

Preliminary communication

A RIGID PENTACOORDINATE SILICON STRUCTURE GENERALIZATION OF PSEUDOROTATION

ROBERT J.P. CORRIU, MUHAMMAD MAZHAR, MONIQUE POIRIER and GERARD ROYO

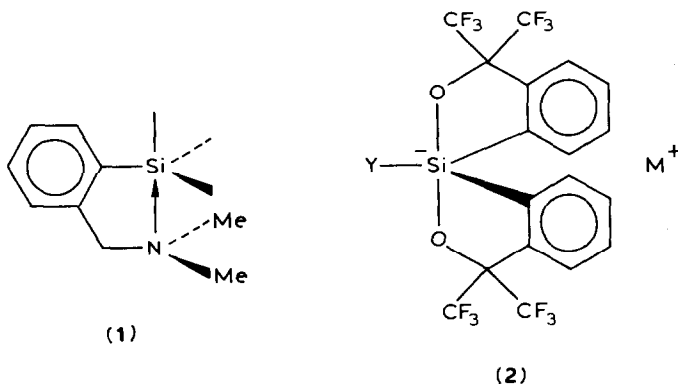
Institut de Chimie fine, Hétérochimie et amino-acides, UA 1097, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cedex (France)

(Received January 17th, 1986)

Summary

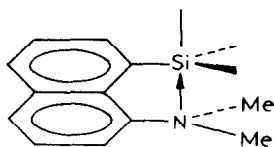
Examination of an organosilicon compound with a structure very favorable for pentacoordination shows the generality of the pseudorotation at silicon for bi- and tri-functional compounds. In contrast monofunctional compounds do not undergo pseudorotation, the ΔG^* being estimated to be $> 20 \text{ kcal } M^{-1}$.

Pseudorotation in the silicate species [1] has been suggested to be the most reasonable mechanism for accounting for the enantiomerization involving intramolecular ligand exchange. Recently pseudorotation in pentacoordinated organosilicon structures 1 and 2 has been observed [2, 3].



A clear distinction between pseudorotation and ring opening-and-closing processes has been obtained for species 1 and the corresponding energies were determined [3, 4]. However the measurement of ΔG^* for the pseudorotation was prevented by the relatively low N—Si breaking energy.

This paper describes the results obtained with the rigid structure A [5], which is known to be very favorable for extra-coordination $N \rightarrow Si$ [6] and which permits the study of mono-, bi- and tri-functional silicon compounds.



(A)

Monofunctional and heterobifunctional silanes

The room temperature 1H NMR spectra of monofunctional silanes A_1 and A_2 and heterobifunctional silanes A_3 always show 2 nonequivalent methyls of NMe_2 groups (see Table 1). This is consistent with a TBP geometry with electronegative groups in apical position, the $Si-H$ and $Si-C\leq$ bonds occupying equatorial positions [6, 1, 7].

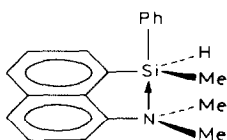
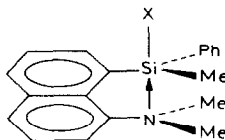
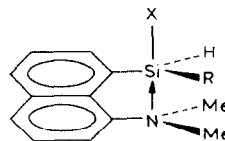
(A₁)(A₂: X = Cl, F;
X = OCH₃)(A₃: X = Cl, R = Me;
X = Cl, R = Ph;
X = Br, R = Ph)

TABLE 1

1H NMR CHEMICAL SHIFTS OF COMPOUNDS A

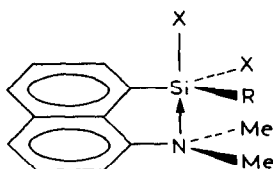
(Shifts measured on a VARIAN HA 100 in dichlorobenzene, are reported relative to internal TMS.)

Monofunctional silanes A_1 and A_2			
$-SiR^1R^2X$	$\delta((CH_3)_2N)$ (ppm)		ΔG^* (kcal M^{-1})
	$20^\circ C$ (2 signals)		
	$+130^\circ < T < +200^\circ C$		
$-SiPhMeH$	2.44, 2.14	2.30 (s)	22
$-SiPhMeX$, X = Cl	2.32, 1.48	1.96 (s)	20
$-SiPhMeX$, X = F	2.13, 1.46	2.02 (s)	23
$-SiPhMe(OMe)$	2.15, 1.46	2.08 (s)	22
Heterobifunctional silanes A_3			
$-SiRHX$	$\delta((CH_3)_2N)$ (ppm)		ΔG^* (kcal M^{-1})
	$20^\circ C$ (2 signals)		
	$+150^\circ < T < +200^\circ C$		
$-SiPhHX$, X = Cl	2.40, 1.90	[equivalence not obtained]	>22
$-SiPhHX$, X = Br	1.66, 2.00		>21
$-SiMeHCl$	2.56, 2.26	2.32	22

Equivalence is observed above 130°C and all the ΔG^* values are > 20 kcal M^{-1} . These energies reflect high tendency towards pentacoordination in A, and we assume they correspond to the N \rightarrow Si bond-breaking energy. It follows that the pseudorotation energy must have higher values.

Homo bifunctional silanes

In contrast, the 1H NMR spectra of bifunctional silanes A_4 at room temperature (see Table 2), always show equivalence of the Me groups attached to N.



(A_4 : X = F, Cl, R = Ph;
 X = OCH₃, R = Ph;
 X = Cl, R = Me)

Diastereotopy is observed at low temperatures in the range $9 < \Delta G^* < 12$ kcal M^{-1} , showing the presence of dissymmetric trigonal bipyramidal structures.

TABLE 2

1H NMR CHEMICAL SHIFTS OF HOMO BIFUNCTIONAL SILANES A_4

(Chemical shifts were measured on a VARIAN HA 100 in CD_2Cl_2 , relative to internal TMS.)

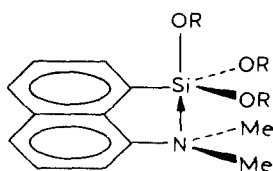
	$\delta((CH_3)_2N)$ (ppm)		ΔG^* (kcal M^{-1})
	20°C	$T < 0^\circ C$ (2 signals)	
—SiPhX ₂ , X = Cl	2.10 (s)	2.66, 1.64	11
—SiPhX ₂ , X = F	2.22 (s)	2.58, 1.85	12
—SiPh(OCH ₃) ₂	2.02 (s)	2.42, 1.54	9 ^a
—SiMeCl ₂	2.72 (s)	2.96, 2.54	9

^aThe value of ΔG^* calculated from (OCH₃)₂ is also 9 kcal mol⁻¹.

Furthermore the very high activation energy difference between the two types of compounds having the same rigid geometry indicates clearly that we are obtaining energies for two processes. Values $\Delta G^* > 20$ kcal M^{-1} probably refer to the opening-closing process and reflect the difficulty of breaking the N \rightarrow Si bond. The low ΔG^* values obtained for bifunctional structures containing a more electrophilic silicon correspond to the pseudorotation energy.

Trifunctional silanes

The case of trialkoxysilanes A_5 is interesting since it is not possible to distinguish the chemical shifts of potentially non equivalent Me or Et groups. See Table 3.

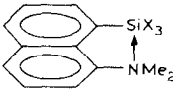


(A_5 :R = Me, Et)

TABLE 3

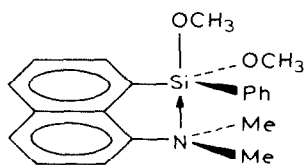
^1H AND ^{19}F NMR CHEMICAL SHIFTS (in ppm) OF TRIFUNCTIONAL COMPOUNDS:

(Chemical shifts were measured on a VARIAN 390, in CD_2Cl_2 with TMS (^1H) and CFCl_3 (^{19}F) as internal references.)

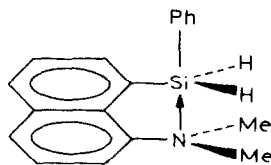
		-20°C	$-100^\circ\text{C} < T < 0^\circ\text{C}$	ΔG^\ddagger (kcal M^{-1})
$-\text{SiF}_3$	δ (F)	-141.1	$\begin{cases} -130.9 \text{ F}_{\text{ax}}(\text{t}) \\ -143.0 \text{ F}_{\text{eq}}(\text{d}) \end{cases}$	12
$-\text{Si}(\text{OMe})_3$	$\delta(\text{OCH}_3)_3$	3.53 (s)	3.52 (s)	<7
$-\text{Si}(\text{OEt})_3$	$\delta(\text{OCH}_2\text{CH}_3)$	1.16 (s)	1.17 (s)	<7
$-\text{Si}(\text{OEt})_3$	$\delta(\text{OCH}_2\text{CH}_3)$	3.82 (s)	3.80 (s)	<7

The ^1H NMR spectrum remains unchanged down to -100°C . As in the case of trihydrogenosilanes [4] this equivalence can be attributed to rapid pseudo-rotation at silicon ($\Delta G^\ddagger < 7$ kcal M^{-1}). The data for the trifluorosilane compound are shown in Table 3 and reveal a triplet for F_{ax} (δ -130.9 ppm) and a doublet for F_{eq} (δ -143 ppm) in the low temperature ^{19}F spectrum. The activation energy for the fluorine equivalence process is 12 kcal M^{-1} . This value is close to the value of ΔG^\ddagger viz. 13.1 kcal M^{-1} found for the trifluorosilane of structure 1 [3, 9].

Finally the ^1H NMR results obtained for the dimethoxysilane A_6 are consistent with a dissymmetric trigonal bipyramidal structure, and recent crystallographic information for the silicon dihydride A_7 [6] enables us to derive the relative order of apicophilicity of groups attached at silicon as $\text{H} < \text{C}_{\text{sp}^2} < \text{OCH}_3$. The presence of Si-H bonds favours pentacoordination [4], but the hydrogen is not apicophilic and prefers the equatorial position. These results extend the scale previously established [8].



(A_6)



(A_7)

These results for the (8-dimethylaminonaphthyl)silanes lead to the following conclusions:

(1) Pseudorotation at silicon takes place with trifunctional silanes. For the trialkoxysilanes studied, as for the previously studied trihydrogenosilanes [4], this process has a low energy barrier ($\Delta G^* < 7 \text{ kcal } M^{-1}$). The value of ΔG^* obtained for the trifluorosilane is similar to those previously observed for compounds with structure 1 [3].

(2) The homobifunctional silanes A_4 (Si-F_2 , Si-Cl_2 , Si(OR)_2) undergo also pseudorotation $9 < \Delta G^* < 12 \text{ kcal } M^{-1}$, as does the silicon difluoride of with structure 1.

(3) The pseudorotation of monofunctional silanes requires a very high energy: $\Delta G^* > 20 \text{ kcal } M^{-1}$. The coalescence of the NMe_2 group found in this energy range can be attributed to $\text{N} \rightarrow \text{Si}$ bond breaking. This is confirmed by the results obtained for hetero bifunctional compounds A_3 : the very high affinity of a Si-H bond for the equatorial position increases the stability of the trigonal bipyramidal complex and the coalescence cannot be observed ($\Delta G^* > 22 \text{ kcal } M^{-1}$).

References

- 1 W.B. Farnham and R.L. Harlow, *J. Am. Chem. Soc.*, **103** (1981) 4608.
- 2 W.H. Stevenson III, S. Wilson, J.C. Martin and W.B. Farnham, *J. Am. Chem. Soc.*, **107** (1985) 6340; W.H. Stevenson III and J.C. Martin, *ibid.*, **107** (1985) 6352.
- 3 R.J.P. Corriu, A. Kpoton, M. Poirier and G. Royo, *J. Organomet. Chem.* **277** (1984) C25.
- 4 J. Boyer, R.J.P. Corriu, A. Kpoton, M. Mazhar, M. Poirier and G. Royo, *J. Organomet. Chem.*, **301** (1986) 131.
- 5 J.T.B.H. Jastrzebski, C.T. Knaap and G. Van Koten, *J. Organomet. Chem.*, **255** (1983) 287.
- 6 C. Brelière, F. Carré, R.J.P. Corriu, M. Poirier and G. Royo, *Organometallics*, **5** (1986) 388.
- 7 R. Corriu, C. Guérin and J. Moreau, *Topics in Stereochemistry*, Wiley-Interscience, New York, vol. **15**, 1984, p. 43.
- 8 R.J.P. Corriu, M. Poirier and G. Royo, *J. Organomet. Chem.*, **233** (1982) 165.
- 9 C. Brelière, F. Carré, R.J.P. Corriu, A. De Saxeé, M. Poirier and G. Royo, *J. Organomet. Chem.*, **205** (1981) C1.