

Preliminary communication

PENTACOORDINATE SILICON COMPOUNDS: PSEUDOROTATION AT SILICON

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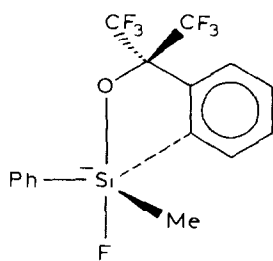
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Summary

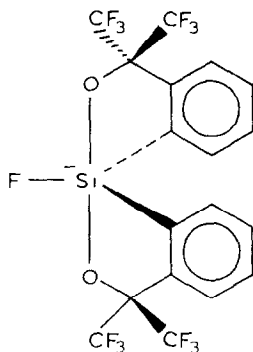
The variation with temperature of the ^{19}F and ^1H NMR spectra of penta-coordinate fluorosilanes which contain an intramolecular Si—N coordination has been examined. A clear distinction between pseudorotation and ring opening-closing processes has been obtained for the first time and the corresponding activation energies determined.

The isomerization of pentacoordinate phosphorus structures through pseudorotational processes are well documented [1,2]. It is of interest to know whether or not the concepts developed in the field of phosphorus chemistry are applicable to organosilicon compounds [3,4]. The pioneering work of Klanberg and Muetterties on the pentafluorosilicates, SiF_5^- , RSiF_4^- and R_2SiF_3^- suggested the possibility of pseudorotation at silicon [5]. Later, Janzen et al. [6] showed that the exchange of fluorine atoms, as observed by ^{19}F NMR spectroscopy, could also be explained by a rapid equilibrium between five- and six-coordinated geometries. Recently, Farnham and Harlow [7a] have published a report concerning the pentacoordinated spiro-siliconate anions, I and II, and Stevenson and Martin has studied the behavior of III towards weak nucleophiles [7b].

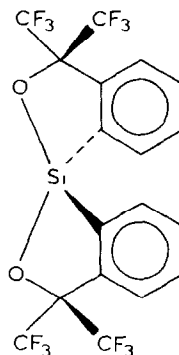
The isomerization at silicon is followed by the exchange of diastereotopic CF_3 groups as shown in the ^{19}F NMR spectrum. The values of activation energies are 16.6 and 17 to 19 kcal/mol for I and II, respectively. These energies are high and perhaps are in the range for possible cleavage of the Si—O bond in ionic systems. In both of these cases, the authors proposed



(I)



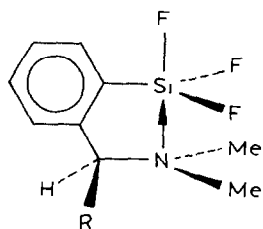
(II)



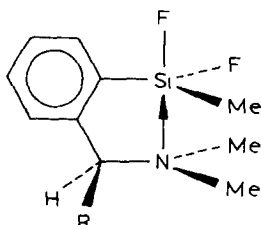
(III)

isomerization via pseudorotation, but a process involving an equilibrium between tetra- and penta-coordinate structures cannot be eliminated "stricto sensu".

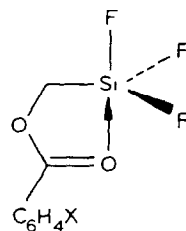
Our first studies [8] on the apicophilicities of groups attached to penta-coordinate silicon have shown an order different from that observed for penta-coordinate phosphorus compounds. The order for silicon appears to be related to the ease of stretching of the Si—X bond and not directly to the electronegativity of X. For this reason we started to study the fluorosilanes, IV and V which probably have the trigonal bipyramidal (TBP) structure of their tin analogs [9]. In both IV and V the fluorine atoms preferentially occupy the positions axial to nitrogen and the aryl (and methyl) substituents prefer the equatorial positions, in agreement with our previous studies [8]. Another example of a neutral TBP has recently been reported, namely compound VI [10]. Systems IV and V were chosen because the intramolecular coordination helps avoid the problems with impurities which were found by Klanberg and Muettterties [5] and Janzen et al. [6]. Finally, the models discussed here represent nucleophilic displacement at silicon more closely than the Stevenson and Martin's system [7].



(IVa, R = H;
IVb, R = CH₃)

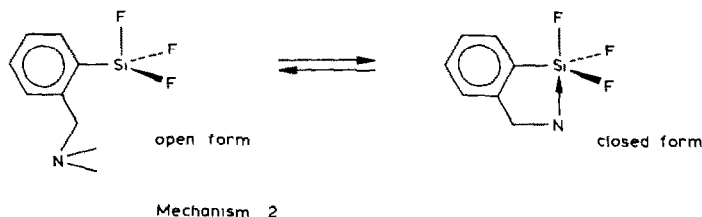
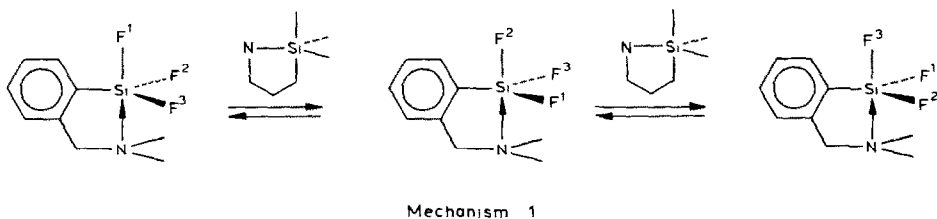


(V, R = H;
Vb, R = CH₃)



(VI)

The ^{19}F and ^1H NMR data for Va show that the fluorine atoms, the methyl groups (of NMe_2) and the benzylic protons are nonequivalent at low temperature (Table 1) which become equivalent at room temperature. The values of the activation energy determined from the F, the $\text{N}(\text{CH}_3)_2$ and the CH_2 data are all close in value, at about 9 kcal/mol, and this result suggests that a single process is occurring. The mechanism which makes the fluorines equiv-



alent at higher temperature may be one of the following: (i) pseudorotation via Berry or turnstile processes (mechanism 1); (ii) an equilibrium between open and closed forms (mechanism 2); (iii) a combination of the two processes.

We have studied the behaviour of compounds IVb and Vb as a function of temperature. In these systems it is possible to distinguish between the two processes, because mechanism 1 does not eliminate the diastereotopism of the Me groups (NMe_2) which is the result of the chirality of the benzyl group, whereas mechanism 2 provides for the complete disappearance of diastereotopism of the NMe_2 group since conversion to the open form allows rotation and inversion at the nitrogen center to occur.

The ^{19}F and ^{29}Si NMR data are listed in Table 1. The changes in the ^1H NMR spectra of IVb and Vb with temperature are shown in Fig. 1. The data show the following features.

(a) The ^{29}Si — ^{19}F coupling constants are observed in all cases and at all temperatures.

(b) In all cases, the ^{29}Si chemical shift of the nitrogen-containing compounds is consistent with a pentacoordinate species in solution, and is temperature dependent.

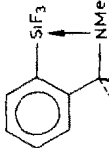
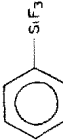
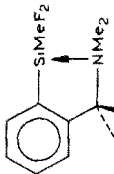
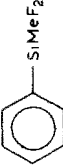
(c) For the compounds without the possibility of intramolecular coordination there is essentially no change in the ^{29}Si chemical shifts with temperature.

(d) The values of ΔG^\ddagger for the fluoro compounds in the present study are lower than those obtained previously for I, II and III.

Since ^{29}Si — ^{19}F coupling is observed over the temperature range studied, the process which is responsible for the fluorine equivalence does not involve

TABLE 1

 ^{19}F AND ^{29}Si NMR DATA ^a FOR FLUOROSILANES ^b

Compounds	$\delta(^{19}\text{F})$ (ppm)		$\delta(^{29}\text{Si})$ (ppm)				$J(^{29}\text{Si}-^{19}\text{F})$ (Hz)			
	IVa	IVb	IVa	IVb	IVc	IVa	IVc	IVa	IVc	
 IVa, R = H IVb, R = Me	25° C	100° C	25° C	100° C						
	-40° C	-50° C								
 IVc	-142	-141	60° C	-126 F _a	-72.83	236.3	267.2			
	{ -128 F _a -148 F _e		0° C	{ -143 F _f -149 F _e	-72.92	231.5	267.4			
	ΔG^* 11.7 kcal/mol	ΔG^* 13.1 kcal/mol	-60° C		-73.14	225.9	267.4			
 Va, R = H Vb, R = Me	Va c	Vb	Va	Vb	Vc	Va	Vc	Va	Vc	
	25° C	20° C	25° C	20° C						
 Vc	-137	-138	30° C	-108 F _a	-12.07	268.9	290.5			
	{ -111 F _a -154 F _e	{ -131d -138	0° C	{ -150 F _e -114 F _f ' -159 F _e ' ΔG^* 9.3 kcal/mol	-11.90	267.0	290.1			
	ΔG^* 9 kcal/mol	ΔG^* 9.3 kcal/mol	-60° C		-11.40	262.7	290.1			

^a Chemical shifts were measured on a Bruker WP 200 SY (^{29}Si) or a VARIAN EM 390 (^{19}F) in CDCl_3 or CD_2Cl_2 using TMS (^{29}Si) or CFCl_3 (^{19}F) as internal references. Negative values are to high field. ^b See also ref. 11. ^c The value of ΔG^* for Va calculated from F, from $\text{N}(\text{CH}_3)_2$ and from CH_3 , was respectively, 8.5, 9.4 and 9.6 kcal/mol. ^d In the open form the two fluorine atoms are diastereotopic.

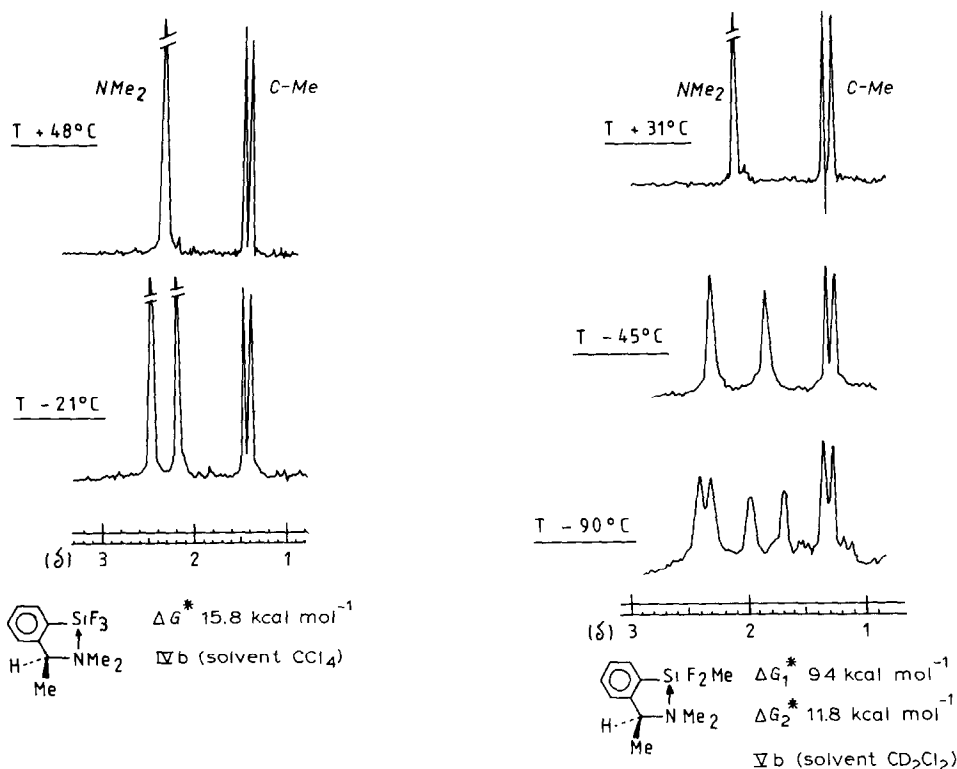


Fig. 1. ^1H NMR spectra of IVb and Vb at different temperatures. IVb: Solvent CCl_4 , $\Delta G^* 15.8 \text{ kcal/mol}$. Vb: Solvent CD_2Cl_2 , $\Delta G_1^* 9.4 \text{ kcal/mol}$, $\Delta G_2^* 11.8 \text{ kcal/mol}$.

intermolecular fluorine exchange but may be attributed to an intramolecular process. The variation of the ^{29}Si chemical shift with temperature could be explained by an increase in the number of pentacoordinate species with decreasing temperature or by the formation of the most stable five-coordinate intermediate (mechanism 1) as the temperature is decreased.

In the case of IVa and Va it is not possible to distinguish between mechanisms 1 and 2. However, in the case of Vb by using proton spectra, Fig. 1, it is possible to obtain the value of ΔG^* for two processes. When the temperature is increased the first coalescence corresponds to a dynamic process at silicon with $\Delta G^* 9.4 \text{ kcal/mol}$ (mechanism 1). The second coalescence would then correspond to the breaking of the silicon–nitrogen bond, $\Delta G^* 11.8 \text{ kcal/mol}$ (mechanism 2). The first result is supported by the variable temperature ^{19}F NMR data, where the energy of the equivalence process, $\Delta G^* 9.3 \text{ kcal/mol}$, agrees well with the value obtained from the ^1H NMR spectra. For IVb, the ^{19}F NMR data provide the value of the energy corresponding to the fluorine equivalence, $\Delta G^* 13.1 \text{ kcal/mol}$ (mechanism 1) and the ^1H NMR data give the energy of the NMe_2 equivalence, $\Delta G^* 15.8 \text{ kcal/mol}$ (mechanism 2). At low temperatures, the CMe group in Vb might be expected to give a doublet of doublets. However, only a single doublet is observed and this may be because the chemical shift differences are too small to be detected in this study.

The results taken altogether support an unambiguous assignment of a pseudorotation mechanism for isomerization at silicon, as was recently predicted [12]. In the compounds studied, the energy barrier for the pseudorotational process is lower than the energy for the equilibrium between the open and closed forms (mechanism 2). The strength of the intramolecular interaction at silicon appears to depend on the Lewis acidity of silicon (compare the energies for the ring opening process in IV and V) as well as by the ease of stretching of the bond to the group which becomes *trans* to the newly-formed coordinate covalent (The substituent in the apical position in the TBP species generated). Although the pseudorotation of V involves a form in which a carbon atom could be apical (with two fluorine atoms equatorial) or where the five-membered ring is diequatorial, the energy barrier for pseudorotation is still lower than in the trifluoro derivative, IV.

Further studies are in progress with five-coordinate compounds with other functional groups at silicon, in order to determine the parameters which control the stability of pentacoordinate silicon and the energy barrier for pseudorotation.

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