

PENTACOORDINATE SILICON DERIVATIVES: RELATIVE APICOPHILICITY OF FUNCTIONAL GROUPS ATTACHED TO A SILICON ATOM

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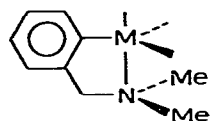
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Summary

For bifunctional organosilanes $o\text{-(Me}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_4\text{SiXFR}$ the relative order of apicophilicity of substituent X versus the apicophilicity of F is determined as $\text{H, OR, NR}_2 < \text{F} < \text{Cl, OCOC}_6\text{H}_5\text{X}$. The results show that the major trigonal bipyramidal conformer is not influenced by the electronegativity of the F atom.

Recently we reported the trigonal bipyramidal (TBP) geometry for penta-coordinated silicon and germanium derivatives of structure I [1].

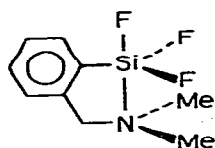


M = Si, Ge, Sn, Pb

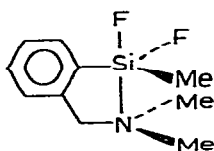
(I)

This TBP geometry is also observed in organotin and lead halides with the same built-in ligand [2,3], and in organosilanes coordinated by other ligands [4,5].

The low temperature ^{19}F spectra of fluorosilanes II and III are also consistent with TBP geometry about silicon and two or one fluorine atoms, respectively, in equatorial positions. In the present work we draw on the spectroscopic data to define a scale of relative apicophilicities for bifunctional groups attached to a silicon atom.



(II)



(III)

TABLE 1
 ^{19}F NMR CHEMICAL SHIFTS OF COMPOUNDS IV—VII

Products ^a	δ (ppm) ^b		$\Delta\delta$ (ppm)
	Room temperature	-90°C)	
MeArSiFH (IV)	-134.5	-122.5 (F _{ax})	+12
MeArSiF(O-t-Bu) (V)	-129	-119 (F _{ax})	+10
MeArSiF(NEt ₂) (VI)	-130	-120 (F _{ax})	+10
MeArSiFCl (VII)	-136	-142 (F _{eq})	-6

^a Ar = *o*-C₆H₄CH₂NMe₂. ^b Chemical shifts were measured relative to internal CFCl₃ in CD₂Cl₂ (Varian EM 390; 84.67 MHz). Negative values are to high fields.

In agreement with the results observed for organophosphorus and sulfur systems [6], we have observed that for II and III the apical ^{19}F signal is downfield and the equatorial signal is at high field [1]. Details of the low temperature ^{19}F spectra of other fluorosilanes are shown in Table 1.

The variable temperature spectroscopic results for IV, V and VI differ from those for VII. At lower temperatures, the ^{19}F signals for IV, V and VI shift downfield, whereas the signal for VII shifts upfield. In each system the favored structure is TBP but with F axial in the former cases and equatorial in the latter case.

The results obtained for fluorobenzoyloxysilanes VIII, IX and X are more complex (Fig. 1). It is possible to see two pentacoordinated TBP conformers below the coalescence temperature. The major configuration has the fluorine substituent in the equatorial position. The ratio of F_{eq}/F_{ax} depends on the nature of the *para* substituent on the benzoyloxy group, the *p*-NO₂ group giving the highest ratio and the *p*-OMe group the lowest.

For bifunctional organosilanes, R₂SiFX the sequence of apicophilicities of substituent X compared with the apicophilicity of F is increasing in the order: H, OR, NR₂ < F < Cl, OCOC₆H₅X. This is the same as the sequence derived previously [7] from the rate of racemization of halosilanes, the substitution of R₃SiX with inversion of configuration and for pentacoordination at silicon. The results show that the major TBP conformer is not determined by the electro-negativity of the F atom.

Related chemical studies have shown that in reactions of 1-Np(Fc)SiFCl only the chlorine is replaced, and inversion of configuration occurs [8]. In 1-Np(Fc)-SiFOR only the fluorine is displaced and inversion of configuration is also generally observed [9]. In each case the group displaced in the substitution reaction is

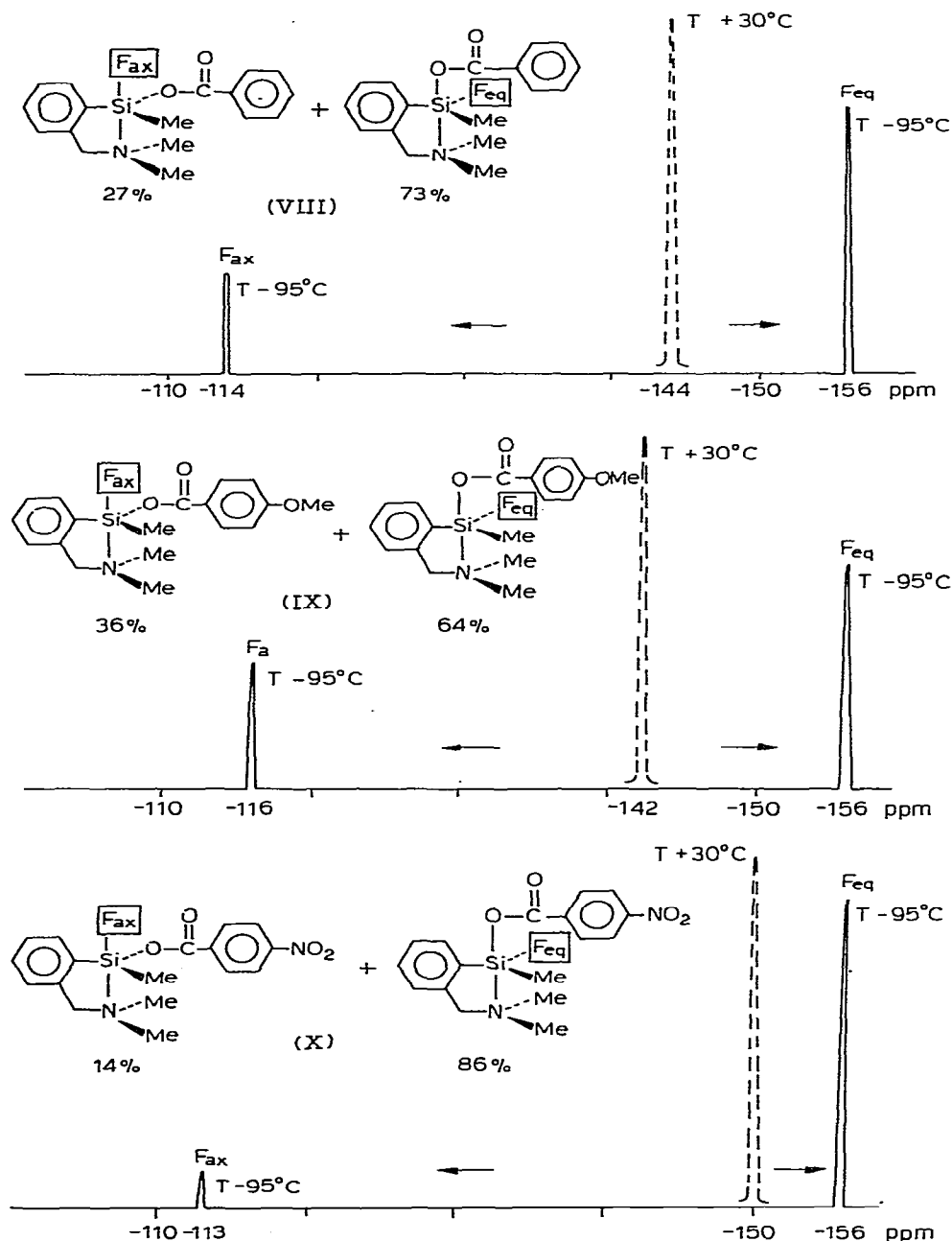


Fig. 1. The ^{19}F NMR spectra of VIII, IX and X in CD_2Cl_2 (recorded on a Varian EM 390 spectrometer at 84.67 MHz). Chemical shifts were measured relative to internal CFCl_3 . Negative values are to high field.

also the one which is found in the apical position in the present study. A parallel exists between monofunctional silanes, R_3SiX , and bifunctional silanes R_2SiFX . If substitution of X (H, OR, NR_2) proceeds with retention in R_3SiX , F is apical in the related bifunctional derivative R_2SiFX . However when X = Cl, OCOR substitution occurs with inversion for R_3SiX and F is equatorial in R_2SiFX . The

polarity rule which is used in the case of fluorophosphoranes [10] cannot be applied to pentacoordinated fluorosilanes.

Further studies are in progress to detect pseudorotation at a silicon centre.

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