# Co-ordinative Interactions in Chelated Complexes of Silicon. Part 7.[1] Dynamic Nuclear Magnetic Resonance Studies of Fluorine Exchange at Five-co-ordinated Silicon †

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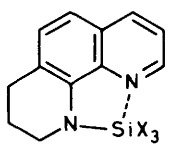
Recently, *X*-ray diffraction has revealed a trigonal-bipyramidal co-ordination for silicon in the chelated complex 1-(trifluorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline, $(C_{12}H_{11}N_2)SiF_3$. At −90 °C in solution $^{19}$F n.m.r. data are in good agreement with the crystalline structure. At room temperature, rapid positional exchange of fluorine atoms is detected. The rearrangement occurs as an intramolecular reaction by an irregular mechanism involving the instability of co-ordinative bonding. An energy barrier of 7.5(2) kcal mol$^{-1}$ for the equilibration of fluorine nuclei has been derived from spectroscopic data by line-shape analysis. Intermolecular fluorine transfer between molecules is also observed, but this exchange remains very slow on the n.m.r. time-scale up to 130 °C.

*X*-Ray diffraction has revealed trigonal-bipyramidal co-ordinated silicon in substituted silyl derivatives of 1,2,3,4-tetrahydro-1,10-phenanthroline: structures (1b)—(1e).[2-4] In these chelated complexes the five-co-ordination of silicon is achieved by intramolecular Lewis acid–base interaction between silicon and the non-bonding electrons on nitrogen in the less saturated ring of the aromatic system. The co-ordinative bond is only 14—15% longer than the other internal Si–N single bond formed by a chemical substitution reaction.

In the solid state the molecular geometry is almost 'frozen in,' whereas in solution dynamic processes can more clearly indicate the strength of co-ordinative bonding. In $CDCl_3$ the static n.m.r. parameters ($^1$H, $^{13}$C, $^{15}$N, and $^{29}$Si chemical shifts in the series of compounds) demonstrate co-ordinative interactions in (1b)—(1e) at room temperature.[1] In (1a) these interactions seem to be very weak or totally absent. Investigation of static n.m.r. shifts does not allow any conclusion as to the stability of the co-ordinative bond as a function of time. Conformational rearrangements of the complexes (1a)—(1f), which result from the lability of the co-ordinative bond, should give rise to temperature-dependent n.m.r. properties. Dynamic exchange processes of fluorine nuclei have been found for the chelated complexes (1e) and (1f). The chlorodifluorosilyl complex (1f) is formed by an intermolecular exchange reaction between (1d) and (1e). The results of the dynamic $^{19}$F n.m.r. studies are reported in this paper.



| $SiX_3$ | |
|---|---|
| $SiMe_3$ | (1a) |
| $SiMe_2Cl$ | (1b) |
| $SiMeCl_2$ | (1c) |
| $SiCl_3$ | (1d) |
| $SiF_3$ | (1e) |
| $SiClF_2$ | (1f) |

## Experimental

The compounds (1d) and (1e) were prepared as described in the literature [3,5] and purified by sublimation. A solution (*ca.* 20—40 mg cm$^{-3}$) was prepared in $CD_2Cl_2$ and dried over molecular sieve; $CFCl_3$ was added as an internal fluorine standard. The $^{19}$F n.m.r. spectra were recorded on Bruker WH 360 and WP 100 MG spectrometers. For (1e), $\delta$ ($CFCl_3$, 188 K): $F_{eq}$ −130.08, $F_{ax}$ −135.97 p.p.m., $J_{FF} = 30.5$ Hz. For (1f), $\delta$ ($CFCl_3$, 188 K): $F_{eq}$ −99.85, $F_{ax}$ −116.80 p.p.m., $J_{FF} =$ 39.1 Hz. For (1e), $\delta$ ($CFCl_3$, 299 K): F −132.04 p.p.m. For (1f), $\delta$ ($CFCl_3$, 299 K): F −108.33 p.p.m. Temperatures are considered accurate to ±3 °C. Spectra were calculated by using the DNMR3 program [6] on a DEC 1091 computer. A visual fit of observed and calculated spectra at various temperatures provides the rate constants shown in Figures 1 and 2. The activation parameters were calculated from the rate constants by the method of Eyring with the ACTPAR program.[7] The estimated standard deviations for $\Delta H^\ddagger$ are given in parentheses after the values given below.

## Results and Discussion

The $^{19}$F n.m.r. spectrum of (1e) shows at room temperature only one signal of three equivalent fluorine atoms, whereas at −90 °C a doublet and a triplet are found (Figure 1). These results are in good agreement with the crystalline trigonal-bipyramidal structure. Assuming the exchange process to be of first order, the numerical line-shape analysis indicates that the equilibration of fluorine nuclei is connected with an energy barrier of $\Delta H^\ddagger = 7.5(2)$ kcal mol$^{-1}$ (31.5 kJ mol$^{-1}$). Because of the Si–F coupling pattern in the $^{29}$Si n.m.r. spectrum (quartet) of (1e), fast intermolecular fluorine exchange can be neglected at ambient temperature. The positional exchange of fluorine is considered as an intramolecular process by a regular or irregular isomerisation.[8] Regular processes occur without breaking and reforming of bonds, conserving five-co-ordination in all steps of the reaction path (Berry pseudorotation, turnstile rotation). In this case the co-ordinative bond has to be expressed as a strong interaction, comparable with a normal single bond. Irregular rearrangement occurs under fission and reformation of the co-ordinative bond involving a more or less hindered rotation of an intermediate tetragonal trifluorosilyl group. In the present case the second process is more likely.[9-11] It indicates the dative Si···N bonding [13.7% extended in (1e) compared with the other Si–N bond [3]] to be a weak interaction amounting to less than 7.5 kcal mol$^{-1}$. This barrier has to be attributed to the total energy necessary for

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† *Non-S.I. unit employed:* cal = 4.184 J.

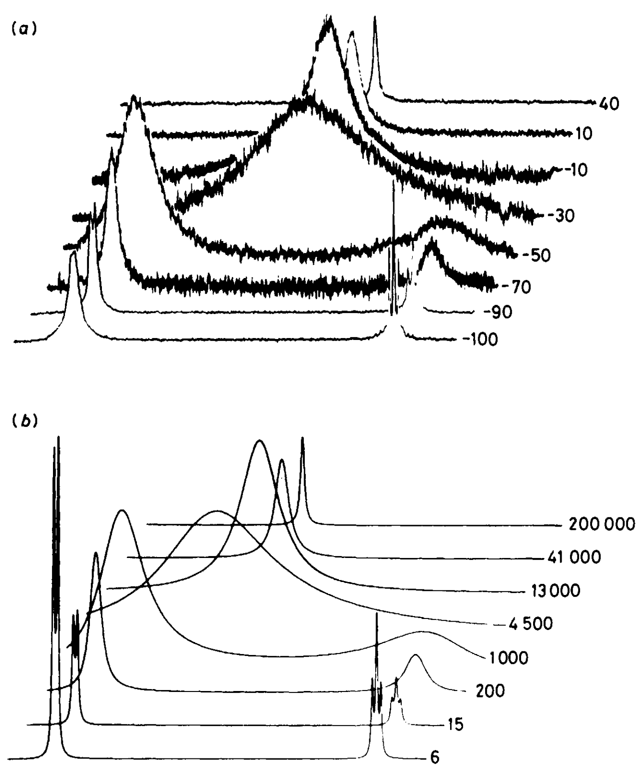

**Figure 1.** (*a*) Observed and (*b*) calculated $^{19}F$ n.m.r. spectra of (1e) as functions of temperature (°C) and rate constant ($s^{-1}$) respectively

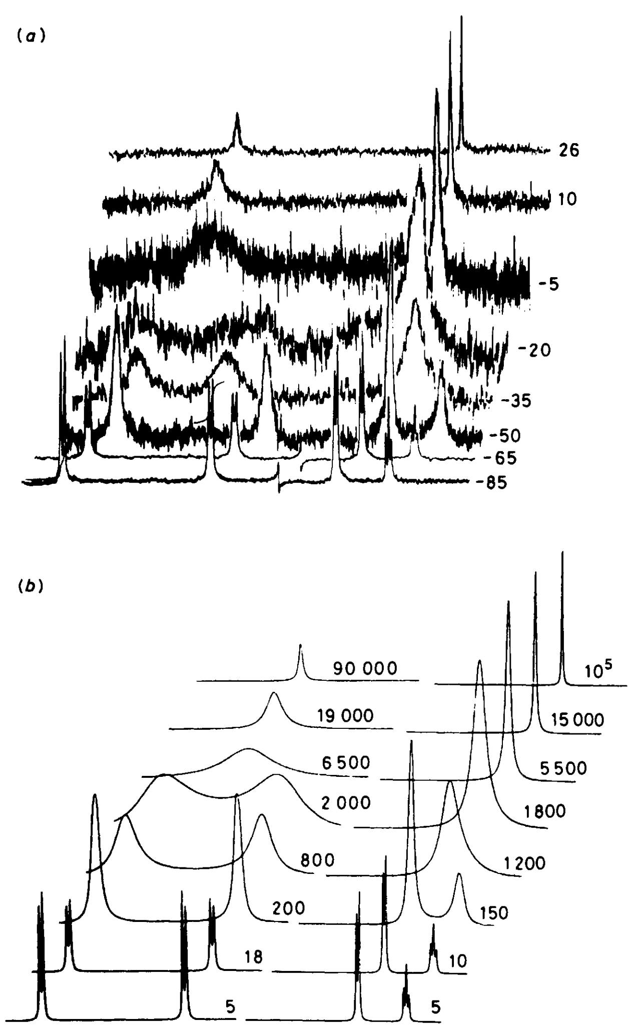

**Figure 2.** (*a*) Observed and (*b*) calculated $^{19}F$ n.m.r. spectra of a mixture of (1e) and (1f) as functions of temperature (°C) and rate constant ($s^{-1}$) respectively

the positional exchange of fluorine and it includes the energy required to overcome the co-ordinative interaction. The energy barrier is in the same range as that for the hindered rotation of bulky side groups, such as t-butyl on aromatic ring systems.[12] Whether co-ordinative interaction really contributes to the height of the barrier of rotation, which governs the rotational movement of the $SiF_3$ group, remains in question.

Structural studies in the crystalline state revealed (1d) and (1e) to be isomorphous. In order to show whether any intermolecular exchange processes play a significant role, a mixture of (1d) and (1e) was prepared in $CD_2Cl_2$. After one month at room temperature the $^{19}F$ n.m.r. spectroscopic properties were recorded as a function of temperature (Figure 2). The spectra indicate two different fluorosilyl complexes. One is identified as the incipient compound (1e), the other one as (1f), formed by intermolecular fluorine exchange between (1d) and (1e). The dichlorofluorosilyl complex is definitely absent, whereas the presence of (1d) cannot be excluded. As the coupling pattern shows, (1f) has at low temperature an axial and an equatorial fluorine atom, the chlorine atom in the silyl group occupies another equatorial site. The complex (1f) represents a chiral arrangement around silicon. The presence of fluorine in the axial and chlorine in the equatorial positions contradicts the assumption of higher apicophilicity of chlorine compared with fluorine.[13]

The formation of (1f) as a reaction product of (1d) and (1e) proves the occurrence of intermolecular fluorine exchange processes. However, the fluorine transfer is slow on the n.m.r. time-scale at room temperature. The different fluorine complexes represent signals of different chemical shift (25 p.p.m. apart). Measurements in $C_2D_2Cl_4$ revealed that the intermolecular exchange remains slow up to 130 °C, no broadening of the resonance signals could be observed. Therefore any dynamic process indicated by the coalescing coupling pattern below room temperature is clearly due to an intramolecular rearrangement, as described above. The activation enthalpies for the two compounds are very similar [(1e), $\Delta H^{\ddagger} = 10.1(10)$; (1f), 9.9(6) kcal $mol^{-1}$]. The deviation of the energy barrier for (1e) in the pure solution and in the mixture may be explained by the different conditions which were present during the spectroscopic analyses of the pure and the mixed samples.

In (1d) and (1f) the intermolecular fluorine transfer (slow on the n.m.r. time-scale) may occur *via* an ionic mechanism involving intermediate four-co-ordinated silicon or *via* a six-co-ordinated transition state with aggregated molecules connected through halogen atoms.[14–16]

Intermolecular fluorine exchange has been discussed in several cases to explain the n.m.r. spectroscopic data of extra-co-ordinated fluorosilyl complexes. Rapid exchange on the n.m.r. time-scale is only found if the co-ordination numbers at Si in the exchanging species are different from each other. Furthermore, it has been pointed out [17] that fluorine transfer can be catalyzed by acid impurities such as HF. It is difficult to exclude traces of acid from investigations of compounds such as (1d), (1e), and (1f), which are all strongly sensitive to moisture. More detailed studies of the mixture (1d)/(1e) as a function of concentration and reaction time should elucidate the fluorine-transfer mechanism and the formation of the reaction products.

## Acknowledgements

We thank Dr. M. Feigel (University of Bremen, West Germany) and Professor C. Beguin (University of Grenoble, France) for recording the $^{19}$F n.m.r. spectra.

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*Received 28th March* 1983; *Paper* 3/501