a polymeric structure.

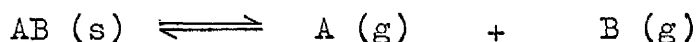
Both $HSiF_3 \cdot 2 \beta$ -picoline and $HSiF_3 \cdot 2 \gamma$ -picoline proved difficult to mull and poor resolution was obtained in the infrared spectra. The most significant features of these spectra were the appearance of bands in the SiH stretching region; 2100 and 2010cm^{-1} for the β -picoline adduct, and 2110 and 2010cm^{-1} for the γ -picoline adduct, whereas only a single band at 1960cm^{-1} is reported for $HSiF_3 \cdot 2\text{pyridine}$ (13). Only one absorption is expected for $HSiF_3$ adducts and the appearance of the second band is difficult to explain. Several possible explanations can be tentatively presented. The presence of both the cis and trans isomers would cause two Si-H absorptions, and so would the existence of two lattice sites in the crystal structure. Halogen exchange between $HSiF_3$ and the sodium chloride optical plates is possible,

although $\nu_{\text{SiH}} = 2088\text{cm}^{-1}$ in $\text{HSiCl}_3 \cdot 2\text{py}$ (13). A final possibility is that Si-F hydrolysis of the spectrum sample would result in the presence of two SiH bonds, one in the adduct and the other in the hydrolysis product.

2.13. The Thermodynamics of Complex Formation

In any discussion on Lewis acid-Lewis base complexes, it is important to understand what is meant by the stability of a complex. To refer to the stability of a complex as "the presence of a solid for which the partial pressures of both its constituents in the vapour phase, in equilibrium with the solid, are lower than the vapour pressures at the pure constituents" (82) is not sufficient as this only states criteria for complexation to occur in the first place. Instead it is necessary to define stability on a comparative, rather than an absolute scale, and in the present work, the measured heats of dissociation of the complexes are taken as the index of stability. The thermodynamic functions of the isolable complexes prepared in this work were determined from the variation of dissociation vapour pressure over a range of temperatures. Graphs were drawn of $\log_{10} p_{\text{mm.}}$ against $1/T^\circ\text{A}$, and if the relationship was linear, thermodynamic functions were determined for the complex.

For the formation of a 1:1 complex which undergoes complete dissociation in the vapour phase, and for which the vapour phase is in equilibrium with the solid state at any chosen temperature, the following equilibrium can be assumed,



If the solid is assumed to have unit activity, and ideal behaviour is assumed in the vapour phase, then the equilibrium constant may be expressed as,

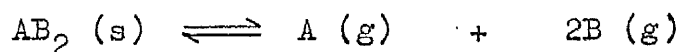
$$K_p = \frac{p_A \cdot p_B}{1}$$

where p_A and p_B are the partial pressures of each component;

$$\text{or } K_p = \frac{\frac{1}{2}P \cdot \frac{1}{2}P}{1} = \frac{P^2}{4}$$

where P is the equilibrium vapour pressure (atmospheres) above the solid at a chosen temperature.

For a 1:2 complex, i.e.,



the equilibrium constant is likewise given by,

$$K_p = \frac{4P^3}{27}$$

From the calculation of K_p at different temperatures, the heat of dissociation can be evaluated; the Van't Hoff equation relates the change in equilibrium constant with temperature to the enthalpy change involved, by the equation:

$$\int_0^T \frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

$$\text{or } \log_{10} K_p = - \frac{\Delta H}{2.303R} \cdot \frac{1}{T} + C$$

Hence if $\log_{10} K_p$ is plotted against $1/T^\circ A$, the heat of dissociation can be calculated from the gradient.

The reaction isotherm relates the standard free energy

change at any temperature to the equilibrium constant:

$$\Delta G = -RT \ln K_p$$

which in turn can be used to calculate the entropy of complex formation;

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

By the use of these graphs and equations, the heat of dissociation, standard free energy change and entropy of complex formation were obtained. It is necessary to assume in these calculations that the solid is involatile and also dissociates completely in the vapour phase; the experimentally determined linear graphs of $\log_{10} K_p$ against $1/T^\circ A$ are justification for these assumptions.

Before going on to discuss the significance of these thermodynamic data, it is important to understand what has been determined in these experiments. It was realised in section 1.10. that the most desirable index of complex stability would be that based on the gas phase dissociation of the complex (ΔH_D); i.e., a direct measurement of the strength of the Si-N bond. However, most Group IVB complexes, and certainly those under consideration here, are not sufficiently stable to exist in the gas phase. Instead, an enthalpy change ($\Delta H'$) is measured that is related to the gas phase heat of dissociation (ΔH_D) by the Born-Haber cycle (section 1.10.); viz.,

$$\Delta H' = \Delta H_D + U$$

where U is the lattice energy. There is not sufficient data about the structure of these compounds to allow calculation of the parameters which determine the lattice energy terms and so ΔH_D is a seemingly indeterminate term at present. However, for a series of like compounds, such as some of the present silane-amine adducts, it is reasonable to assume that

Table 2.25.Heats of Dissociation (kcal.mole⁻¹) of the Silane-AmineComplexes.

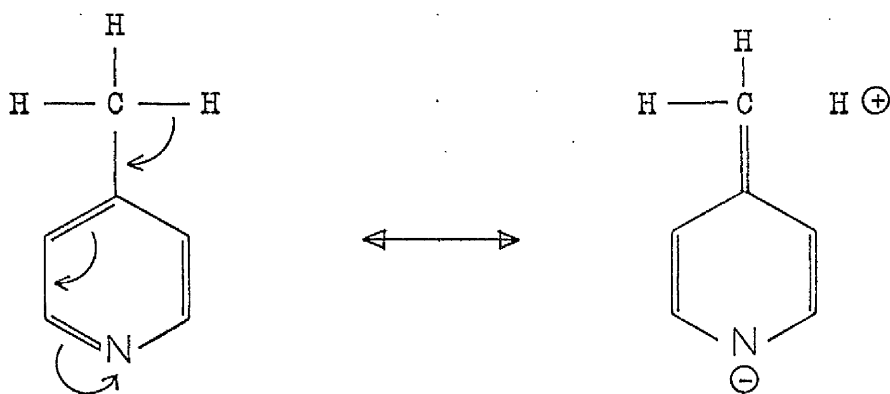
<u>Silane</u> \ <u>Amine</u>	<u>Me₃N</u>	<u>py</u>	<u>β-pic</u>	<u>γ-pic</u>
Cl ₃ SiCH ₂ CHF ₂	-	-	21.42	22.31
SiF ₄	-	28.41	32.52	35.86
Cl ₃ SiCHFCHF ₂	-	-	28.23	31.87
F ₃ SiCHFCHF ₂	-	-	32.68	34.46
H ₃ SiCHFCHF ₂	11.77	-	-	-
Cl ₃ SiCF ₂ CHF ₂	-	-	30.71	34.28
F ₃ SiCF ₂ CHF ₂	-	31.37	38.49	39.60
H ₃ SiCF ₂ CHF ₂	-	-	28.11	28.40
F ₃ SiH	-	-	51.25	56.11

the lattice energies might be comparable for two compounds, so that $\Delta H'$ bears some resemblance to the magnitude of ΔH_D .

The heats of dissociation changes are given in Table 2.25., and the majority of the data agrees with intuitive chemical ideas. The reactions of $F_3Si.CF_2.CHF_2$ and study of its isolable complexes, give the most complete order of amine Lewis basicity:

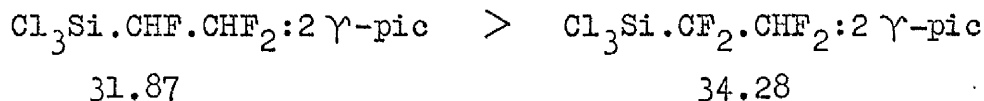
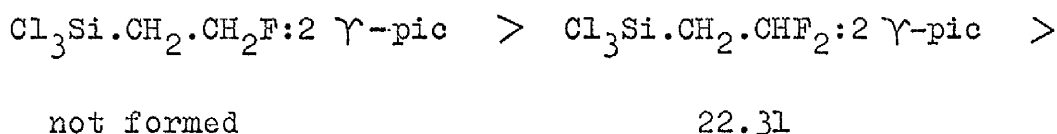


α -picoline ($pK_a = 5.96$) is a stronger base than pyridine ($pK_a = 5.2$) because of the inductive and hyperconjugative effects of the methyl group substituted in the 2-position. However, the methyl group in the 2-position hinders the access of the nitrogen to the central acceptor atom and thus makes complexation more difficult. For β -picoline and γ -picoline, the methyl groups substituted in the 3- and 4- positions are sufficiently far removed from the site of donation for little or no steric strain to be set up. Thus for β -picoline and γ -picoline, the complex stability should be determined essentially by the base strength of the amine. γ -picoline ($pK_a = 6.05$) is a stronger base than β -picoline ($pK_a = 5.66$) by virtue of the hyperconjugative effect of the methyl group in the 4-position which permits contributions of the type,



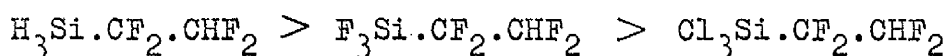
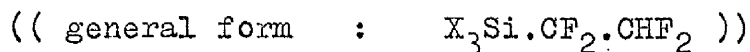
γ -picoline is thus able to form the more stable complexes.

There is a definite increase in stability, for a given amine, as the degree of fluorination in the fluoroalkyl group of the fluoroalkylsilanes is increased, as is shown by the heats of dissociation (kcal.mole^{-1}):

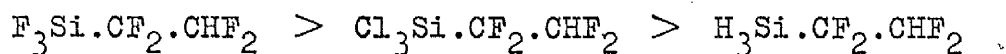


and is best explained by the increase in the electropositive character of the silicon effected by the increased σ -inductive effect on greater fluorine substitution in the fluoroalkyl chain. It would appear however that the presence of a single, β -fluorine atom in the fluoroalkyl group is not sufficient to overcome the not inconsiderable steric effects of the organic group.

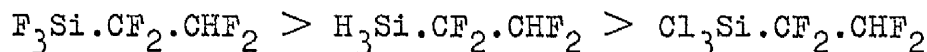
For a consideration of the effects of the $\text{X}_3\text{Si}-$ group, it is convenient to compare the silanes, $\text{X}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ ($\text{X} = \text{H}, \text{Cl}, \text{F}$). From steric considerations, the order of Lewis acidity should be:



But based on electronegativity considerations, a different order is predicted.



A combination of these two factors might be expected to give an overall order of stability,



But a comparison of the heats of dissociation of the β -picoline and γ -picoline adducts (Table 2.24.) shows that such a prediction is probably not correct. However, only the solid

$\text{F}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ and $\text{Cl}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ complexes can be meaningfully compared, since $\text{H}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ forms liquid complexes.

The only data which are consistent with the predicted stability sequence are the vapour pressures of the trimethylamine adducts (105). The most remarkable data, however,

Table 2.26

<u>Trimethylamine complex of</u>	<u>ΔH kcal.mole⁻¹.</u>	<u>Dissociation Vapour Pressure</u>	<u>ΔG kcal.mole⁻¹.</u>
$\text{F}_3\text{SiCF}_2\text{CHF}_2$	23.8	80.4mm. / 74.2°	-6.8
$\text{Cl}_3\text{SiCF}_2\text{CHF}_2$	25.1	79.5mm. / 10°	-3.1
$\text{H}_3\text{SiCF}_2\text{CHF}_2$	15.3	79.5mm. / 19°	-2.1

are the heats of dissociation of these same trimethylamine adducts; the high heat of dissociation of $\text{Cl}_3\text{Si}.\text{CF}_2.\text{CHF}_2:\text{NMe}_3$ is not consistent with its high vapour pressure. While no explanation other than unusual crystal packing can be offered for this anomaly, it is interesting to note that the free energy changes do give the predicted order of stability, for the fluoro and chloro adducts.

It appears therefore that trimethylamine produces a different order of stability to that produced by β -picoline and γ -picoline. The major difference between the trimethylamine and picoline adducts is the co-ordination of the silicon; it is conceivable that the promotion and hybridisation energies involved in five and six co-ordination of silicon are critical in determining the magnitude of $\Delta H'$.

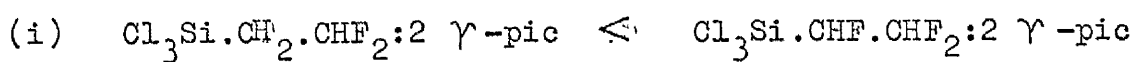
It has been mentioned that the heats of dissociation show $\text{F}_3\text{Si}.\text{CF}_2.\text{CHF}_2$ to be the strongest fluoroalkylsilane acceptor. What is perhaps surprising therefore is that this silane should appear to be a stronger Lewis acid than silicon tetrafluoride.

If the adducts of $F_3Si.CF_2.CHF_2$ and SiF_4 were to differ in their structure, the order could be explained, for the formation of a cis 1:2 adduct results in a higher heat of dissociation than for the analogous trans adduct (12). Such an explanation would require the SiF_4 adducts to be trans, in agreement with their infrared spectra, and the $F_3Si.CF_2.CHF_2$ adducts, and presumably the fluoroalkyl-silane adducts in general, to be cis. However, this argument has been used to assign a cis stereochemistry to the adducts of F_3SiH , and it is difficult to credit the difference of almost 20 kcal.mole⁻¹ for the heats of dissociation between the adducts of $F_3Si.CF_2.CHF_2$ and F_3SiH to the effect of the $-CF_2.CHF_2$ group, as the large size of this group is compensated by a strong +I effect. Therefore it is unlikely that the adducts of $F_3Si.CF_2.CHF_2$ are the cis isomers.

Instead it is preferable to consider the fluoroalkyl-silane adducts as the trans isomers, and attribute the considerably reduced Lewis acidity of silicon tetrafluoride to $d\pi - p\pi$ bond formation between silicon and fluorine. This phenomenon is well authenticated in silicon chemistry (e.g. see Introduction) and the donation of non-bonded p fluorine electrons into the silicon 3d-orbitals would decrease the electropositivity of the silicon. This reduction in Lewis acidity would be expected to be larger for SiF_4 (four Si-F bonds) than for $F_3Si.CF_2.CHF_2$ (only three Si-F bonds).

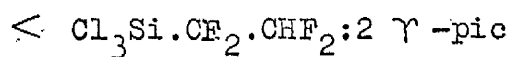
It is of interest to compare the two orders of stability based on the heats of dissociation ($\Delta H'$) and free energy changes (ΔG). ΔG is a measure of the spontaneity of a chemical process at a chosen temperature, and a spontaneous process always occurs in the direction of a decrease in free energy. Consequently, the larger the negative value of

ΔG , the greater is the tendency for complex formation to occur at that temperature. A comparison of the orders of complex stability based on ΔH (kcal.mole⁻¹) and ΔG (kcal.mole⁻¹) shows that, except for the trimethylamine adducts of $X_3Si.CF_2.CHF_2$, both functions give the same order of stability.



ΔH 22.31 31.87

ΔG 3.19/-25° 10.62



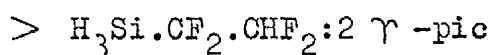
ΔH 34.28

ΔG 11.24



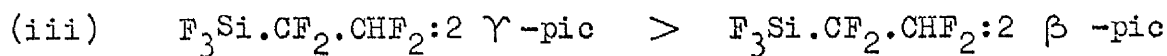
ΔH 39.60 34.28

ΔG 12.63 11.24



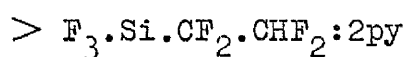
ΔH 28.40

ΔG 2.19



ΔH 39.60 38.49

ΔG 12.63 12.36



ΔH 31.37

ΔG 11.28

The entropies of formation cover a very wide range (~ -21 to -152 entropy units). It is not really possible to explain satisfactorily the differences in entropy of formation without a fuller knowledge of the crystalline state of the complexes. In general however, one would expect a large entropy change for the formation of a solid complex. In fact, the entropy changes for the liquid complex $\text{H}_3\text{Si} \cdot \text{CF}_2 \cdot \text{CHF}_2$:2 γ -pic (-25.02 e.u.) was smaller than for the comparable solid complex of $\text{F}_3\text{Si} \cdot \text{CF}_2 \cdot \text{CHF}_2$ (-90.29 e.u.) Also one would expect a larger entropy change for the formation of a 1:2 complex than for the formation of a 1:1 complex. The experimental data appear to confirm this; e.g., $\text{F}_3\text{Si} \cdot \text{CF}_2 \cdot \text{CHF}_2 \cdot \text{NMe}_3$, $\Delta S = -57.3$ e.u. (105) and $\text{F}_3\text{Si} \cdot \text{CF}_2 \cdot \text{CHF}_2$:2 γ -pic, $\Delta S = -90.29$ e.u.

The entropy changes are therefore in agreement with intuitive ideas; but in view of the uncertain structures of the complexes, it is probably unwise to analyse the changes any further.

For the same reason, it is probably unwise to attempt a correlation of the heats of dissociation. Several successful correlations have been made between ν_{SiH} and the Taft constant of some silanes (139, 140, 141). Complex stability is however, not solely a function of inductive characteristics; it is also dependent on steric considerations and not enough is known at the present time about the magnitudes of these two effects to justify a correlation with the heats of dissociation.

2.14. Accuracy of the Thermodynamic Data

The experimentally determined heats of dissociation of the complexes represent the average values for the temperature range studied, and are calculated from the gradient of a Van't Hoff isochore. They would therefore be subject to errors in drawing the "best" straight line through a set of points. To eliminate this visual error, the results were computer programmed, and the gradient and intercept of the straight line determined by a least mean squares method. The standard deviations of the gradients showed that the accuracy of the initial pressure and temperature measurements was good, varying from 0.07 to 0.46 kcal.mole $^{-1}$ for the complexes studied.

The free energy changes are dependent only on the vapour pressure and temperature which can be measured reasonably accurately ($\pm 0.02\text{mm.}$ and $\pm 0.2^\circ$). Therefore the error in ΔG should be lower than $\Delta H'$ and is in fact assessed at $\pm 0.1 \text{ kcal.mole}^{-1}$.

The entropy changes, being determined from the equation, $\Delta G = \Delta H - T\Delta S$, is dependent on the accuracy of ΔH , ΔG and T . The accuracy of ΔS is assessed at $\pm 1 \text{ e.u.}$ and because of its dependence on three other terms, is the least accurate of the thermodynamic data.

EXPERIMENTAL

3.1. General Techniques

Since many of the compounds prepared and used in this investigation possessed a high vapour pressure at room temperature and a high susceptibility to hydrolysis, a vacuum system was constructed so that they could be easily manipulated.

The system was of a conventional type, being constructed from Pyrex glass and standard Quickfit ground glass joints and taps. It consisted of a section of storage bulbs, a Regnault molecular weight section and a fractional condensation train. An Edwards two-stage Speedivac rotary pump was used to evacuate the main manifold and gave pressures of ca. 10^{-3} mm. Hg. By use of a mercury diffusion pump in series with the rotary pump, pressures down to ca. 10^{-4} - 10^{-5} mm.Hg. could be achieved when required.

Gases were transferred from one vessel to another by condensation using liquid nitrogen.

Volatile reaction products were separated by low pressure fractional condensation. The mixture was allowed to warm slowly from -196° and the vapours were passed through a series of traps cooled in "slush-baths" at successively lower temperatures, the final trap being cooled in liquid nitrogen. The "slush-baths" were prepared from common organic solvents cooled to their melting points with either liquid nitrogen or solid carbon dioxide. The process of fractional condensation is a convenient, though not always totally efficient, method of separation if the compounds used have boiling points differing by ca. $30-40^{\circ}$.

Molecular weights of desired products were determined by Regnault's method using a calibrated molecular weight bulb.

Gas volumes were measured by allowing the gases to expand into calibrated bulbs or traps, and measuring the pressure generated. The volumes were corrected to S.T.P.

Pure compounds were characterised by elemental analyses carried out by the microanalytical department, and in the case of a known compound, by comparison with the known physical constants of the compound.

Infrared spectra were recorded on a Perkin-Elmer Double Beam Spectrophotometer (Model 21), a Perkin-Elmer Infracord Spectrophotometer (Model 137) or a Perkin-Elmer Grating Infrared Spectrophotometer (Model 257). Gas samples were examined in a 10cm. gas cell, and liquids as capillary films. Because the silane-amine adducts prepared in this investigation undergo extremely rapid hydrolysis, solid samples were prepared by the technique employed by Campbell-Ferguson and Ebsworth (13). A sample of the adduct was prepared in a tube attached to the vacuum line. The tube was then sealed and transferred to a dry box. The tube was broken open and the mull prepared in the normal way using Nujol or HCB in excess. This spread out to the edge of the plates when they were pressed together and acted as a fairly effective seal in preventing hydrolysis and oxidation during the recording of the spectrum.

The nuclear magnetic resonance spectra were obtained on a Perkin-Elmer R.10 Spectrometer (60 Mc/s. for ^1H and 56.4 Mc/s. for ^{19}F). All samples were sealed in vacuo and unless otherwise stated, tetramethylsilane was used as an internal reference for the proton spectra and a capillary of trifluoroacetic acid used as an external reference for the fluorine spectra.

3.2. Preparation of Starting Materials

3.2.1. Purification of Tertiary Amines

Commercial samples (Koch-Light Chemicals, purissimo grade) of pyridine, α -picoline, β -picoline and γ -picoline were allowed to stand over A.R. potassium hydroxide pellets for several days. They were filtered and fractionally distilled through a 1 metre silvered column packed with glass helices. The "middle-cut" was distilled onto freshly calcined (6 hours, 300°) 4A molecular sieves. The amines were stored over the sieves until required for use.

Trimethylamine was purified by fractional condensation through a series of "slush-baths" and finally condensed onto freshly calcined (6 hours, 300°) anhydrous barium oxide. The trimethylamine was then condensed into ampoules for storage.

When the tertiary amines were required for use, the last traces of moisture were removed by a process of "mutual drying" using silicon tetrachloride or trichlorosilane. A small amount of the chlorosilane was condensed onto a sample of the amine in vacuo and allowed to reach room temperature. Any remaining water in the amine would then hydrolyse the chlorosilane to involatile silica or siloxane polymers and liberate hydrogen chloride, which would then combine with the amine to form the involatile amine hydrochloride. The excess chlorosilane would complex with the amine to form an involatile solid. The amine was then removed by vapourisation from the involatile solids into the storage ampoules.

This technique of "mutual drying" was found to be most efficient, and all the amines were characterised by microanalysis, infrared and nuclear magnetic resonance spectroscopy.

3.2.2. Purification of Trichlorosilane.

A commercial sample (Midland Silicones Chemicals) of trichlorosilane was purified by distillation through a 1 metre silvered column packed with glass helices. The fraction boiling at $33-35^{\circ}$ was collected and distilled in a vacuum system through "slush-baths" at -78° , -96° and -196° to remove most of the hydrogen chloride. The purified trichlorosilane was then sealed into small ampoules until required for further use. The purity of the trichlorosilane was checked by molecular weight determinations, infrared spectroscopy and by comparison of the vapour pressure obtained with that given by a pure sample.

3.2.3. Preparation of 2-fluoroethyltrichlorosilane.

In a typical reaction, trichlorosilane (15.6g., 0.116mole) and vinyl fluoride (2.65g., 0.058 mole) were sealed in a 350 ml. silica tube and irradiated on a mechanical shaker for 150 hours at a distance of 30 cm. from a 500 watt mercury resonance lamp.

The products were fractionated in vacuo through traps maintained at -24° , -78° and -196° to give (i) crude 2-fluoroethyltrichlorosilane, (ii) unreacted trichlorosilane and (iii) vinyl fluoride (0.10g., 0.0025 mole; 4% recovery) respectively. An involatile material remained in the tube.

The crude 2-fluoroethyltrichlorosilane was purified by fractionation under nitrogen at atmospheric pressure through a 130 x 8 mm. vacuum jacketed column, packed with glass helices and fitted with a partial reflux take-off head, b.p. 116-119°/760mm. yield 9.98g., 0.055 mole, 94.5%. (Found: C, 13.4; H, 2.1. Calc. for $C_2H_4Cl_3FSi$: C, 13.2; H, 2.2%.)

The infrared spectrum showed the absence of trichlorosilane (ν Si-H at 4.6μ), and the infrared and n.m.r. spectra were consistent with pure 2-fluoroethyltrichlorosilane (142).

3.2.4. Preparation of 2,2-Difluoroethyltrichlorosilane.

In a typical reaction, trichlorosilane (17.5g., 0.132 mole) and 1,1-difluoroethylene (4.25g., 0.066mole) were sealed in a 350 ml. silica tube and irradiated on a mechanical shaker for 24 hours at a distance of 30cm. from a 500 watt mercury resonance lamp.

The products were fractionated in vacuo through traps maintained at -24° , -78° , and -196° to give crude 2,2-difluoroethyltrichlorosilane, unreacted trichlorosilane and 1,1-difluoroethylene (0.41g., 0.0064 mole; 10% recovery) respectively. An involatile material remained in the reaction tube.

The crude 2,2-difluoroethyltrichlorosilane was purified by fractionation under nitrogen at atmospheric pressure through a 130 x 8mm. vacuum jacketed column, packed with glass helices and fitted with a partial reflux take-off head, b.p. 108-110°/760mm. Yield 11.32g., 0.0568 mole, 86%. (Found : C, 12.3; H, 1.6 Calc. for $C_2H_3Cl_3F_2Si$ = C, 12.1 ; H, 1.5%).

The infrared spectrum showed the absence of trichlorosilane (ν Si-H at 4.6μ), and the infrared and n.m.r. spectra were consistent with pure 2,2-difluoroethyltrichlorosilane (142).

3.2.5. Preparation of 2,2-Difluoroethyltrifluorosilane.

2,2-Difluoroethyltrichlorosilane (41.6g., 0.209 mole) was passed repeatedly, in the vapour phase, through a horizontal glass tube (40 x 2cm.i.d.) packed with antimony trifluoride (50g., and dried over phosphorus pentoxide in vacuo for three days) dispersed with glass-wool plugs and moistened with antimony pentachloride (1ml.). Heat was evolved and some blackening of the solid occurred.

After twelve passes, the products were separated by fractional condensation in vacuo through traps maintained at -23° , -78° and -196° to yield unreacted 2,2-difluoroethyltrichlorosilane and crude 2,2-difluoroethyltrifluorosilane in the first two traps respectively. There was no evidence for the presence of silicon tetrafluoride and vinyl fluoride, formed from the decomposition of the required product, as reported by previous workers (147,148).

The crude 2,2-difluoroethyltrifluorosilane was purified by fractionation under nitrogen at atmospheric pressure through a 130 x 8 mm. vacuum jacketed column, packed with glass helices and fitted with a partial reflux take-off head, b.p. $45-46^{\circ}/760\text{mm}$. Yield 23.4g., 0.156 mole, 75%. (Found : C, 16.2; H, 2.1; M, 149. Calc. for $\text{C}_2\text{H}_3\text{F}_5\text{Si}$: C, 16.0 ; H, 2.0% ; M, 150).

The infrared and n.m.r. spectra were consistent with pure 2,2-difluoroethyltrifluorosilane (136).

3.2.6. Preparation of 1-Bromo-2-chloro-1,1,2-trifluoroethane.

Hydrogen bromide (32.0g., 0.4 mole) and 1,1,2-trifluoro-2-chloroethylene ("Kel-F") (46.6g., 0.4 mole) were introduced into a 20 litre irradiation bulb fitted with a mercury manometer and a silica insert containing a 500 watt Hanovia mercury resonance lamp. The gases were irradiated until no further pressure change occurred; this took about $2\frac{1}{2}$ hours.

The products were condensed out into a -196° trap and distilled in vacuo through two -63° traps and a -196° trap to yield (i) a colourless liquid containing a small amount of "Kel-F" and (ii) some unreacted hydrogen bromide and "Kel-F". The colourless liquid was distilled under nitrogen at atmospheric pressure through a 60cm. silvered column and the fraction boiling at $51-52^{\circ}/760\text{mm}$. was collected (71.0g., 0.361 mole; 90% yield). The infrared spectrum of this product was consistent with pure 1-bromo-2-chloro-1,1,2-trifluoroethane (143).

3.2.7. Preparation of Trifluoroethylene.

Zinc dust (150g., 2.25 mole), contained in a 500ml. three necked flask, was activated by 5N hydrochloric acid and washed three times with dry ethanol.

The flask was fitted with a dropping funnel, a magnetic stirrer and a double surface condenser leading to a series of

traps at -23° , -120° (x2) and -196° . Outlets to the atmosphere were closed with drying tubes.

Dry ethanol (112.5ml.) was added to the zinc and heated to its reflux temperature. 1-Bromo-2-chloro-1,1,2-trifluoroethane (150g., 0.75 mole) was slowly added to the reflux mixture; the mixture was maintained at its reflux temperature for a further two hours. The product that condensed in the two -120° traps was transferred to the vacuum system and fractionated to give a major fraction condensing at -120° . Yield 51.25g., 0.6288 mole; 84%. (Found : \underline{M} , 82.5. Calc. for C_2HF_3 : \underline{M} , 82). The infrared spectrum was consistent with pure 1,1,2-trifluoroethylene (144).

3.2.8. Preparation of 1,2,2-trifluoroethyltrichlorosilane.

In a typical reaction, trichlorosilane (37.6g., 0.2775 mole) and trifluoroethylene (4.55g., 0.0555 mole) were sealed in a 350ml. silica tube and irradiated on a mechanical shaker for 100 hours at a distance of 30cm. from a 500 watt mercury resonance lamp.

The products were fractionated in vacuo through traps maintained at -24° , -78° and -196° to give crude 1,1,2-trifluoroethyltrichlorosilane, unreacted trichlorosilane and trifluoroethylene (0.36g., 0.0044 mole ; 8% recovery) respectively. An involatile material remained in the reaction tube.

The crude 1,2,2-trifluoroethyltrichlorosilane was purified by fractionation under nitrogen at atmospheric pressure through a 130 x 8mm. vacuum jacketed column, packed with glass helices and fitted with a partial reflux take-off head, b.p. $101-102^{\circ}/760\text{mm}$. Yield 10.16g., 0.0464 mole, 84%. (Found : C, 11.3 ; H 1.1. Calc. for $C_2H_2Cl_3F_3Si$: C, 11.1 ; H, 0.9%).

The infrared spectrum showed the absence of trichlorosilane (ν Si-H at 4.6μ), and the infrared and n.m.r. spectra were consistent with pure 1,2,2-trifluoroethyltrichlorosilane (145).

The product was investigated by g.l.c. analysis. Using a 4m. "silicone" (M.S.550) column, a single peak was obtained with a retention time of 14.3min. at 150° and a nitrogen flow rate of 74ml. min.^{-1} at 1 kg. cm.^{-2} . The isomeric product, $Cl_3SiCF_2CH_2F$, has a retention time of 12.8min. under similar conditions (142)

3.2.9. Preparation of 1,2,2-Trifluoroethyltrichlorosilane.

1,2,2-Trifluoroethyltrichlorosilane (6.16g., 0.0367 mole) was passed repeatedly, in the vapour phase, through a horizontal glass tube (40 x 2cm.i.d.) packed with antimony trifluoride (50g., and dried over phosphorus pentoxide in vacuo for three days) dispersed with glass-wool plugs and moistened with antimony pentachloride (1ml.). Heat was evolved and some blackening of the solid occurred.

After ten passes, the products were separated by fractional condensation in vacuo through traps maintained at -23° , -78° and -196° , to give unreacted 1,2,2-trifluoroethyltrichlorosilane and crude 1,2,2-trifluoroethyltrifluorosilane in the first two traps respectively.

The crude 1,2,2-trifluoroethyltrichlorosilane was purified by fractional condensation in vacuo through traps maintained at -23° , -45° , -78° and -196° to yield 4.04g., 0.024 mole, 65%, in the -45° trap (Found : C, 12.6; H, 1.3. $\text{C}_2\text{H}_2\text{F}_5\text{Si}$ requires C, 12.3; H, 1.2%).

The infrared (Appendix A.1) and n.m.r. (Appendix B.1) spectra of this compound have been recorded.

3.2.10. Preparation of 1,2,2-trifluoroethylsilane

Di-n-butyl ether was stood for 24 hours over anhydrous magnesium sulphate, filtered and stood for a further 24 hours over fresh sodium wire. It was then fractionally distilled from fresh sodium wire, and the middle cut (b.p. 141°) stored over a third batch of fresh sodium wire.

1,2,2-Trifluoroethyltrichlorosilane (19.58g., 0.09 mole) was condensed in vacuo onto a stirred suspension of lithium aluminium hydride (6g.) in di-n-butyl ether (150ml.). The mixture was allowed to warm slowly to room temperature, and then warmed to 70° on a water bath. The mixture was maintained at this temperature for 2 hours and the products collected in a series of traps maintained at -23° , -45° , -78° , -120° and -196° . The contents of the -23° , and -45° traps were found to be a mixture of di-n-butyl ether and unreacted 1,2,2-trifluoroethyltrichlorosilane. Crude 1,2,2-trifluoroethylsilane condensed at -78° and -120° . A trace of silane was found to be present in the -196° trap.

The 1,2,2-trifluoroethylsilane was purified by fractionation in vacuo through traps maintained at -45° , -78° , -120° and -196° to yield 9.73g., 0.0675 mole, 75%, in the -120° trap. (Found : \underline{M} , 113.5 . $\text{C}_2\text{H}_5\text{F}_3\text{Si}$ requires \underline{M} , 114).

The infrared (Appendix A.2.) and n.m.r. (Appendix B.2.) spectra of this compound have been recorded.

3.2.11. Preparation of 1,1,2,2-Tetrafluoroethyltrichlorosilane

In a typical reaction, trichlorosilane (8.66g., 0.064mole) and tetrafluoroethylene (3.22g., 0.032mole) were sealed in a 350 ml. silica tube and irradiated on a mechanical shaker for 40 hours at a distance of 30 cm. from a 500 watt mercury resonance lamp.

The products were fractionated in vacuo through traps maintained at -24° , -78° and -196° to give crude 1,1,2,2-tetrafluoroethyltrichlorosilane, unreacted trichlorosilane and tetrafluoroethylene (0.2g., 0.0020mole; 6% recovery) respectively. An involatile material remained in the reaction tube.

The crude 1,1,2,2-tetrafluoroethyltrichlorosilane was purified by fractionation under nitrogen at atmospheric pressure through a 130 x 8 mm. vacuum jacketed column, packed with glass helices and fitted with a partial reflux take-off head, b.p. $86-89^{\circ}/760\text{mm}$. Yield 4.15g., 0.01762mole, 55%. (Found : C, 10.4 ; H, 0.5. Calc. for $\text{C}_2\text{HCl}_3\text{F}_4\text{Si}$: C, 10.2 ; H, 0.4%).

The infrared spectrum showed the absence of trichlorosilane (ν Si-H at 4.6μ), and the infrared and n.m.r. spectra were consistent with pure 1,1,2,2-tetrafluoroethyltrichlorosilane (105).

3.2.12. Preparation of 1,1,2,2-Tetrafluoroethyltrifluorosilane

1,1,2,2-Tetrafluoroethyltrichlorosilane (7.56g., 0.03210 mole) was passed repeatedly, in the vapour phase, through a horizontal glass tube (40. x 2 cm.i.d.) packed with antimony trifluoride (50g., and dried over phosphorus pentoxide in vacuo for three days) dispersed with glass-wool plugs and moistened with antimony pentachloride (1ml.). Heat was evolved and some blackening of the solid occurred.

After fourteen passes, the products were separated by

fractional condensation in vacuo through traps maintained at -45° , -78° , -120° and -196° to give unreacted 1,1,2,2-tetrafluoroethyltrichlorosilane, and crude 1,1,2,2-tetrafluoroethyltrifluorosilane which condensed in the -78° and -120° traps. This crude product was purified by further fractional condensation in vacuo, using the same trap temperatures, to yield 4.48g., 0.0241mole, 75%. (Found : C, 12.8 ; H, 0.6; M, 185. Calc. for $C_2H_7F_7Si$: C, 12.9 ; H, 0.5%; M, 186).

The infrared and n.m.r. were consistent with pure 1,1,2,2-tetrafluoroethyltrifluorosilane (105).

3.2.13. Preparation of 1,1,2,2-Tetrafluoroethylsilane

1,1,2,2-Tetrafluoroethyltrichlorosilane (7.07g., 0.030 mole) was condensed in vacuo onto a stirred suspension of lithium aluminium hydride (2g.) in dry di-n-butyl ether (50ml.). The mixture was allowed to warm slowly to room temperature, and then warmed to 70° on a water bath. The mixture was maintained at this temperature for 2 hours and the products collected in a series of traps maintained at -23° , -45° , -78° , -120° and -196° . Di-n-butyl ether and unreacted 1,1,2,2-tetrafluoroethyltrichlorosilane condensed at -23° and -45° . The contents of the -78° and -120° traps were found to be crude 1,1,2,2-tetrafluoroethylsilane. A trace of silane was found to be present in the -196° trap.

The crude 1,1,2,2-tetrafluoroethylsilane was purified by fractionation in vacuo through traps maintained at -45° , -78° , -120° and -196° to yield 3.67g., 0.0255 mole, 77%, in the -120° trap. (Found : M, 131. Calc. for $C_2H_4F_4Si$: M, 132).

The infrared and n.m.r. spectra of this compound were consistent with pure 1,1,2,2-tetrafluoroethylsilane (105).

3.2.14. Preparation of 1,1,2,2-Tetrafluoroethyldeuterosilane.

1,1,2,2-Tetrafluoroethyltrichlorosilane (3.04g., 0.016 mole) was condensed in vacuo onto a stirred suspension of lithium aluminium deuteride (1g.) in dry di-n-butyl ether (50ml.). The mixture was allowed to warm slowly to room temperature, and then warmed to 70° on a water bath. The mixture was maintained at this temperature for 2 hours and the products collected in a series of traps maintained at -23° , -45° , -78° , -120° and -196° . Di-n-butyl ether and unreacted 1,1,2,2-tetra-

fluoroethyltrichlorosilane condensed at -23° and -45° . The contents of the -78° and -120° traps were found to be crude 1,1,2,2-tetrafluoroethyldeuterosilane. A trace of deuterosilane was found to be present in the -196° trap.

The crude 1,1,2,2-tetrafluoroethyldeuterosilane was purified by fractionation in vacuo through traps maintained at -45° , -78° , -120° and -196° to yield 1.62g., 0.012 mole, 75%, in the -120° trap. (Found : \underline{M} , 134.5 $\text{C}_2\text{HD}_3\text{F}_4\text{Si}$ requires \underline{M} , 135).

The infrared (Appendix A.3.) and n.m.r. (Appendix B.3.) spectra of this compound have been recorded.

3.3. Preparation and Study of Silane-Amine Complexes.

3.3.1. Technique for Studying Complex Formation

It has been found that the conventional vacuum taps and joints allow sufficient diffusion of water through the grease to cause hydrolysis of the silicon-halogen bond in halosilanes (146). A greaseless section was therefore constructed and attached to the main manifold of the conventional vacuum system. This section consisted of two calibrated storage ampoules; their cross-sectional areas were determined by a mercury displacement method. Also attached to this section was a reaction chamber, of 30-40ml. capacity, attached to a mercury manometer, a side-arm for solubility experiments, and a small ampoule fitted with a capillary mercury -manometer for vapour pressure measurements.

This system was constructed throughout of Pyrex glass and the vacuum taps used were Springham 4mm. diaphragm taps fitted with neoprene valves. The system was constructed so that the arm of the greaseless tap which contained the diaphragm orifice was attached to the ampoule; this assured that the smallest possible surface area of the valve was exposed to the reactants, and the slow swelling of the valve caused by the halosilanes, kept to a minimum. The neoprene valves were replaced periodically.

3.3.2. Stoichiometric Studies and Typical Operation of the Greaseless Section.

Unless otherwise stated, the procedure that is described

below was that followed in each of the silane-amine systems described in this research.

A known quantity of mutually dried amine was condensed into the reaction chamber from the calibrated storage ampoule. The amount was calculated by measuring the decrease in the height of the liquid in the calibrated ampoule with a 1 metre cathotometer fitted with a Vernier gauge; knowing the cross-sectional area of the ampoule and the density of the liquid, the amount of amine was calculated.

Small aliquots of the silane were condensed into the reaction chamber. After each addition, the system was allowed to attain equilibrium at the temperature chosen for the study, and the vapour pressure in the reaction chamber measured. Aliquots of silane were added until generally a mole ratio > 1 was reached.

A graph was drawn of vapour pressure against composition, expressed as mole ratio of silane to amine. The mole ratio at which the vapour pressure rose sharply (or if both the amine and silane were gases, when the vapour pressure was a minimum) gave the stoichiometry of the complex.

3.3.3. Tensiometric Studies and Dissociation Vapour Pressure Measurements.

For the calculation of thermodynamic functions (ΔH , ΔG , etc.,) of stable complexes from dissociation vapour pressure-temperature studies, a sample of the complex was formed and sealed in vacuo in an ampoule fitted with a capillary mercury manometer. The tensiometer was totally immersed in a stirred water bath and the apparatus allowed to come to equilibrium at the required temperature. Temperatures were measured ($\pm 0.2^\circ$) with a $0-110^\circ$ thermometer that had been calibrated against a set of standard thermometers. The dissociation vapour pressure at this temperature was then calculated by measuring ($\pm 0.02\text{mm.}$) the difference in the heights of the mercury capillary in the manometer with a cathotometer. The cathotometer had a 1 metre brass scale, mounted on a heavy metal base, and fitted with a sliding Vernier gauge. The heights of the mercury capillary were observed through a telescope mounted on the Vernier gauge by the method of non-parallel.

The temperature of the water bath was increased and a series of pressure measurements obtained when no further movement was observed in the mercury capillary (i.e. the system had attained equilibrium at the required temperature). To ensure that the dissociation of the complex was a reversible process, the sample was allowed to cool to the initial temperature and the pressure checked against the original pressure reading.

The temperature-vapour pressure data were computer programmed using a least mean squares method. $\log_{10} p_{\text{mm}}$ was plotted against $1/T^{\circ}\text{A}$ to ensure that the results gave a linear relationship over the temperature range studied; i.e.,

$$\log_{10} p_{\text{mm}} = a - \frac{b}{T}$$

where a is the intercept on the $\log_{10} p_{\text{mm}}$ axis, and b is the gradient of the straight line. A Van't Hoff isochore was then obtained by plotting $\log_{10} K_p$ against $1/T^{\circ}\text{A}$; i.e.,

$$\log_{10} K_p = A + \frac{B}{T}$$

where A is the intercept on the $\log_{10} K_p$ axis and B is the gradient of the straight line. The values of the dissociation constant, K_p , at 25° and 50° were obtained from the graph. The heat of formation was calculated from the gradient of the isochore, and then used to calculate other thermodynamic quantities; the free energy change, ΔG , and the entropy change, ΔS , on complex formation.

3.4. Reactions of 2-Fluoroethyltrichlorosilane.

Aliquots of 2-fluoroethyltrichlorosilane (v.p. = 27.2mm. at 20°) were condensed onto samples of dried amines using the technique already described. The results of these additions are tabulated below.

3.4.1. Trimethylamine

Trimethylamine = 0.049g., 0.827mmole at 19°.

TABLE 3.1.

<u>Cl₃SiCH₂CH₂F</u> <u>mmoles</u>	<u>mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	201
0.084	0.102	187
0.215	0.260	180
0.314	0.380	177
0.391	0.472	172
0.474	0.574	170
0.547	0.662	170
0.609	0.737	165
0.628	0.759	164
0.777	0.940	164
0.920	1.112	166
1.015	1.227	165

The pressure measurements indicate that little or no reaction occurred; no reaction was observed.

3.4.2. Pyridine

Pyridine = 0.138g., 1.745 mmoles at 20°.

Table 3.2.

<u>Cl₃SiCH₂CH₂F</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm.)</u>
0.000	0.000	12.0
0.197	0.113	13.4
0.406	0.244	15.5
0.639	0.366	17.8
0.843	0.483	20.6
0.892	0.511	21.7
1.016	0.582	23.2
1.284	0.736	27.1
1.576	0.903	27.4
1.873	1.074	27.3

The pressure measurements indicate that little or no reaction occurred; no reaction was observed.

3.4.3. α - Picoline

α -picoline = 0.174g., 1.869 mmoles at 21°

Table 3.3.

<u>Cl₃SiCH₂CH₂F</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm.)</u>
0.000	0.000	10.1
0.179	0.096	14.8
0.201	0.107	15.3.
0.237	0.127	17.5
0.376	0.201	19.1
0.547	0.294	21.3
0.668	0.357	23.9
0.821	0.439	25.0
0.952	0.510	27.3
1.037	0.555	27.2

The pressure measurements indicate that little or no reaction occurred; no reaction was observed.

3.4.4. β -Picoline

β -picoline = 0.156g., 1.675 mmoles at 22°.

Table 3.4.

<u>Cl₃SiCH₂CH₂F</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm.)</u>
0.000	0.000	6.0
0.239	0.143	7.9
0.416	0.248	9.7
0.657	0.392	13.3
0.824	0.492	16.2
0.885	0.528	17.3
0.978	0.570	19.1
1.381	0.824	25.1
1.520	0.907	27.9
1.722	1.028	28.0

A small amount of white solid formation was observed after the third addition. The reaction was repeated at -23°, but again the stoichiometry of the complex could not be determined from the vapour pressure-molar composition measurements.

3.4.5. γ -Picoline

γ -picoline = 0.187g., 2.008 mmoles at 21°.

Table 3.5.

<u>$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{F}$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm.)</u>
0.000	0.000	6.8
0.206	0.103	7.5
0.444	0.221	9.6
0.697	0.347	13.1
0.963	0.480	17.5
1.094	0.545	20.1
1.257	0.626	23.5
1.611	0.802	27.4
1.875	0.934	27.6
2.101	1.046	27.5

A small amount of white solid formation was observed after the third addition. The reaction was repeated at -23°, but again the stoichiometry of the complex could not be determined from the vapour pressure-molar composition measurements.

3.4.6. Infrared Spectra

An infrared spectrum of the vapour phase of reaction 4.1. showed a mixture of trimethylamine and 2-fluoroethyltrichlorosilane, while the infrared spectra of the vapour phases of reactions 4.2. to 4.5. showed only 2-fluoroethyltrichlorosilane to be present.

3.5. Reactions of 2,2-Difluoroethyltrichlorosilane

Aliquots of 2,2-difluoroethyltrichlorosilane (v.p. = 34.7 mm. at 20°) were condensed onto samples of dried amines using the technique already described. The results of these additions are tabulated below.

3.5.1. Trimethylamine

Trimethylamine = 0.0432 g., 0.732 mmole at 22°.

Table 3.6.

<u>Cl₃SiCH₂CHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	174
0.128	0.175	169
0.208	0.283	164
0.292	0.398	163
0.354	0.483	165
0.451	0.616	164
0.593	0.809	165

No solid formation was observed, and although the reaction was repeated at -23°, there was no evidence of any reaction occurring.

3.5.2. Pyridine

Pyridine = 0.1126g., 1.423 mmoles at 22°.

Table 3.7.

<u>Cl₃SiCH₂CHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	16.8
0.106	0.075	19.6
0.199	0.140	22.4
0.310	0.218	25.3
0.385	0.270	29.9
0.526	0.370	34.7
0.610	0.429	34.8
0.690	0.485	34.7
0.796	0.560	34.9

A small amount of white solid was formed during the reaction, but could not be characterised either at this temperature or by repeating the reaction at -23°.

3.5.3. α -Picoline

α -picoline = 0.0880g., 0.9462 mmole at 20°.

Table 3.8.

<u>$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	10.0
0.137	0.145	16.4
0.208	0.220	23.9
0.261	0.276	28.4
0.310	0.327	31.9
0.420	0.444	34.3
0.526	0.556	34.2
0.628	0.664	34.2

No solid formation was observed, and although the reaction was repeated at -23°, there was no evidence of any reaction occurring.

3.5.4. β -Picoline

(a) Reaction at 20° β -picoline = 0.1778g., 0.955 mmole.

Table 3.9.

<u>$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	5.9
0.044	0.046	8.7
0.168	0.176	16.6
0.252	0.264	22.2
0.363	0.380	29.9
0.419	0.449	35.5
0.535	0.560	35.4
0.610	0.639	35.3
0.720	0.736	35.6

A small amount of white solid was formed during the reaction, but could not be characterised at this temperature.

(b) Reaction at -23° β -picoline = 0.1778g., 0.955 mmole.

Table 3.10.

<u>$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	1.6
0.079	0.083	1.8
0.168	0.176	1.8
0.230	0.241	1.9
0.354	0.371	1.8
0.482	0.505	7.8
0.531	0.556	9.9
0.641	0.672	10.3
0.717	0.750	10.4
0.796	0.834	10.5

A white solid was formed during the addition and the pressure measurements at this temperature indicate that the complex has a molar composition (silane/amine) of 0.5.

A tensiometric study of the complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.11.

Table 3.11.

<u>Temp. °C.</u>	<u>p.measured, mm.</u>	<u>p.amine, mm.</u>	<u>p.silane, mm.</u>
-10.0	4.09	0.88	3.21
- 5.9	4.55	1.19	3.36
- 1.5	5.23	1.57	3.66
+ 2.1	6.03	1.97	4.06
+ 5.0	6.51	2.34	4.17
+ 8.8	7.49	2.97	4.52
+12.4	8.42	3.67	4.75
+16.2	9.70	4.63	5.07

The measured vapour pressures indicate that the dissociation vapour pressure of the adduct is too high for all the dissociated β -picoline to be in the vapour phase. So the silane vapour pressure was calculated, knowing the saturation vapour pressure of β -picoline at the experimental temperatures. The p-silane values were processed in the manner described previously, and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 2.77 - \frac{598}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = -0.11 - \frac{598}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.5.5. γ -Picoline

(a) Reaction at 19° γ -picoline = 0.102g., 1.091 mmoles.

Table 3.12.

<u>$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	6.4
0.127	0.139	9.6
0.263	0.287	13.7
0.389	0.424	19.8
0.463	0.505	27.0
0.525	0.573	33.6
0.584	0.637	35.0
0.690	0.753	35.2
0.812	0.886	35.2
0.929	1.013	35.1
1.044	1.139	35.2

A small amount of white solid was formed during the reaction, but could not be characterised at this temperature.

(b) Reaction at -23° γ -picoline = 0.103g., 1.105 mmoles.

Table 3.13.

<u>$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	1.1
0.133	0.120	1.5
0.243	0.220	1.3
0.336	0.304	1.5
0.416	0.376	1.5
0.504	0.456	1.9
0.584	0.528	8.4
0.655	0.593	9.1
0.721	0.653	9.1
0.805	0.729	9.3

A white solid was formed during the reaction and the pressure measurements at this temperature indicate that the complex has a molar composition (silane/amine) of 0.5.

A tensiometric study of this complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.14.

Table 3.14.

<u>Temp. °C.</u>	<u>p.measured,mm.</u>	<u>p.amine,mm.</u>	<u>p.silane,mm.</u>
-11.2	3.83	0.70	3.13
- 7.0	4.39	0.92	3.47
- 4.1	4.76	1.11	3.65
- 0.9	5.33	1.38	3.95
+ 3.8	6.34	1.88	4.46
+ 8.2	7.68	2.48	5.20
+12.9	8.78	3.31	5.47
+16.0	9.92	3.99	5.93
+20.6	11.68	5.19	6.49

The measured vapour pressures indicate that the dissociation vapour pressure of the adduct is too high for all the dissociated γ -picoline to be in the vapour phase. So the silane vapour pressure was calculated, knowing the saturation vapour pressure of γ -picoline at the experimental temperatures. The p-silane values were processed in the manner described previously, and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 3.50 - \frac{790}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 0.59 - \frac{779}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.5.6. Infrared Spectra

An infrared spectrum of the vapour phase of reaction 5.1. showed a mixture of trimethylamine and 2,2-difluoroethyltri-chlorosilane, while the infrared spectra of reactions 5.2. to 5.5. showed only 2,2-difluoroethyltrichlorosilane to be present.

3.6. Reactions of 2,2-Difluoroethyltrifluorosilane

Aliquots of 2,2-difluoroethyltrifluorosilane (v.p. = 27.7cm. at 20°) were condensed onto samples of dried amines using the technique already described. The results of these additions are tabulated below.

3.6.1. Pyridine

Pyridine = 0.0701g., 0.8874 mmole at 22°

Volume of reaction vessel = 62.3 ml.

Table 3.15.

<u>F₃SiCH₂CHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure*mm.</u>	<u>Mmoles</u> <u>of gas</u>	<u>% gas</u> <u>evolved**</u>
0.000	0.000	0.0	0.000	-
0.131	0.148	39.9	0.137	93.0
0.222	0.250	67.6	0.232	92.0
0.336	0.379	102.2	0.343	92.7
0.393	0.442	119.9	0.412	92.8
0.450	0.507	136.5	0.469	92.7
0.512	0.577	156.0	0.535	-
0.620	0.699	188.7	0.648	-

* corrected for vapour pressure of pyridine.

** expressed as % of F₃SiCH₂CHF₂ added.

On adding aliquots of 2,2-difluoroethyltrifluorosilane to the pyridine, a white solid was formed and a gas was evolved. The gas was identified by infrared spectroscopy and molecular weight measurements as vinyl fluoride. The infrared spectra indicate that vinyl fluoride was liberated up to a mole ratio of ~ 0.5, and that the increase in vapour pressure produced by subsequent additions of 2,2-difluoroethyltrifluorosilane was due to the presence of excess 2,2-difluoroethyltrifluorosilane.

This indicates that reaction had stopped at a mole ratio of ~ 0.5 , and that the complex has a molar composition (added silane/amine) of ~ 0.5 . No further change in pressure was observed on leaving the reaction for 48 hours, indicating that no more vinyl fluoride was liberated.

The vinyl fluoride and excess 2,2-difluoroethyltrifluoro-silane were pumped off and the solid residue warmed to 65° . A further 0.0304mmoles (equivalent to 6.8% of the stoichiometric amount of silane required for a 1:2 complex) of vinyl fluoride were liberated.

An infrared spectrum was obtained of the heated solid residue and is recorded in Appendix A.4.

A tensiometric study was carried out on the heated solid residue and the temperature-vapour pressure data are recorded in Table 3.16. for this system.

Table 3.16.

<u>Temperature $^{\circ}\text{C}.$</u>	<u>p, mm.</u>
22.1	4.13
28.0	5.43
35.0	7.55
43.1	11.85
49.5	14.41
55.0	19.93
60.9	26.12

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 7.54 - \frac{2048}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 13.37 - \frac{6209}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.6.2. α -Picoline

A preliminary study of this reaction showed that reaction was slow. So α -picoline (0.0587g., 0.630mmole) and 2,2-difluoroethyltrifluorosilane (0.0473g., 0.315mmole) were sealed in a break-seal tube and left for 28 days in the dark. During this time a very pale yellow solid was formed in the tube. The tube was then opened and the products analysed using the techniques described in Section 6.5.

Table 3.17.

<u>Trap</u>	<u>Compound</u>	<u>Mmoles</u>
-23°	$\text{F}_3\text{SiCH}_2\text{CHF}_2$	0.0694
-78°	$\text{CH}_2=\text{CHF}$	0.2065
Hydrolysis	$\text{CH}_2=\text{CHF}$	0.0328
		0.3087
	Mass Balance	= 98%

3.6.3. β -Picoline

β -picoline = 0.0713g., 0.765 mmole at 20°

Volume of reaction vessel = 46.2 ml.

Table 3.18.

<u>F₃SiCH₂CHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour</u> <u>Pressure* mm.</u>	<u>Mmoles</u> <u>of gas</u>	<u>% gas</u> <u>evolved**.</u>
0.000	0.000	0.0	0.000	-
0.114	0.149	42.4	0.107	94.2
0.211	0.275	78.9	0.199	94.4
0.341	0.426	127.2	0.322	94.2
0.398	0.500	147.6	0.374	94.1
0.594	0.647	184.4	0.466	-
0.609	0.795	224.9	0.567	-

* corrected for vapour pressure of β -picoline

** expressed as % of F₃SiCH₂CHF₂ added.

This reaction was treated in an analogous manner to the pyridine reaction (Section 6.1.). The white solid formed corresponded to a molar composition of 0.5, and on warming the solid to 65°, a further 0.0421 mmoles of vinyl fluoride (equivalent to 5.5%) were liberated. An infrared spectrum of the heated solid residue was obtained and is recorded in Appendix A.5.

A tensiometric study was carried out on the heated solid residue and the temperature-vapour pressure data for this system are recorded in Table 3.19.

Table 3.19.

<u>Temperature °C.</u>	<u>p, mm.</u>
21.6	2.65
26.2	3.19
30.9	4.49
34.9	5.24
39.0	6.80
44.4	9.19
49.1	11.88
54.6	15.79

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 8.39 - \frac{2356}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 15.80 - \frac{7105}{T}$$

and the thermodynamic data which are recorded in Appendix C.

3.6.4. γ -Picoline

γ -picoline = 0.0727g., 0.781 mmole at 20°.

Volume of reaction vessel = 75.3 ml.

Table 3.20.

<u>F₃SiCH₂CHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour</u> <u>pressure*,mm.</u>	<u>Mmoles</u> <u>of gas</u>	<u>% gas</u> <u>evolved**</u>
0.000	0.000	0.0	0.000	-
0.091	0.117	21.2	0.088	96.1
0.171	0.219	39.0	0.162	95.9
0.273	0.350	63.3	0.263	96.2
0.353	0.452	81.4	0.338	95.8
0.387	0.495	90.1	0.374	95.9
0.421	0.539	98.7	0.410	-
0.512	0.656	119.0	0.494	-
0.609	0.780	135.3	0.562	-
0.706	0.903	158.7	0.658	-
0.808	1.035	187.0	0.776	-
0.888	1.136	202.9	0.843	-

* corrected for vapour pressure of γ -picoline

** expressed as % of F₃SiCH₂CHF₂ added.

This reaction was treated in an analogous manner to the pyridine reaction (Section 6.1.). The white solid formed corresponded to a molar composition of ~ 0.5 , and on warming the solid to 65°, a further 0.0273 mmoles of vinyl fluoride (equivalent to 3.5%) were liberated. An infrared spectrum of the heated solid residue was obtained and is recorded in Appendix A.6.

A tensiometric study was carried out on the heated solid residue and the temperature-vapour pressure data for this system are recorded in Table 3.21.

Table 3.21.

<u>Temperature °C.</u>	<u>p,mm.</u>
22.5	1.78
26.4	2.24
30.3	2.88
36.0	4.19
40.4	5.51
45.4	7.43
49.8	9.77
54.9	13.00

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 9.08 - \frac{2613}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 17.75 - \frac{7836}{T}$$

and the thermodynamic data which are recorded in Appendix C.

3.6.5. Trimethylamine

A preliminary study of this reaction showed that reaction was slow and that liberation of vinyl fluoride was equally slow.

So a series of reactions were carried out so that the degree of reaction could be determined from an estimation of the amounts of reactants and products.

These reactions were carried out using equimolar amounts of trimethylamine and 2,2-difluoroethyltrifluorosilane which were sealed in a break-seal tube and left in the dark. The tubes were opened and the volatile materials condensed into a -196° trap. These were then fractionated in vacuo and the components identified by infrared spectroscopy. The solid residues in the tubes were hydrolysed by adding an excess of water and the quantity of vinyl fluoride liberated was measured after fractionation in vacuo. Yields are based on the amount of 2,2-difluoroethyltrifluorosilane used.

(a) Reaction at 20° for 72 hours.

Me_3N	0.0409g., 0.6930 mmole
$\text{F}_3\text{SiCH}_2\text{CHF}_2$	0.1040g., 0.6930 mmole.

Table 3.22.

<u>Trap</u>	<u>Compound</u>	<u>Mmoles</u>	<u>%</u>
-23°	$\text{F}_3\text{SiCH}_2\text{CHF}_2$	0.1322	19
-78°	$\text{CH}_2 = \text{CHF}$	0.1509	21
Hydrolysis	$\text{CH}_2 = \text{CHF}$	0.4028	58
Mass Balance			98

(b) Reaction at 20° for 192 hours.

Me_3N 0.0407g., 0.6916 mmole
 $\text{F}_3\text{SiCH}_2\text{CHF}_2$ 0.1038g., 0.6916 mmole.

Table 3.23.

<u>Trap</u>	<u>Compound</u>	<u>Mmoles</u>	<u>%</u>
-23°	$\text{F}_3\text{SiCH}_2\text{CHF}_2$	0.2709	39
-78°	$\text{CH}_2 = \text{CHF}$	0.3018	43
Hydrolysis	$\text{CH}_2 = \text{CHF}$	0.1058	15
Mass Balance			97

(c) Reaction at -10° for 28 days

Me_3N 0.0343g., 0.5811 mmole
 $\text{F}_3\text{SiCH}_2\text{CHF}_2$ 0.0872g., 0.5811 mmole.

Table 3.24.

<u>Trap</u>	<u>Compound</u>	<u>Mmoles</u>	<u>%</u>
-23°	$\text{F}_3\text{SiCH}_2\text{CHF}_2$	0.2040	35
-78°	$\text{CH}_2 = \text{CHF}$	0.2478	42.5
Hydrolysis	$\text{CH}_2 = \text{CHF}$	0.1217	21
Mass Balance			98.5

(d) Reaction at -23° for 28 days

Me_3N	0.0343g.,	0.5811 mmole
$\text{F}_3\text{SiCH}_2\text{CHF}_2$	0.0872g.,	0.5811 mmole.

Table 3.25.

<u>Trap</u>	<u>Compound</u>	<u>Mmoles</u>	<u>%</u>
-23°	$\text{F}_3\text{SiCH}_2\text{CHF}_2$	0.0790	13.5
-78°	$\text{CH}_2 = \text{CHF}$	0.1358	23.5
Hydrolysis	$\text{CH}_2 = \text{CHF}$	0.3484	60
Mass Balance			97

3.7. Reactions of 1,2,2-Trifluoroethyltrichlorosilane

Aliquots of 1,2,2-trifluoroethyltrichlorosilane (v.p. = 30.2mm. at 20°) were condensed onto samples of dried amines using the technique already described. The results of these additions are tabulated below.

3.7.1. Trimethylamine

Trimethylamine = 0.0421g., 0.713 mmole at 21°

Table 3.26.

<u>$\text{Cl}_3\text{SiCHFCHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour pressure(mm)</u>
0.000	0.000	170
0.101	0.141	169
0.237	0.328	161
0.380	0.546	158
0.498	0.694	157
0.651	0.913	156
0.843	1.183	155
0.884	1.241	155
1.003	1.408	155
1.145	1.607	154

No solid formation was observed and although the reaction was repeated at -23° , there was no evidence of any reaction occurring.

3.7.2. Pyridine

Pyridine = 0.988g., 1.243 mmoles at 18° .

Table 3.27.

<u>$\text{Cl}_3\text{SiCHFCHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	16.0
0.090	0.072	16.2
0.124	0.099	16.5
0.200	0.161	17.1
0.247	0.199	19.0
0.285	0.229	19.3
0.385	0.310	27.7
0.495	0.398	27.4

A small amount of white solid was formed during the reaction, but could not be characterised either at this temperature or by repeating the reaction at -36° .

3.7.3. α -Picoline

α -picoline = 0.173g., 1.862 mmoles at 22° .

Table 3.28.

<u>$\text{Cl}_3\text{SiCHFCHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	9.7
0.068	0.037	28.5
0.149	0.080	30.9
0.273	0.147	30.3
0.414	0.222	30.4
0.686	0.369	30.5
0.921	0.495	30.3
1.045	0.561	30.4

3.7.4. β -Picoline

β -picoline = 0.115g., 1.23 mmoles at 20°.

Table 3.29.

<u>Cl₃SiCHFCHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	4.8
0.055	0.045	5.3
0.179	0.146	5.7
0.286	0.232	6.3
0.311	0.253	6.3
0.345	0.281	6.4
0.401	0.326	5.8
0.520	0.423	6.0
0.575	0.468	5.6
0.631	0.513	17.3
0.699	0.569	26.7
0.771	0.627	26.8
0.887	0.721	27.0
0.985	0.801	27.1
1.053	0.856	26.8
1.168	0.950	27.0
1.236	1.006	27.2
1.296	1.057	26.8

A white solid was formed during the addition and the pressure measurements indicate that the complex has a molar composition (silane/amine) of 0.5. The infrared spectrum of the complex was obtained and recorded in Appendix A.7.

A tensiometric study of the complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.30.

Table 3.30.

<u>Temperature °C.</u>	<u>p,mm.</u>
18.1	4.39
22.0	5.19
25.8	6.51
29.8	8.00
31.9	8.79
34.6	10.37
37.1	11.39
40.0	13.30
43.4	16.24
46.0	17.90
48.7	20.11
51.1	22.40
54.0	25.24

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 7.69 - \frac{2056}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 13.60 - \frac{6168}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.7.5. γ -Picoline

γ -picoline = 0.187g., 2.012 mmoles at 21°.

Table 3.31.

<u>Cl₃SiCHFCHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	6.1
0.155	0.077	6.0
0.315	0.158	6.1
0.407	0.202	6.2
0.516	0.256	6.4
0.576	0.285	6.4
0.704	0.350	6.4
0.749	0.372	6.4
0.868	0.432	6.3
0.914	0.454	6.2
0.978	0.486	6.0
1.097	0.545	23.4
1.169	0.581	27.4
1.229	0.611	29.9
1.430	0.711	30.2
1.617	0.803	30.3
1.885	0.922	30.2
2.006	0.997	30.4
2.157	1.024	30.3
2.357	1.172	30.3

A white solid was formed during the addition and the pressure measurements indicate that the complex has a molar composition (silane/amine) of 0.5. The infrared spectrum of the complex was obtained and recorded in Appendix A.8.

A tensiometric study of the complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.32.

Table 3.32.

<u>Temperature °C.</u>	<u>p,mm.</u>
9.9	1.51
14.9	1.95
18.7	2.96
24.9	3.97
30.4	5.33
34.9	6.71
40.1	9.90
44.8	11.25
49.8	14.97
54.7	20.06

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 8.30 - \frac{2298}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 15.66 - \frac{6964}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.7.6. 2,2'-Bipyridyl

2,2'-Bipyridyl was stored in vacuo over barium oxide for 3 days. 2,2'-Bipyridyl (0.322g., 2.06mmoles) was placed in the reaction chamber and evacuated continuously for 6 hours to remove any final traces of moisture. Aliquots of 1,2,2-tri-fluoroethyltrichlorosilane were added to this sample and the results are recorded in Table 3.33.

Table 3.33.

<u>Cl₃SiCHFCHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	0.0
0.209	0.101	25.8
0.298	0.145	26.1
0.401	0.195	26.0
0.522	0.255	26.2

No reaction was observed to have taken place.

3.7.7. 2,2,2-Bicyclo-1,4-diazo-octane. ("Dabco").

A sample of "Dabco" was stored in vacuo for 3 days. "Dabco" (0.207g., 1.84 mmoles) was placed in the reaction chamber and evacuated continuously for 6 hours to remove any final traces of moisture. Aliquots of 1,2,2-trifluoroethyltri-chlorosilane were added to this sample and the results recorded in Table 3.34.

Table 3.34.

<u>Cl₃SiCHFCHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	0.4
0.085	0.046	11.4
0.170	0.093	13.4
0.281	0.153	15.7
0.367	0.199	16.1
0.503	0.273	16.4
0.563	0.305	18.1
0.699	0.379	19.4
0.793	0.430	20.6
0.937	0.509	21.5
1.017	0.551	22.7
1.177	0.653	24.9
1.278	0.694	27.8
1.363	0.740	27.8
1.509	0.818	27.9
1.704	0.924	27.8
1.843	0.999	28.0
1.958	1.074	27.8

During the course of the reaction, the solid amine changed from a near-white powder to a very pale yellow solid. But the pressure measurements indicate that reaction was not sufficient for any product to be characterised.

3.7.8. Infrared Spectra

An infrared spectrum of the vapour phase of reaction 7.1. showed a mixture of trimethylamine and 1,2,2-trifluoroethyltrichlorosilane, while the infrared spectra of reactions 7.2. to 7.7. showed only 1,2,2-trifluoroethyltrichlorosilane to be present.

3.8. Reactions of 1,2,2-Trifluoroethyltrifluorosilane

Aliquots of 1,2,2-trifluoroethyltrifluorosilane (v.p. = 384 mm. at 20°) were condensed onto samples of dried amines using the techniques already described. The results of these additions are tabulated below.

3.8.1. β -Picoline

β -picoline = 0.0830g., 0.890 mmole at 22°.

Table 3.35.

<u>$\text{F}_3\text{SiCHFCHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	5
0.111	0.125	5
0.210	0.236	5
0.309	0.347	7
0.389	0.437	8
0.439	0.493	8
0.519	0.583	15
0.637	0.715	30
0.730	0.819	53
0.835	0.936	78
0.952	1.068	102

During the course of the reaction a white solid was formed and the pressure measurements indicate that the complex has a molar composition (silane/amine) of 0.5. The infrared spectrum

of the complex was obtained and recorded in Appendix A.9.

A tensiometric study of the complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.36.

Table 3.36.

<u>Temperature °C.</u>	<u>p, mm.</u>
19.4	3.18
23.0	4.22
26.1	5.25
29.5	6.75
32.1	8.10
35.0	10.34
37.8	11.97
41.0	14.88
43.8	17.80
46.2	20.43
50.0	24.64

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 10.20 - \frac{2383}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 21.32 - \frac{7142}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.8.2. γ -Picoline

γ -picoline = 0.0915g., 0.983 mmole at 21.5°.

Table 3.37.

<u>$\text{F}_3\text{SiCH}_2\text{CHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	4
0.129	0.132	4
0.235	0.239	5
0.343	0.348	5
0.447	0.454	6
0.519	0.528	10
0.612	0.627	23
0.717	0.730	39
0.841	0.855	62
0.952	0.968	85
1.058	1.076	95
1.113	1.145	109

During the course of the reaction a white solid was formed and the pressure measurements indicate that the complex has a molar composition (silane/amine) of 0.5. The infrared spectrum of the complex was obtained and recorded in Appendix A.10.

A tensiometric study of the complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.38.

Table 3.38.

<u>Temperature °C.</u>	<u>p, mm.</u>
18.2	6.40
21.8	8.22
26.0	10.93
30.0	13.86
35.0	18.64
39.6	25.20
43.1	30.23
46.5	37.57
50.0	47.51

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 9.43 - \frac{2510}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 18.81 - \frac{7532}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.8.3. Infrared Spectra.

The infrared spectra of the vapour phase of reactions 8.1. and 8.2. showed only 1,2,2-trifluoroethyltrifluorosilane to be present.

3.9. Reactions of 1,2,2-Trifluoroethylsilane

Aliquots of 1,2,2-trifluoroethylsilane (vapour at room temperature) were condensed onto samples of dried amine using the techniques already described. The results of these additions are tabulated below.

3.9.1. Trimethylamine

(a) Reaction at 21° Trimethylamine = 0.0607g., 1.028mmoles.

Table 3.39.

<u>H₃SiCHFCHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour</u> <u>pressure(mm)</u>	<u>Pressure(mm) ex-</u> <u>pected for no reaction</u>
0.000	0.000	437	437
0.077	0.975	451	470
0.212	0.208	459	528
0.306	0.298	465	567
0.419	0.407	472	615
0.525	0.511	470	660
0.647	0.619	492	708
0.769	0.748	504	764
0.851	0.828	514	799
0.932	0.907	523	833
1.006	0.978	532	864
1.078	1.045	542	904
1.196	1.163	559	945

A small amount of colourless liquid was formed during the reaction, but could not be characterised at this temperature.

(b) Reaction at -23° Trimethylamine = 0.0599g., 1.015mmoles.

Table 3.40.

<u>H₃SiCHFCHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	201
0.117	0.115	176
0.225	0.222	156
0.336	0.324	137
0.448	0.442	121
0.586	0.577	91
0.700	0.690	75
0.808	0.797	57
0.890	0.877	45
0.956	0.942	36
0.996	0.981	31
1.026	1.011	33
1.069	1.054	40
1.177	1.158	48
1.273	1.255	61
1.364	1.344	74
1.476	1.455	90
1.623	1.600	112
1.750	1.725	135
1.843	1.816	148
1.972	1.944	176
2.037	2.008	192
2.146	2.115	214

A colourless liquid became observable during the reaction and the pressure measurements indicate that the complex has a molar composition (silane/amine) of 1:1 at this temperature.

The dissociation vapour pressure of the complex was too high at room temperature to permit an infrared spectrum to be obtained. The n.m.r. spectra of the complex was obtained and is recorded in Appendix B.4.

A tensiometric study of the complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.41.

Table 3.41.

<u>Temperature °C.</u>	<u>p,mm.</u>
-40.4	19.21
-35.0	23.19
-30.1	30.72
-25.7	37.92
-20.3	49.59
-15.6	61.79
-10.1	80.08
- 5.2	97.61
- 0.6	118.75
+ 5.0	143.00

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 6.78 - \frac{1286}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 7.21 - \frac{2572}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.9.2. β -Picoline(a) Reaction at 21° β -picoline = 0.134g., 1.450 mmoles.Table 3.42.

<u>$\text{H}_3\text{SiCHFCHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure (mm)</u>
0.000	0.000	5
0.166	0.115	26
0.340	0.234	46
0.501	0.346	65
0.663	0.458	83
0.715	0.493	89
0.775	0.536	93
0.925	0.683	112
1.080	0.745	127
1.244	0.858	157
1.496	1.032	180

(b) Reaction at -23° β -picoline = 0.139g., 1.497 mmoles.Table 3.43.

<u>$\text{H}_3\text{SiCHFCHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	1
0.149	0.099	6
0.297	0.199	12
0.452	0.302	20
0.613	0.409	32
0.684	0.457	38
0.751	0.502	48
0.813	0.543	54
0.964	0.644	71
1.094	0.730	86
1.263	0.844	103
1.422	0.950	121
1.537	1.027	135
1.701	1.136	154

Although the addition at $+21^{\circ}$ indicates that reaction was negligible at that temperature, some complexation is indicated in the addition at -23° by the low pressure readings obtained for the first few additions. But any complex formed could not be characterised.

3.9.3. γ -Picoline

(a) Reaction at 21° γ -picoline = 0.127g., 1.363 mmoles.

Table 3.44.

<u>$\text{H}_3\text{SiCHFCHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	6
0.154	0.113	13
0.297	0.219	24
0.469	0.345	40
0.613	0.450	57
0.676	0.497	62
0.739	0.543	69
0.892	0.656	86
1.056	0.776	107
1.240	0.911	122
1.387	1.020	139

(b) Reaction at -23° γ -picoline = 0.140g., 1.508 mmoles.

Table 3.45.

<u>H₃SiCHFCHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	1
0.165	0.109	11
0.309	0.205	14
0.456	0.303	32
0.617	0.400	50
0.680	0.451	58
0.750	0.497	66
0.795	0.527	72
0.865	0.574	81
0.998	0.662	96
1.174	0.779	118
1.326	0.880	139
1.439	0.954	154
1.602	1.062	174
1.755	1.164	192

Although the reaction at $+21^{\circ}$ indicates that reaction was negligible at that temperature, some complexation is indicated in the addition at -23° by the low pressure readings obtained for the first few additions. But any complex formed could not be characterised.

3.9.4. Infrared Spectra

The infrared spectrum of the vapour phase of reaction 9.1.(a) showed only excess 1,2,2-trifluoroethylsilane to be present. The infrared spectra of reactions 9.2. and 9.3. showed only 1,2,2-trifluoroethylsilane to be present.

3.10. Reactions of 1,1,2,2-Tetrafluoroethyltrichlorosilane

The stoichiometric additions of this silane have been carried out and evidence was obtained for the formation of 1:2 adducts with β - and γ -picolines (105).

3.10.1. Tensiometric Study of $\text{Cl}_3\text{SiCF}_2\text{CHF}_2$ 2 β -picoline

The temperature-vapour pressure data for this system are recorded in Table 3.46.

Table 3.46.

<u>Temperature °C.</u>	<u>p, mm.</u>
18.0	1.40
28.9	2.50
38.2	4.50
45.4	6.26
51.0	8.56
58.4	11.66

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 7.82 - \frac{6709}{T}$$

They yield the following Vant't Hoff isochore,

$$\log_{10} K_p = 13.99 - \frac{6709}{T}$$

and the thermodynamic data which are recorded in Appendix C.

3.10.2. Tensiometric Study of $\text{Cl}_3\text{SiCF}_2\text{CHF}_2$.2 γ -picoline

The temperature-vapour pressure data for this system are recorded in Table 3.47.

Table 3.47.

<u>Temperature °C.</u>	<u>p, mm.</u>
22.1	2.11
35.9	4.94
40.2	6.32
49.2	10.47
55.3	14.45
59.6	18.20

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 8.60 - \frac{2442}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 16.88 - \frac{7490}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.10.3. Infrared Spectrum

The infrared spectrum of the γ -picoline adduct of 1,1,2,2-tetrafluoroethyltrichlorosilane was obtained and is recorded in Appendix A.11.

3.11. Reactions of 1,1,2,2-Tetrafluoroethyltrifluorosilane

Aliquots of 1,1,2,2-tetrafluoroethyltrifluorosilane (v.p. = 260 mm. at 21°) were condensed onto samples of dried amines using the techniques already described. The results of these additions are tabulated below.

3.11.1. Pyridine

Pyridine = 0.112g., 1.411 mmoles at 20°.

Table 3.48.

<u>F₃SiCF₂CHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	14
0.102	0.072	20
0.199	0.112	23
0.315	0.223	23
0.390	0.276	24
0.497	0.360	25
0.626	0.444	25
0.684	0.485	28
0.750	0.532	59
0.803	0.569	80
0.923	0.654	111
1.042	0.738	159
1.183	0.838	210
1.334	0.945	256
1.466	1.039	299

During the reaction, a white solid was formed and the pressure measurements indicate that the complex has a molar composition (silane/amine)0.5. The infrared spectrum of the complex was obtained and is recorded in Appendix A.12.

A tensiometric study of the complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.49.

Table 3.49.

<u>Temperature °C.</u>	<u>p,mm.</u>
23.5	2.39
32.9	3.85
41.2	5.76
50.6	10.80
56.8	13.55
61.9	17.75

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm.}} = 8.07 - \frac{2285}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 14.72 - \frac{6855}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.11.2. α -Picoline

α -picoline = 0.133g., 1.431 mmoles at 21°.

Table 3.50.

<u>$F_3SiCF_2CHF_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	7
0.134	0.094	43
0.331	0.231	50
0.491	0.343	58
0.630	0.440	79
0.695	0.486	84
0.762	0.533	100
0.872	0.609	120
1.079	0.754	136
1.240	0.867	180
1.446	1.011	228

During the reaction, a very small amount of white solid was formed but it could not be characterised from the pressure measurements. The reaction was left in the dark for 96 hours; no change in the pressure was observed, indicating that no further reaction had occurred.

3.11.3. Tensiometric Study of $F_3SiCF_2CHF_2 \cdot 2 \beta$ -picoline

The stoichiometry of this adduct has been determined by Cook (105). The temperature-vapour pressure data for this system are recorded in Table 3.51.

Table 3.51.

<u>Temperature °C.</u>	<u>p, mm.</u>
22.9	1.24
30.6	1.93
38.9	3.33
47.3	5.60
53.2	8.83
57.8	11.50
61.0	14.44
64.4	17.00

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm.}} = 9.54 - \frac{2803}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 19.14 - \frac{8410}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.11.4. γ -Picoline

γ -picoline = 0.0964g., 1.035 mmoles at 22°.

Table 3.52.

<u>F₃SiCF₂CHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	5
0.104	0.101	5
0.188	0.181	5
0.294	0.284	4
0.380	0.367	4
0.444	0.429	4
0.499	0.483	4
0.556	0.537	20
0.684	0.661	70
0.815	0.788	132
0.933	0.922	168
1.066	1.030	208

During the reaction, a white solid was formed and the pressure measurements indicate that this complex has a molar composition (silane/amine) of 0.5. An infrared spectrum of the complex was obtained and is recorded in Appendix A.13.

A tensiometric study of the complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.53.

Table 3.53.

<u>Temperature °C.</u>	<u>p, mm.</u>
23.0	1.08
31.6	1.74
39.9	3.16
47.4	5.50
54.4	8.76
58.6	11.43
63.7	15.25

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm.}} = 9.76 - \frac{2892}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 19.76 - \frac{8653}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.11.5. Infrared Spectra

The infrared spectra of the vapour phases of reactions 11.1., 11.2., and 11.3., showed only 1,1,2,2-tetrafluoroethyl-trifluorosilane to be present.

3.12. Reactions of 1,1,2,2-Tetrafluoroethylsilane

Aliquots of 1,1,2,2-tetrafluoroethylsilane (vapour at room temperature) were condensed onto samples of dried amine using the techniques already described. The results of these additions are tabulated below.

3.12.1. Pyridine

Pyridine = 0.114g., 1.442 mmoles at 19°

Table 3.54.

<u>H₃SiCF₂CHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	10
0.122	0.085	28
0.276	0.192	41
0.432	0.299	55
0.570	0.396	74
0.701	0.464	88
0.758	0.526	111
0.818	0.580	128
0.967	0.670	148
1.146	0.795	182
1.292	0.896	204
1.461	1.013	245
1.594	1.106	260

The pressure measurements indicate that no reaction occurred, and no reaction was observed.

3.12.2. α -Picoline

α -picoline = 0.101g., 1.088 mmoles at 21°

Table 3.55.

<u>$\text{H}_3\text{SiCF}_2\text{CHF}_2$</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	6
0.111	0.101	27
0.209	0.192	46
0.295	0.271	68
0.384	0.353	79
0.466	0.428	101
0.529	0.468	124
0.615	0.565	150
0.762	0.701	173
0.924	0.849	220
1.063	0.976	251
1.192	1.110	281

The pressure measurements indicate that no reaction occurred, and no reaction was observed.

3.12.3. Tensiometric Study of $\text{H}_3\text{SiCF}_2\text{CHF}_2$.2 β -picoline

The stoichiometry of this adduct has been determined by Cook(105). The temperature-vapour pressure data for this system are recorded in Table 3.56.

Table 3.56.

<u>Temperature</u> <u>°C.</u>	<u>p measured,mm.</u>	<u>p amine,mm.</u>	<u>p silane,mm.</u>
23.2	21.72	6.89	14.83
28.2	28.52	9.00	19.52
34.0	39.18	12.16	27.02
39.1	46.69	15.70	33.99
43.8	62.80	19.68	43.12
50.0	85.52	26.30	56.22
55.0	103.13	33.12	70.01

The measured vapour pressure values indicate that the dissociation vapour pressure of the adduct is too high for all the dissociated β -picoline to be in the vapour phase. So the silane vapour pressure was calculated, knowing the saturation vapour pressure of β -picoline at the experimental temperatures. The p-silane values were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 8.13 - \frac{2061}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 5.25 - \frac{2061}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.12.4. γ -Picoline

γ -picoline = 0.148g., 1.595 mmoles at 21°.

Table 3.57.

<u>H₃SiCF₂CHF₂</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	5
0.141	0.089	20
0.294	0.184	24
0.459	0.288	24
0.577	0.362	26
0.676	0.424	25
0.728	0.456	26
0.776	0.486	31
0.825	0.517	36
0.880	0.552	50
1.022	0.641	72
1.164	0.729	103
1.384	0.845	130
1.477	0.925	174
1.602	1.004	206
1.723	1.080	234

The volume of liquid in the reaction vessel appeared to increase considerably during the reaction, and the pressure measurements indicate that this colourless liquid complex has a molar composition of 0.5 at this temperature. An infrared and a n.m.r. spectra were obtained of the complex and are recorded in Appendix A.14. and Appendix B.5. respectively.

A tensiometric study of the complex was carried out and the temperature-vapour pressure data for this system are recorded in Table 3.58.

Table 3.58.

<u>Temperature</u> <u>°C.</u>	<u>p measured,mm.</u>	<u>p amine,mm.</u>	<u>p silane,mm.</u>
22.4	21.59	5.92	15.67
28.2	29.90	7.96	21.94
33.1	39.39	10.35	29.04
39.6	54.79	14.72	40.07
45.0	71.08	19.06	52.02
50.1	90.28	25.07	65.21
55.0	112.20	30.55	81.65

The measured vapour pressures indicate that the dissociation vapour pressure of the adduct is too high for all the dissociated γ -picoline to be in the vapour phase. So the silane vapour pressure was calculated, knowing the saturation vapour pressure of γ -picoline at the experimental temperatures. The p-silane values were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 8.40 - \frac{2129}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 5.47 - \frac{2111}{T}$$

and thermodynamic data which are recorded in Appendix C.

3.12.5. Infrared Spectra

The infrared spectra of the vapour phases of reactions 12.1., 12.2., and 12.4., showed only 1,1,2,2-tetrafluoroethylsilane to be present.

3.13. Reactions of Trifluorosilane

Aliquots of trifluorosilane (vapour at room temperature) were condensed onto samples of dried amine using the techniques already described. The results of these additions are tabulated below.

3.13.1. β -Picoline

β -picoline = 0.102g., 1.097 mmoles at 20°.

Table 3.59.

<u>F₃SiH</u> <u>mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	6
0.167	0.152	6
0.294	0.268	7
0.417	0.380	8
0.471	0.429	7
0.556	0.507	9
0.623	0.568	17
0.796	0.726	38
0.874	0.797	48
1.011	0.921	68
1.239	1.130	100

A white solid was formed during the reaction and the pressure measurements indicate that this complex has a molar composition (silane/amine) of 0.5. The excess silane was pumped off and the solid residue was warmed to 75°; but no disproportionation of the adduct was observed.

An infrared spectrum of the complex was obtained and is recorded in Appendix A.15.

A tensiometric study was carried out on the complex and the temperature-vapour pressure data for this system are

recorded in Table 3.60.

Table 3.60.

<u>Temperature°C.</u>	<u>p,mm.</u>
19.7	3.36
29.0	9.11
32.6	14.95
39.1	23.17
46.2	46.77
51.5	75.34

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 14.19 - \frac{3999}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 33.10 - \frac{11200}{T}$$

and the thermodynamic data are recorded in Appendix C.

3.13.2. γ -Picoline

γ -picoline = 0.095g., 1.020 mmole at 21°.

Table 3.61.

<u>F₃SiH mmoles</u>	<u>Mole ratio</u>	<u>Vapour Pressure(mm)</u>
0.000	0.000	6
0.196	0.192	7
0.301	0.295	7
0.408	0.400	8
0.457	0.448	6
0.501	0.491	6
0.579	0.568	18
0.743	0.729	47
0.878	0.860	70
0.992	0.972	97
1.123	1.101	119

A white solid was formed during the reaction and the pressure measurements indicate that this complex has a molar composition (silane/amine) of 0.5. The excess silane was pumped off and the solid residue was warmed to 75°; but no disproportionation of the adduct was observed.

An infrared spectrum of the complex was obtained and is recorded in Appendix A.16.

A tensiometric study was carried out on the complex and the temperature-vapour pressure data for this system are recorded in Table 3.62.

Table 3.62.

<u>Temperature °C.</u>	<u>p,mm.</u>
19.7	0.48
29.0	0.90
32.6	1.93
39.1	3.39
46.2	6.54
51.5	10.56

These data were processed in the manner described previously and can be represented by the equation,

$$\log_{10} p_{\text{mm}} = 13.81 - \frac{4153}{T}$$

They yield the following Van't Hoff isochore,

$$\log_{10} K_p = 32.13 - \frac{12260}{T}$$

and the thermodynamic data which are recorded in Appendix C.

3.14. Solubility Tests.

All the isolable solid complexes prepared in this work were tested for solubility in a wide range of solvents of differing polarities. The solvents used were acetone, acetonitrile, benzene, carbon tetrachloride, chloroform, di-ethyl ether, dimethylformamide, and methylene dichloride. The technique used was to prepare a small amount of the complex in an ampoule (ca. 6 ml. capacity) and the anhydrous solvent condensed into the tube at -196° . The ampoule was sealed, and allowed to warm to room temperature. The ratio of solvent to complex was approximately 10 : 1 by volume. The samples were then warmed to $60-70^{\circ}$.

However, for all the complexes prepared in this work no discernible solubility was observed in any of the solvents used.

APPENDIX A

INFRARED SPECTRA

The infrared spectrum of each pure compound prepared in this research has been determined. The spectra are recorded in wavenumbers (cm^{-1} .) and the letters in parentheses indicate the intensity of the band; (vw = very weak; w = weak; m = medium; s = strong; vs = very strong; br = broad; sh = shoulder).

1. $\text{F}_3\text{SiCHFCHF}_2$ (vapour)= 2981(m); 2925(w); 2184(vw); 2114(vw);
 1992(vw); 1883(vw); 1461(vw); 1399(s);
 1359(s); 1264(s); 1237(s); 1152(s);
 1100(vs); 1060(vs); 1000(vs); 880(vs);
 796(m); 774(m); 753(s); 725(w) cm^{-1} .

2. $\text{H}_3\text{SiCHFCHF}_2$ (vapour)= 3110(vw); 2980(m); 2930(m); 2870(vw);
 2750(vw); 2700(vw); 2450(w); 2270(vs);
 2202(w); 2090(vw); 1875(vw); 1728(vw);
 1710(vw); 1668(vw); 1616(vw); 1464(vw);
 1392(s); 1382(s); 1370(s); 1360(s);
 1296(w); 1282(w); 1242(m); 1146(s);
 1099(vs); 1090(vs); 1043(s); 905(s);
 945(vs); 921(vs); 916(vs); 803(m);
 758(w); 690(m); 635(m) cm^{-1} .

3. $\text{D}_3\text{SiCF}_2\text{CHF}_2$ (vapour)= 3170(vw); 3110(vw); 2980(m); 2870(vw);
 2740(vw); 2720(vw); 2660(vw); 2510(vw);
 2450(vw); 2320(vw); 2300(vw); 2210(w);
 2190(vw); 2160(vw); 2070(vw); 1793(w);
 1778(w); 1704(m); 1677(m); 1620(s);
 1590(m); 1585(s); 1578(m); 1483(vw);
 1381(m); 1376(s); 1370(m); 1350(m);
 1342(m); 1330(m); 1320(m); 1271(m);
 1265(m); 1255(m); 1201(m); 1179(s);
 1170(s); 1160(m); 1122(vs); 1110(vs);
 1102(vs); 1070(s); 1026(m); 936(w);
 930(w); 920(w); 888(vw); 809(m);
 803(m); 769(m); 759(m); 750(m);
 694(s); 686(s); 678(s); 665(s);
 658(s) cm^{-1} .

4. $\text{SiF}_4 \cdot 2\text{py}$ (solid) = 3060(w); 2930(w); 2860(w); 1635(w);
 1624(s); 1610(m); 1536(w); 1488(m);
 1378(w); 1252(w); 1212(m); 1161(m);
 1075(s); 1056(m); 1023(w); 1005(w);
 860(w); 840(m); 803(s); 763(s);
 730(s); 700(m); 688(s); 670(m) cm^{-1} .

5. $\text{SiF}_4 \cdot 2\beta\text{-pic(solid)}$ = 3120(w); 3070(w); 3030(w); 2930(w);
 2110(w); 2010(w); 1950(w); 1910(w);
 1870(w); 1830(w); 1760(s); 1626(m);
 1620(m); 1590(m); 1558(w); 1485(s);
 1465(s); 1420(s); 1390(m); 1380(m);
 1361(m); 1327(m); 1260(w); 1240(w);
 1210(w); 1190(s); 1135(m); 1118(s);
 1082(s); 1050(w); 1040(w); 1000(w);
 954(w); 916(w); 848(s); 829(s);
 800(s); 730(s); 699(s); 675(s). cm^{-1} .

6. $\text{SiF}_4 \cdot 2\gamma\text{-pic(solid)}$ = 3050(w); 3000(w); 2940(w); 1631(s);
 1610(m); 1508(m); 1440(s); 1380(s);
 1233(m); 1213(m); 1068(s); 1048(s);
 1020(w); 876(m); 864(m); 850(w);
 820(s); 803(m); 765(m); 733(m);
 720(s); 669(m). cm^{-1} .

7. $\text{Cl}_3\text{SiCHFCHF}_2 \cdot 2\beta\text{-pic(solid)}$ 3030(m); 2941(w); 2470(br); 2114(m);
 2016(vw); 1984(w); 1631(w); 1613(m);
 1560(s); 1490(m); 1443(w); 1379(m);
 1361(m); 1325(m); 1266(w); 1253(w);
 1227(w); 1182(w); 1117(br); 1089(br);
 1068(br); 1038(br); 1008(br); 952(w);
 913(m); 825(w); 792(s); 775(m);
 720(vw); 699(m); 683(s); 662(w);
 658(w). cm^{-1} .

8. $\text{Cl}_3\text{SiCHFCHF}_2 \cdot 2\gamma\text{-pic(solid)}$ 3020(m); 2960(w); 2484(br); 2116(w);
 1640(w); 1622(m); 1580(w); 1427(m);
 1397(m); 1377(m); 1355(m); 1311(m);
 1220(w); 1200(w); 1174(br); 1121(br);
 1072(br); 1038(br); 1011(br); 951(w);
 906(m); 831(w); 806(s); 698(m);
 685(s); 658(w). cm^{-1} .

9. $\text{F}_3\text{SiCHFCHF}_2 \cdot 2\beta$ -pic = 3220(w); 3170(w); 3125(w); 3095(w);
 (solid) 3070(m); 2930(m); 2860(w); 2714(vw);
 1630(m); 1620(m); 1589(w); 1563(w);
 1559(w); 1552(w); 1492(m); 1484(s);
 1428(m); 1392(m); 1262(m); 1240(vw);
 1209(vw); 1188(m); 1132(w); 1120(m);
 1083(m); 1041(w); 953(w); 918(vw);
 862(vw); 841(m); 810(m); 794(s);
 721(w); 700(s); 675(m); 669(m). cm^{-1} .
10. $\text{F}_3\text{SiCHFCHF}_2 \cdot 2\gamma$ -pic = 3255(w); 3160(w); 3078(w); 2970(w);
 (Solid) 2916(w); 2870(w); 1864(w); 1710(w);
 1658(m); 1635(s); 1608(s); 1569(w);
 1516(m); 1450(m); 1390(m); 1356(w);
 1260(m); 1236(m); 1218(m); 1170(w);
 1160(w); 1140(m); 1078(m); 1056(m);
 1036(w); 1016(vw); 996(vw); 978(vw);
 936(w); 916(m); 826(m); 795(s);
 727(s); 676(w); 668(w). cm^{-1} .
11. $\text{Cl}_3\text{SiCF}_2\text{CHF}_2 \cdot 2\beta$ -pic 2100(w); 1982(w); 1634(w); 1615(m);
 (solid; nujol mull 1588(w); 1560(m); 1327(w); 1255(w);
 only) 1189(m); 1166(m); 1110(s); 1082(m);
 1072(m); 1044(m); 1024(m); 963(m);
 920(w); 825(w); 807(m); 796(s);
 704(m); 687(m); 659(m); 630(s). cm^{-1} .
12. $\text{F}_3\text{SiCF}_2\text{CHF}_2 \cdot 2\text{py}$ = 3140(w); 3100(w); 3070(w); 3050(w);
 (solid; nujol mull only) 2490(vw); 1965(w); 1884(w); 1860(w);
 1672(w); 1640(w); 1623(s); 1614(m);
 1580(m); 1540(w); 1490(m); 1352(m);
 1310(w); 1242(m); 1231(m); 1223(m);
 1200(m); 1170(m); 1090(s); 1070(s);
 1058(s); 1021(m); 980(m); 890(vw);
 820(m); 800(m); 735(s); 700(s);
 650(s). cm^{-1} .

13. $\text{F}_3\text{SiCF}_2\text{CHF}_2 \cdot 2\gamma$ -pic = 3250(w); 3160(w); 3100(w); 2500(w);
(solid; nujol mull only) 2090(w); 1972(w); 1870(w); 1704(w);
1640(s); 1636(s); 1620(m); 1590(w);
1567(w); 1514(m); 1490(w); 1345(w);
1320(w); 1252(w); 1236(m); 1219(m);
1180(s); 1116(s); 1084(s); 1050(s);
1038(s); 980(s); 875(w); 824(s);
802(s); 735(s); 672(m). cm^{-1} .
14. $\text{H}_3\text{SiCF}_2\text{CHF}_2 \cdot 2\gamma$ -pic = 3070(w); 3028(w); 2990(w); 2924(w);
(liquid) 2860(vw); 2360(vw); 2172(s); 1935(w);
1620(s); 1608(vs); 1564(w); 1508(vw);
1496(w); 1439(m); 1413(m); 1380(w);
1222(m); 1210(m); 1184(m); 1160(s);
1084(s); 1040(m); 1018(m); 995(s);
945(s); 800(s); 729(w); 710(vw). cm^{-1} .
15. $\text{F}_3\text{SiH} \cdot 2\beta$ -pic = 2100(s); 2010(w); 1631(m); 1613(m);
(solid; nujol mull only) 1590(w); 1554(m); 1328(w); 1262(m);
1190(m); 1120(m); 1085(m); 1060(vw);
1046(w); 1030(vw); 1000(m); 978(vw);
956(m); 940(vw); 920(vw); 895(w);
843(m); 795(vs); 732(m); 701(m);
681(m); 630(m). cm^{-1} .
16. $\text{F}_3\text{SiH} \cdot 2\gamma$ -pic = 2110(s); 2010(m); 1920(w); 1875(w);
(solid; nujol mull only) 1765(w); 1638(s); 1610(s); 1558(w);
1530(w); 1506(m); 1323(m); 1257(m);
1223(vw); 1208(m); 1070(w); 1047(w);
1010(s); 960(s); 896(vw); 875(w);
805(vs); 740(m); 710(m); 688(m);
654(m); 630(w). cm^{-1} .

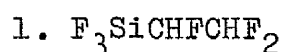
APPENDIX B

NUCLEAR MAGNETIC RESONANCE SPECTRA

The ^1H and ^{19}F n.m.r. spectra of the starting materials used, and the liquid complexes prepared in this work, are tabulated below.

Samples were run as neat liquids. Unless otherwise stated, the chemical shifts were measured from tetramethylsilane as an internal reference for ^1H and trifluoroacetic acid as an external reference for ^{19}F . Positive values are to high field and negative values are to low field of the reference line. The intensities of each band are not given; in each case the measured intensity corresponded to the assigned.

The silicon bonded carbon atom in the silane's fluoroalkyl chain has been called the α -carbon and the terminal carbon atom has been called the β -carbon in this Appendix.



^1H : $-\text{CHF}_2$, -6.15 p.p.m.; triplet structure

$$J_{\beta\text{H}-\beta\text{F}} = 55.2 \text{ c.p.s.}$$

$-\text{CHF}-$, -4.84 p.p.m.; doublet of triplets

$$J_{\alpha\text{H}-\alpha\text{F}} = 55.6 \text{ c.p.s.}$$

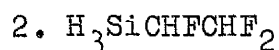
$$J_{\alpha\text{H}-\beta\text{F}} = 15.4 \text{ c.p.s.}$$

The two ^1H resonances overlap to give a
4:8:1:6:1:1:2:1 pattern

^{19}F : $-\text{CHF}_2$, +50.0 p.p.m.; complex structure
as in Figure 3.1.

$-\text{SiF}_3$, +67.8 p.p.m.; complex structure
as in Figure 3.2.

$-\text{CHF}-$, +174.0 p.p.m.; complex structure
as in Figure 3.2.



^1H : $-\text{CHF}_2$, -6.00 p.p.m.; triplet of doublets
of doublets

$$J_{\beta\text{H}-\beta\text{F}} = 56.4 \text{ c.p.s.}$$

$$J_{\beta\text{H}-\alpha\text{F}} = 4.4 \text{ c.p.s.}$$

$$J_{\beta\text{H}-\alpha\text{H}} = 3.6 \text{ c.p.s.}$$

$-\text{CHF}-$, -4.98 p.p.m.; complex structure

$-\text{SiH}_3$, -3.71 p.p.m.; complex structure

The ^1H resonance spectrum is given
in Figure 3.4.

^{19}F : $-\text{CHF}_2$, +48.8 p.p.m.; doublet of doublets of doublets of quartets that overlap to give a 1:3:3:1:1:4:6:4:1:1:3:3:1 pattern of doublets as in Figure 3.5.

$$J_{\beta\text{F}-\beta\text{H}} = 56.5 \text{ c.p.s.}$$

$$J_{\beta\text{F}-\alpha\text{H}} = 18.9 \text{ c.p.s.}$$

$$J_{\beta\text{F}-\alpha\text{F}} = 16.4 \text{ c.p.s.}$$

$$J_{\beta\text{F}-\text{SiH}} = 2.8 \text{ c.p.s.}$$

$-\text{CHF}-$, + 160.4 p.p.m.; complex structure as in Figure 3.6.

3. $\text{D}_3\text{SiCF}_2\text{CHF}_2$

^1H : $-\text{CHF}_2$, -4.99 p.p.m.; triplet of triplets

$$J_{\beta\text{H}-\beta\text{F}} = 55.2 \text{ c.p.s.}$$

$$J_{\beta\text{H}-\alpha\text{F}} = 4.8 \text{ c.p.s.}$$

^{19}F : $-\text{CF}_2-$, +42.6 p.p.m.; complex structure as in Figure 3.7.

$-\text{CHF}_2$ +53.8 p.p.m.; doublet structure

$$J_{\beta\text{F}-\beta\text{H}} = 54.8 \text{ c.p.s.}$$

4. $\text{H}_3\text{SiCHFCHF}_2\cdot\text{NMe}_3$

(a) Spectra recorded at -20° .

^1H : external benzene interchange reference.

$-\text{CHF}_2$, +1.00 p.p.m.

$-\text{CHF}-$, +2.30 p.p.m.

$-\text{SiH}_3$, +3.18 p.p.m.

$\text{N}(\text{CH}_3)_3$, +4.74 p.p.m. singlet structure

Apart from the new NMe_3 resonance and the above chemical shifts, the pattern of the spectrum was identical to that of the free silane (Fig. 3.4.); no change in coupling constants was discernible.

^{19}F : $-\text{CHF}_2$, + 46.0 p.p.m.; complex structure as in Figure 3.8.

$J_{\beta\text{F}-\beta\text{H}} = 55.3 \text{ c.p.s.}$

$J_{\beta\text{F}-\alpha\text{H}} = 16.9 \text{ c.p.s.}$

$-\text{CHF}-$, + 154.2 p.p.m.; complex structure as in Figure 3.9.

(b) The ^1H and ^{19}F spectra were also recorded at 0° and -20° . But no change in the resonances or coupling constants was observed.

5. $\text{H}_3\text{SiCF}_2\text{CHF}_2$. 2 γ -pic

(a) Spectra recorded at $+35^\circ$

^1H : external benzene interchange reference

pic. α -H, -1.26 p.p.m.; complex structure

pic. β -H, -0.10 p.p.m.; complex structure

$-\text{CHF}_2$, +1.17 p.p.m.; triplet of triplets

$$J_{\text{H}-\beta\text{F}} = 55.0 \text{ c.p.s.}$$

$$J_{\text{H}-\alpha\text{F}} = 6.3 \text{ c.p.s.}$$

$-\text{SiH}_3$, +2.71 p.p.m.; triplet of triplets

$$J_{\text{SiH}-\alpha\text{F}} = 11.2 \text{ c.p.s.}$$

$$J_{\text{SiH}-\beta\text{F}} = 2.8 \text{ c.p.s.}$$

pic. $-\text{CH}_3$, +4.88 p.p.m.; singlet.

^{19}F : $-\text{CF}_2-$, +50.4 p.p.m.; quartet of doublets

$$J_{\alpha\text{F}-\text{SiH}} = 11.3 \text{ c.p.s.}$$

$$J_{\alpha\text{F}-\text{H}} = 6.7 \text{ c.p.s.}$$

$-\text{CHF}_2$, +56.5 p.p.m.; doublet of quartets

$$J_{\beta\text{F}-\text{H}} = 55.4 \text{ c.p.s.}$$

$$J_{\beta\text{F}-\text{SiH}} = 2.8 \text{ c.p.s.}$$

(b) The proton resonance spectra were also recorded at $+10^{\circ}$, 0° , -10° and -20° ; but no change in the resonances or coupling constants was observed. At -30° , line broadening and poor line resolution occurred due to solidification of the sample.

6. $\text{H}_3\text{SiCF}_2\text{CHF}_2\cdot\text{NMe}_3$

The n.m.r. spectra of this complex have been recorded previously at $+35^{\circ}$ (105). the ^1H and ^{19}F n.m.r. spectra were recorded at -20° , 0° and $+20^{\circ}$, but no changes in the chemical shifts and coupling constants were observed at these lower temperatures. The parameters for the ^{19}F spectrum are recorded in Table 2.22.

7. $\text{D}_3\text{SiCF}_2\text{CHF}_2\cdot\text{NMe}_3$

The n.m.r. spectra of this complex were recorded at -20° , 0° and $+20^{\circ}$. But apart from some line broadening at the lowest temperature, the spectra were identical.

^1H : external benzene interchange reference

$-\text{CHF}_2$: $+1.44$ p.p.m.; triplet of triplets

$$J_{\text{CH}-\beta\text{F}} = 55.2 \text{ c.p.s.}$$

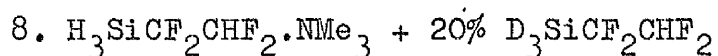
$$J_{\text{CH}-\alpha\text{F}} = 5.7 \text{ c.p.s.}$$

$\text{N}(\text{CH}_3)_3$: $+4.86$ p.p.m.; singlet

^{19}F : $-\text{CF}_2-$, $+46.4$ p.p.m. complex structure as in Figure 3.10.

$+\text{CHF}_2$, $+54.8$ p.p.m.; doublet structure

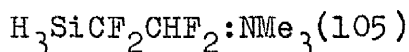
$$J_{\beta\text{F}-\text{CH}} = 54.8 \text{ c.p.s.}$$



The n.m.r. spectra of this mixture were recorded at -20° , 0° and $+20^\circ$, the spectra were identical at each temperature

^1H : external benzene interchange reference

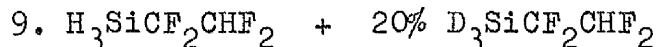
The spectrum was identical to that of



^{19}F : $-\text{CF}_2-$, $+50.2$ p.p.m.; complex structure as in Figure 3.11.

$-\text{CHF}_2$, $+55.4$ p.p.m; doublet structure

$$J_{\beta\text{F}-\text{CH}} = 51.9 \text{ c.p.s.}$$



The n.m.r. spectra were recorded at -20° , 0° and $+20^\circ$; the spectra were identical at each temperature.

^{19}F : $-\text{CF}_2-$, $+43.0$ p.p.m. This resonance (Fig.3.12.) appeared mainly as a quartet of doublets of triplets with the same coupling constants as for $\text{H}_3\text{SiCF}_2\text{CHF}_2$ (105). But to the high field side of the resonance, seven extra bands were observed with a spacing of ~ 1.8 c.p.s.

$-\text{CHF}_2$, $+54.4$ p.p.m.; doublet of multiplets as in Figure 3.13.

$$J_{\beta\text{F}-\text{CH}} = 55.8 \text{ c.p.s.}$$

Figure 3.1.

^{19}F n.m.r. spectrum of $\text{F}_3\text{SiCHFCHF}_2$

$\beta\text{-CHF}_2$ group

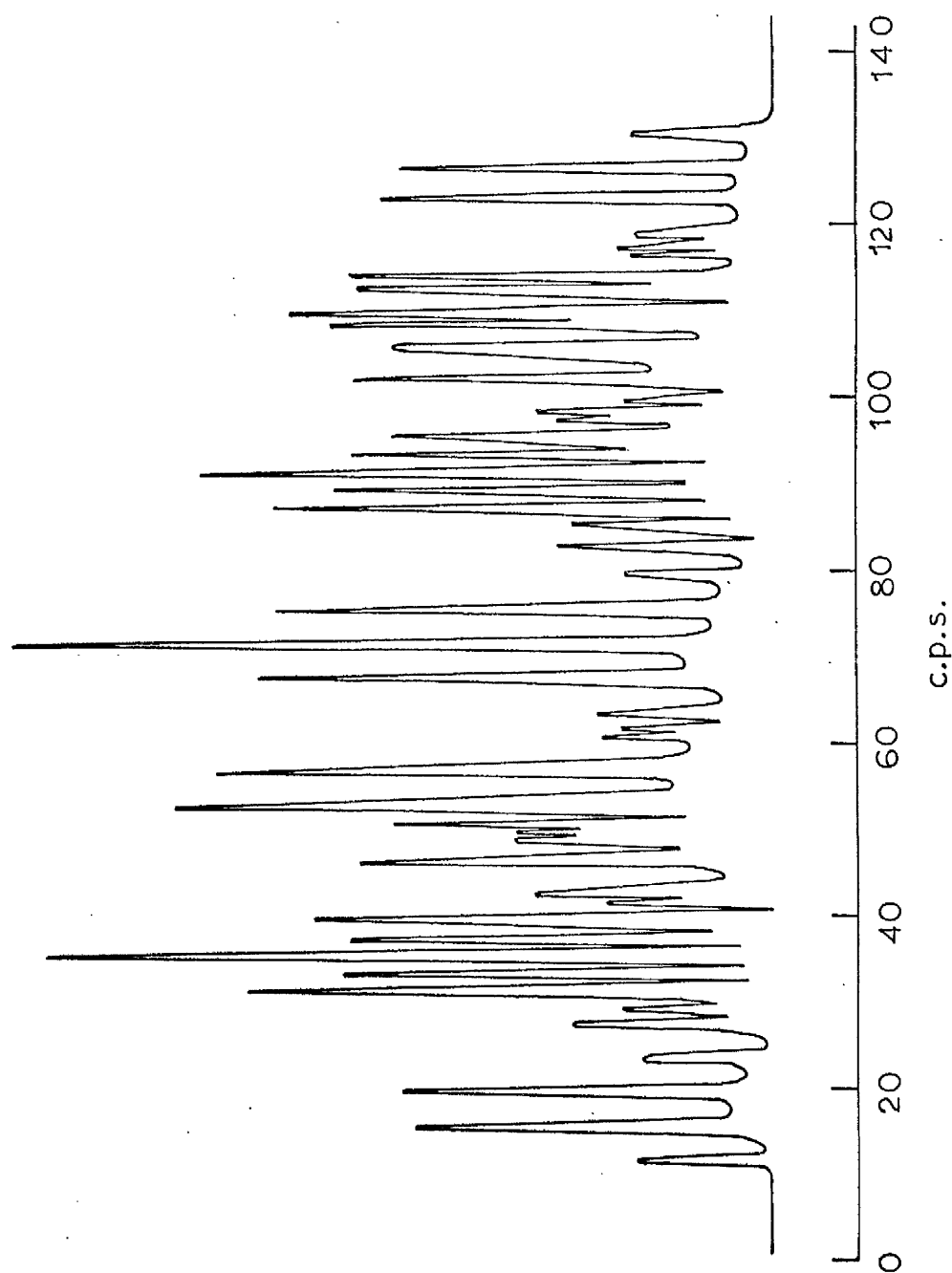


Figure 3.2.

^{19}F n.m.r. spectrum of $\text{F}_3\text{SiCHFCHF}_2$

SiF_3 group

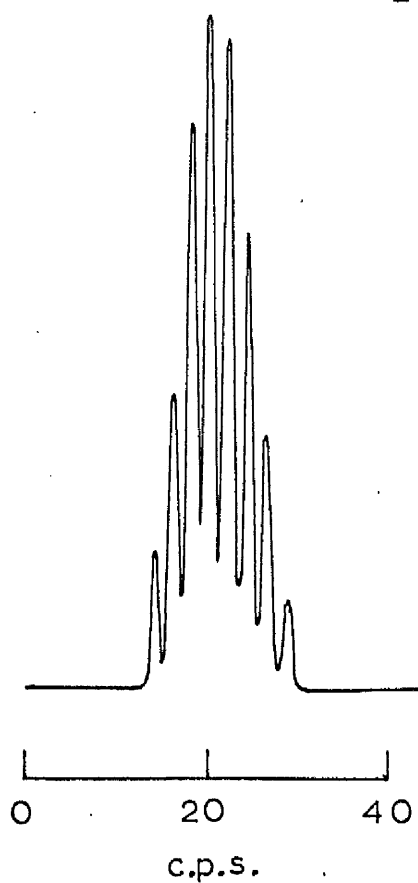


Figure 3.3.

^{19}F n.m.r. spectrum of $\text{F}_3\text{SiCHFCHF}_2$

$\alpha\text{-CHF}$ group

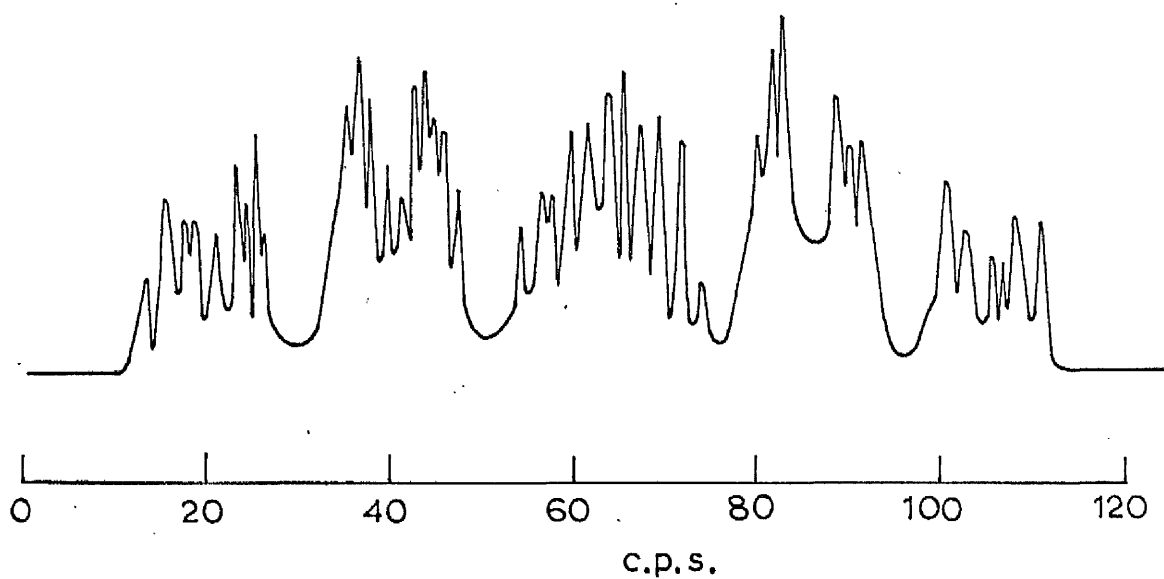


Figure 3.4.

^1H n.m.r. spectrum of $\text{H}_3\text{SiCHFCHF}_2$

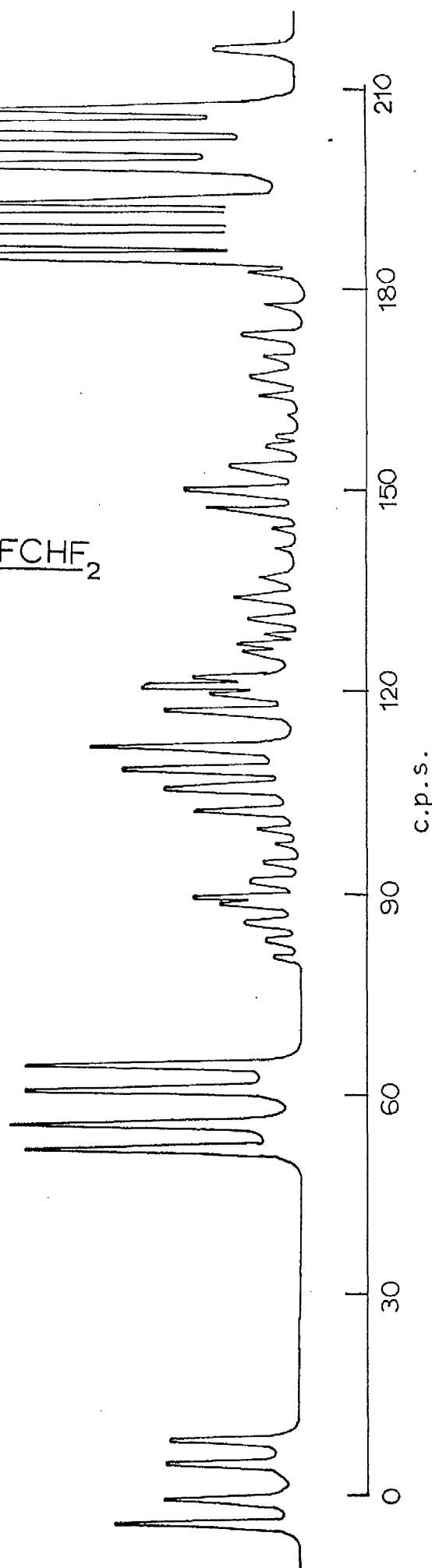


Figure 3.5.

^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCHFCHF}_2$

$\beta\text{-CHF}_2$ group

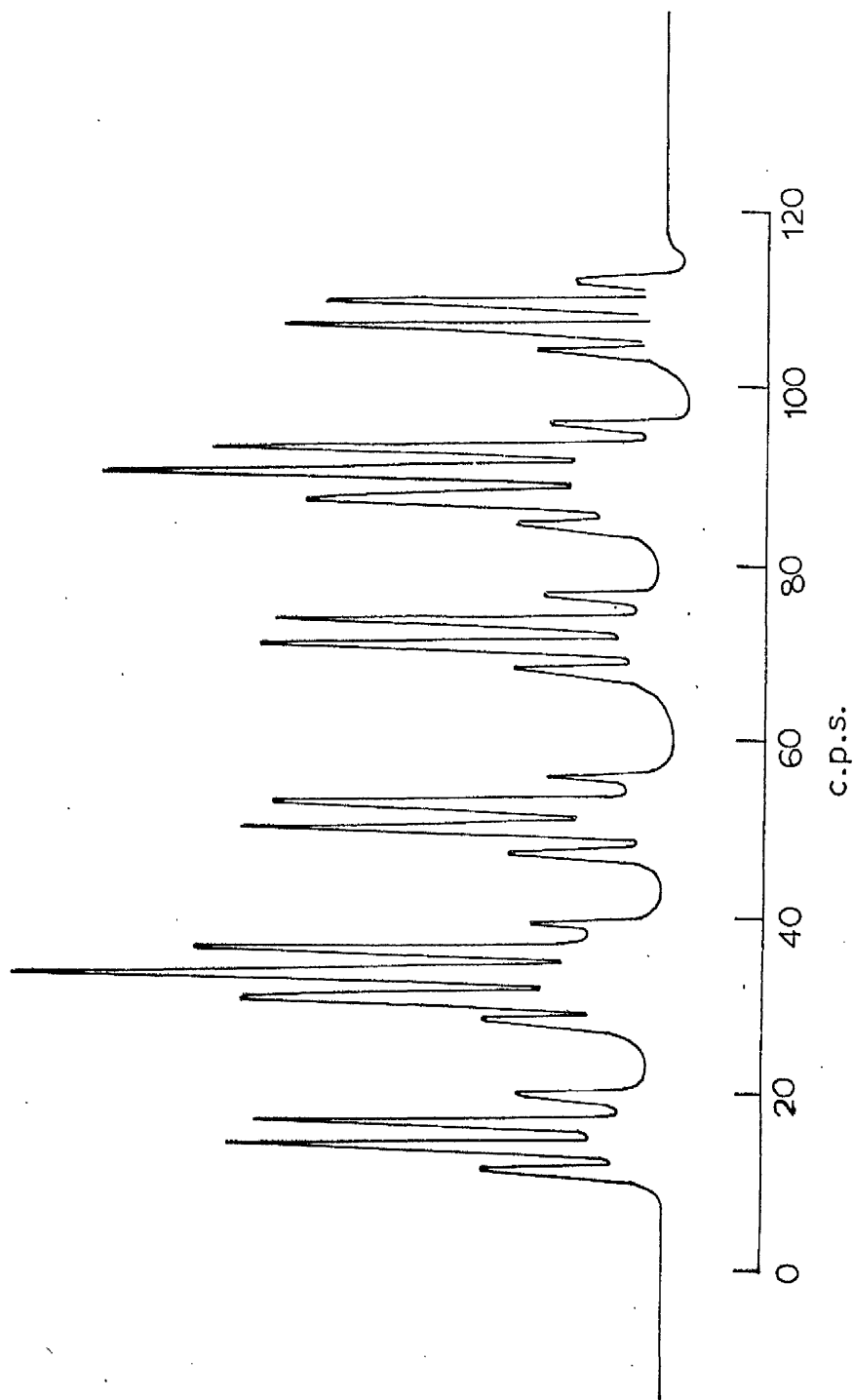


Figure 3.6.

^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCHFCHF}_2$

α -CHF group

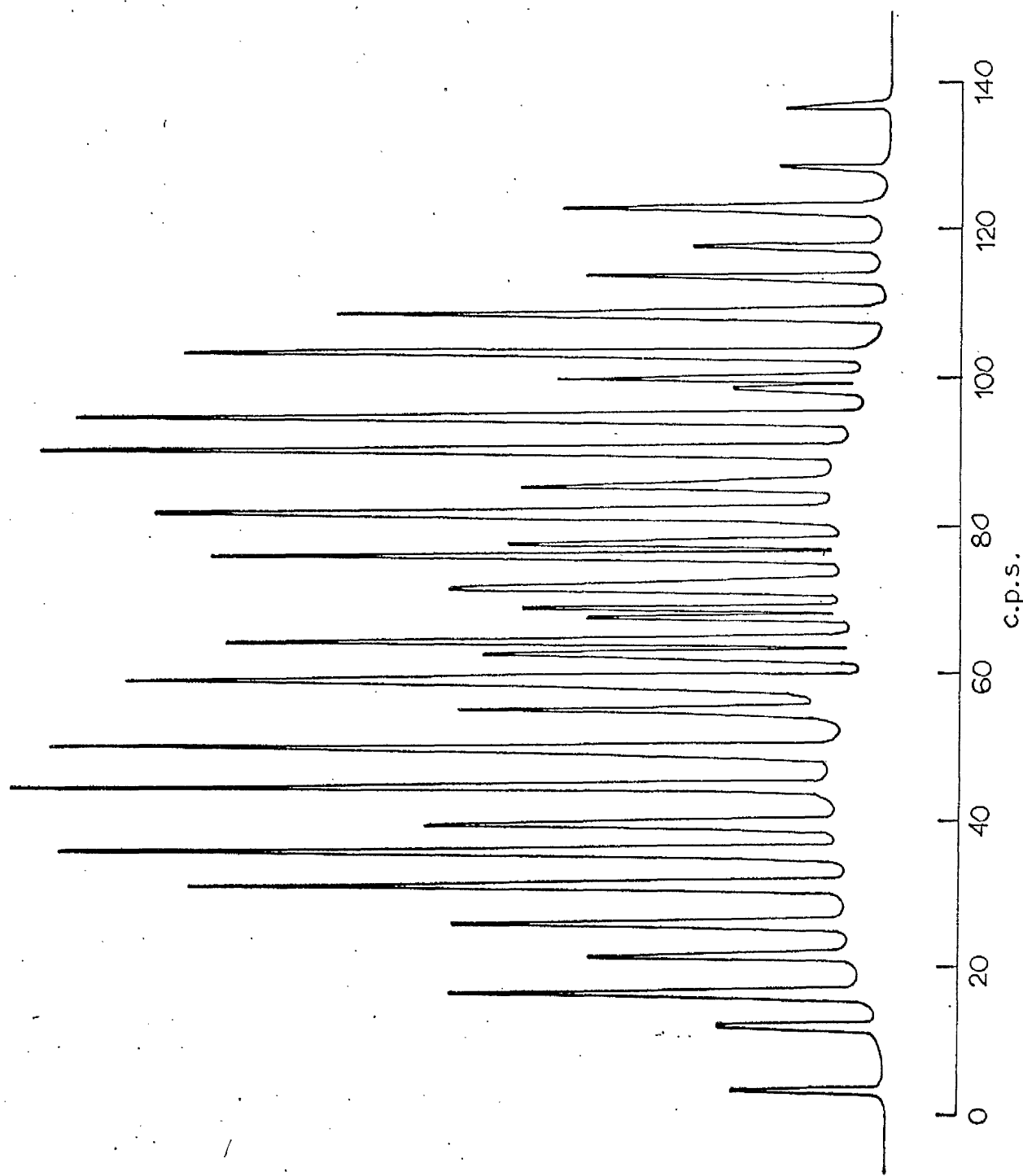


Figure 3.7.

^{19}F n.m.r. spectrum of $\text{D}_3\text{SiCF}_2\text{CHF}_2$

$\beta\text{-CHF}_2$ group

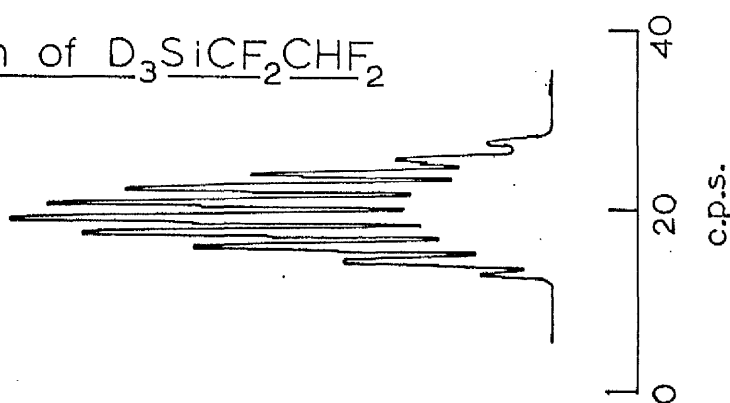


Figure 3.8.

^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCHFCHF}_2\cdot\text{NMe}_3$

$\beta\text{-CHF}_2$ group

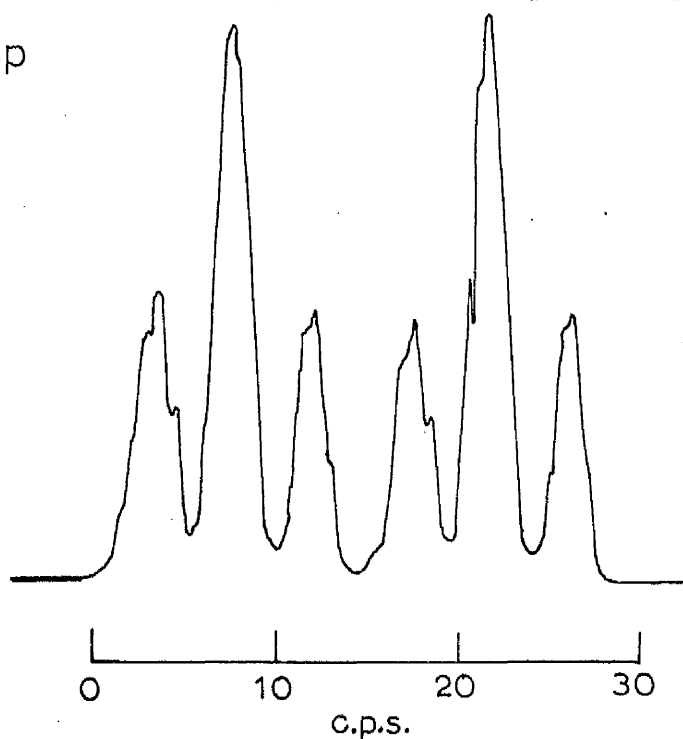


Figure 3.9.

^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCHFCHF}_2\cdot\text{NMe}_3$

$\alpha\text{-CHF}$ group

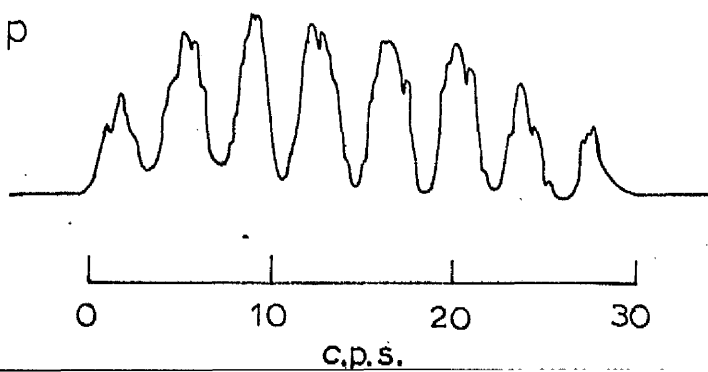


Figure 3.10.

^{19}F n.m.r. spectrum of $\text{D}_3\text{SiCF}_2\text{CHF}_2\cdot\text{NMe}_3$

$\alpha\text{-CF}_2$ group

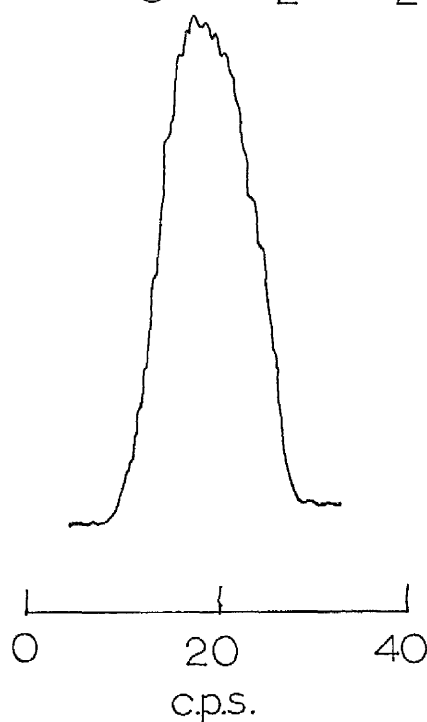
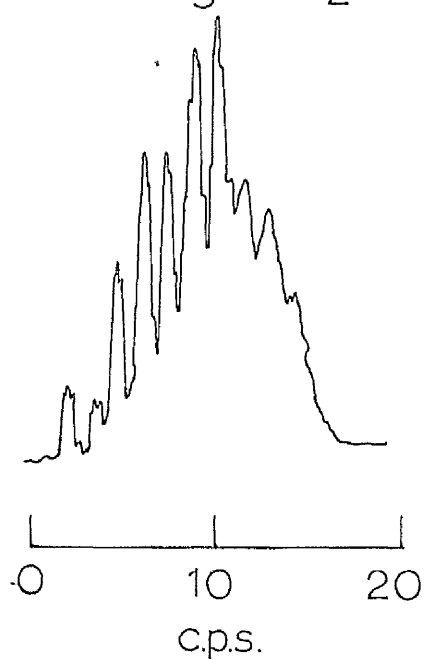


Figure 3.11.

^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCF}_2\text{CHF}_2\cdot\text{NMe}_3 + 20\%$

$\text{D}_3\text{SiCF}_2\text{CHF}_2$

$\alpha\text{-CF}_2$ group



^{19}F n.m.r. spectrum of $\text{H}_3\text{SiCF}_2\text{CHF}_2 + 20\%$

$\text{D}_3\text{SiCF}_2\text{CHF}_2$

Figure 3.12

$\alpha\text{-CF}_2$ group

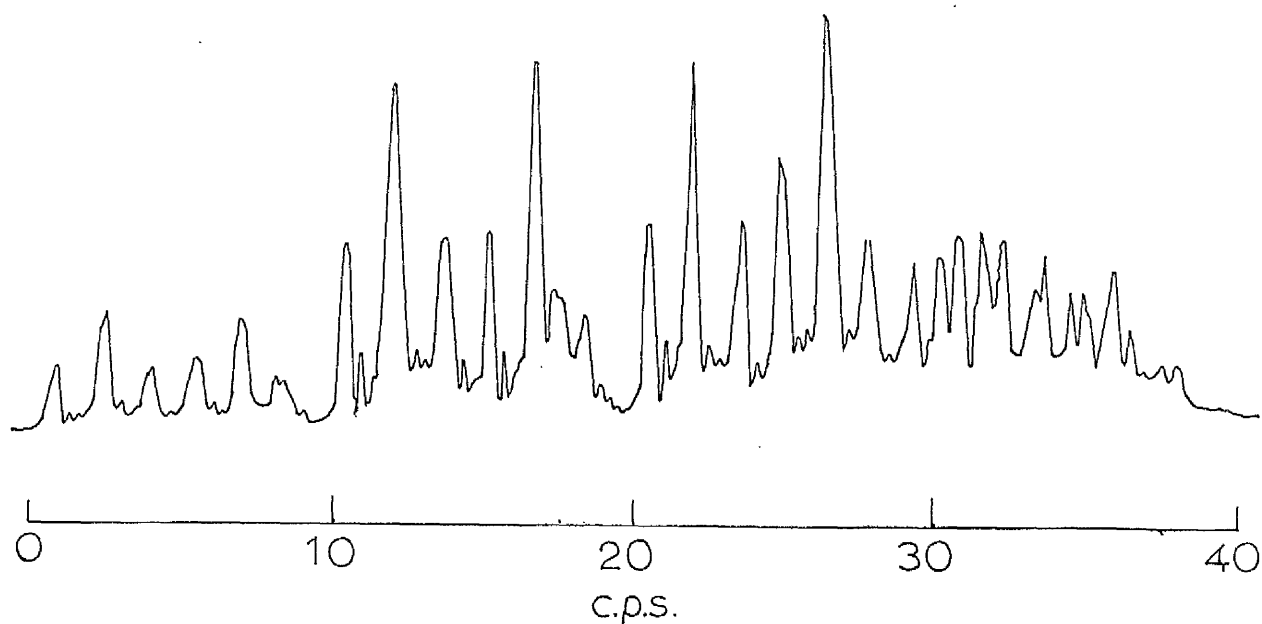
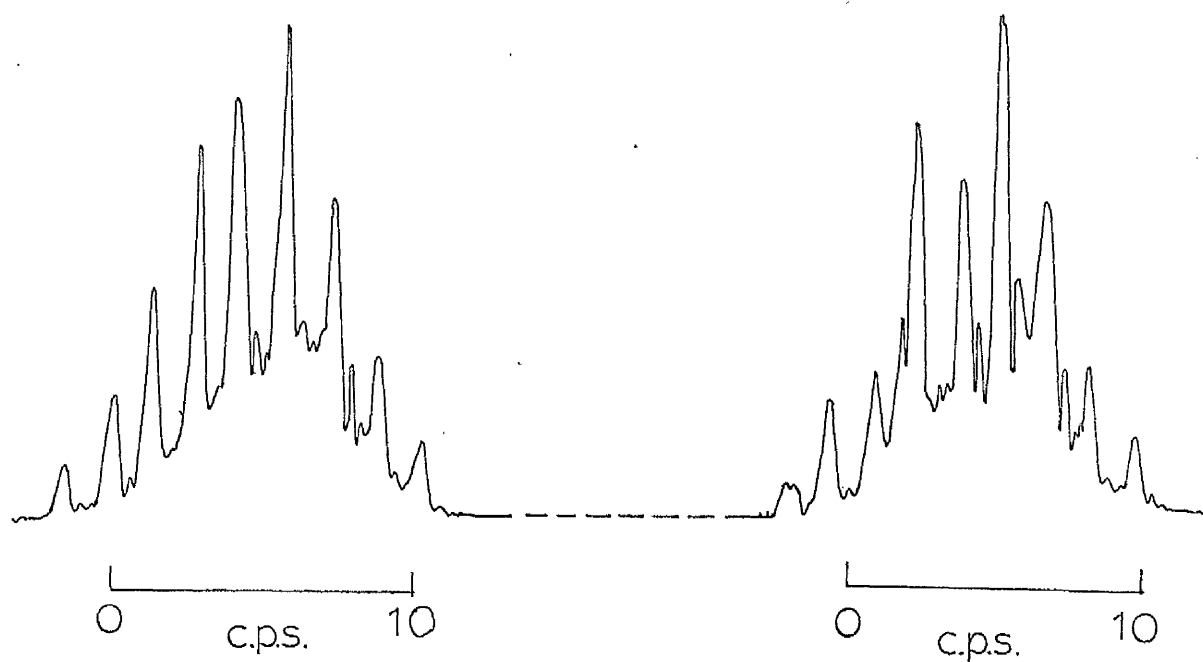


Figure 3.13

$\beta\text{-CHF}_2$ group



APPENDIX C

THERMODYNAMIC FUNCTIONS

The thermodynamic functions of the complexes that were prepared in this work and were stable enough to be characterised, are listed as follows:-

- (i) enthalpy changes,
- (ii) free energy changes,
- (iii) entropy changes,
- (iv) dissociation vapour pressures,
- and (v) dissociation constants.

1. Enthalpy Changes (ΔH) (kcal.mole⁻¹).

The figure quoted below the enthalpy change is the calculated standard deviation.

Silane	Amine	Me ₃ N	py	β -pic	γ -pic
Cl ₃ SiCH ₂ CHF ₂	-	-	-	(2.74)* 21.42 ± 0.23	(3.57)* 22.31 ± 0.25
SiF ₄	-	28.41 ± 0.14	-	32.52 ± 0.07	35.86 ± 0.08
Cl ₃ SiCHFCHF ₂	-	-	-	28.23 ± 0.08	31.87 ± 0.33
F ₃ SiCHFCHF ₂	-	-	-	32.68 ± 0.11	34.46 ± 0.05
H ₃ SiCHFCHF ₂	11.77 ± 0.10	-	-	-	-
Cl ₃ SiCF ₂ CHF ₂	-	-	-	30.71 ± 0.16	34.28 ± 0.46
F ₃ SiCF ₂ CHF ₂	-	31.37 ± 0.21	-	38.49 ± 0.24	39.60 ± 0.25
H ₃ SiCF ₂ CHF ₂	-	-	-	(9.43)* 28.11 ± 0.12	(9.66)* 28.40 ± 0.16
F ₃ SiH	-	-	-	51.25 ± 0.17	56.11 ± 1.61

* This Figure is calculated from the measurement of the dissociation vapour pressure as a function of the pressure

exerted by free silane. The true enthalpy change is calculated by adding the latent heat of vaporisation for the amine.

Latent heat of vaporisation of β -picoline = $9.34\text{kcal.mole}^{-1}$.

Latent heat of vaporisation of γ -picoline = $9.37\text{kcal.mole}^{-1}$.

2. Free Energy Changes (ΔG) at 25° and 50° (kcal.mole⁻¹)

The top figure is the free energy change at 25° and the lower figure is the free energy change at 50°.

Silane	Amine Me ₃ N	py	β-pic	γ-pic
Cl ₃ SiCH ₂ CHF ₂	-	-	3.15* 2.61**	3.19* 2.58**
SiF ₄	-	10.16 8.65	10.95 9.17	11.63 9.62
Cl ₃ SiCHFCHF ₂	-	-	9.65 8.13	10.62 8.86
F ₃ SiCHFCHF ₂	-	-	8.79 6.65	9.05 7.06
H ₃ SiCHFCHF ₂	3.95* 2.51**	-	-	-
Cl ₃ SiCF ₂ CHF ₂	-	-	11.24 9.31	11.60 10.02
F ₃ SiCF ₂ CHF ₂	-	11.28 9.60	12.36 10.19	12.63 10.17
H ₃ SiCF ₂ CHF ₂	-	-	2.26 1.67	2.19 1.57
F ₃ SiH	-	-	6.10 2.29	12.26 8.62

* Calculated at -25°

** Calculated at 0°

3. Entropy Changes (ΔS) (Entropy Units)

Silane Amine	Me_3N	py	β -pic	γ -pic
$\text{Cl}_3\text{SiCH}_2\text{CHF}_2$	-	-	21.10	36.24
SiF_4	-	61.23	72.24	81.27
$\text{Cl}_3\text{SiCHFCHF}_2$	-	-	62.36	71.25
$\text{F}_3\text{SiCHFCHF}_2$	-	-	79.29	86.10
$\text{H}_3\text{SiCHFCHF}_2$	32.70	-	-	-
$\text{Cl}_3\text{SiCF}_2\text{CHF}_2$	-	-	64.08	77.30
$\text{F}_3\text{SiCF}_2\text{CHF}_2$	-	67.54	87.73	90.28
$\text{H}_3\text{SiCF}_2\text{CHF}_2$	-	-	24.03	25.05
F_3SiH_2	-	-	151.5	147.1

4. Dissociation Vapour Pressures (mm.) at 25°.

Silane ^{Amine}	Me ₃ N	py	β-pic	γ-pic
Cl ₃ SiCH ₂ CHF ₂	-	-	3.83*	4.10*
SiF ₄	-	4.74	3.06	2.08
Cl ₃ SiCHFCHF ₂	-	-	6.27	3.97
F ₃ SiCHFCHF ₂	-	-	4.91	3.99
H ₃ SiCHFCHF ₂	119.5*	-	-	-
Cl ₃ SiCHFCHF ₂	-	-	2.12	2.57
F ₃ SiCHFCHF ₂	-	2.53	1.37	1.17
H ₃ SiCHFCHF ₂	-	-	16.71	18.56
F ₃ SiH	-	-	5.93	0.78

* Calculated at 0°

5. Dissociation Constant (Kp) at 25° and 50°.

The top figure is the dissociation constant at 25° and the lower figure is the dissociation constant at 50°.

Silane	Amine	Me ₃ N	py	β-pic	γ-pic
Cl ₃ SiCH ₂ CHF ₂		-	-	3.032.10 ^{-3*} 5.030.10 ^{-3**}	2.782.10 ^{-3*} 5.386.10 ^{-3**}
SiF ₄		-	3.554.10 ⁻⁸ 1.415.10 ⁻⁶	9.450.10 ⁻⁹ 6.102.10 ⁻⁷	2.978.10 ⁻⁹ 3.119.10 ⁻⁷
Cl ₃ SiCHFCHF ₂		-	-	8.388.10 ⁻⁸ 3.189.10 ⁻⁶	1.647.10 ⁻⁸ 1.016.10
F ₃ SiCHFCHF ₂		-	-	3.623.10 ⁻⁷ 3.156.10 ⁻⁵	2.332.10 ⁻⁷ 1.690.10 ⁻⁵
H ₃ SiCHFCHF ₂		6.903.10 ^{-4*} 6.208.10 ^{-3**}	-	-	-
Cl ₃ SiCF ₂ CHF ₂		-	-	5.758.10 ⁻⁹ 5.016.10 ⁻⁷	3.119.10 ⁻⁹ 1.675.10 ⁻⁷
F ₃ SiCF ₂ CHF ₂		-	5.425.10 ⁻⁹ 3.195.10 ⁻⁷	8.666.10 ⁻¹⁰ 1.282.10 ⁻⁷	5.462.10 ⁻¹⁰ 9.276.10 ⁻⁸
H ₃ SiCF ₂ CHF ₂		-	-	2.193.10 ⁻² 7.430.10 ⁻²	2.457.10 ⁻² 8.600.10 ⁻²
F ₃ SiH		-	-	3.377.10 ⁻⁵ 2.810.10 ⁻²	1.023.10 ⁻⁹ 1.479.10 ⁻⁶

* Calculated for -25°

** Calculated for 0°

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