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Hexacoordinate Silicon Species: A Possible Model for Reaction Intermediates. 2. Nondissociative Permutational Isomerization in Solution

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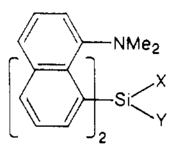
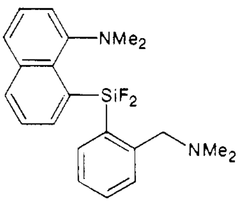
Summary: Studies of intramolecularly hexacoordinated silicon compounds with chelating nitrogen donors have shown for each compound the existence of a pair of enantiomers in fluxional equilibrium. The NMR features are consistent with an isomerization mechanism that occurs without bond cleavage.

In a previous paper,[1] we described the X-ray determination of the structure of the three silicon derivatives 1, 2, and 3.



1: X = H, Y = F
2: X = Y = H
4: X = H, Y = OMe
5: X = H, Y = Me
6: X = Me, Y = Ph



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In all three cases hexacoordination occurs at the silicon atom which largely maintains the basic tetrahedral geometry in spite of the two dative bonds from the nitrogen atoms (see Figure 1). We considered that an investigation of the behavior of such compounds in solution might be interesting for the light that it could shed on a large variety of reactions involving nucleophilic activation at a silicon atom in which hypervalent silicon intermediates may occur.[2] We describe here a dynamic NMR study of bis(8-(dimethylamino)naphthyl)fluorosilane (1), bis(8-(dimethylamino)naphthyl)methoxysilane (4), bis(8-(dimethylamino)naphthyl)methylsilane (5), and bis(8-(dimethylamino)naphthyl)methylphenylsilane (6).

The structures we have investigated (1, 4, 5, and 6) contain two ligands favorable to intramolecular coordination and two different functional groups at silicon in order to have a dissymmetry well suited to ^{1}H NMR studies. If the simplest assumption is made that compound 1 retains the same geometry in solution as in the crystal, the structure of compound 1 can be expected to be as shown in Figure 1.

The ^{1}H NMR is in agreement with this structure although evidence for hexacoordination in all four cases is not provided by the ^{29}Si NMR chemical shifts because in the series with the (dimethylamino)naphthyl ligand, the ^{29}Si NMR chemical shifts are very similar in tetracoordinate, pentacoordinate, and hexacoordinate structures (Table I).[3] However, the Si–H coupling constants are significantly larger ($216.4 < J(\mathrm{SiH}) < 285.45$ for compounds 1, 2, 4, and 5) than the coupling constants observed for the corresponding tetracoordinate compounds (dinaphthylsilane, $J(\mathrm{SiH}) = 197.72$ Hz).[4] This is a reliable indication of hexacoordination in solution.

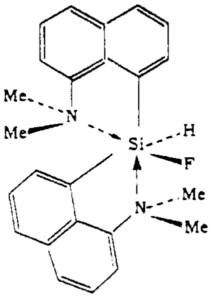

Figure 1. Solid-state geometry of compound 1.

Table I. ^{29}Si Chemical Shifts and ^1J(Si–H) Coupling Constants (Determined by INEPT Technique with $CDCl_3$ as Internal Reference)[a]

compound	δ, ppm	J(SiH), Hz	J(SiF), Hz
tetracoordinate			
$(Np)_2SiH_2$	−38.73	197.72	
NpPhMeSiH	−19.84	194.15	
$NpPhSiH_2$	−35.38	199.8	
pentacoordinate			
ArPhMeSiH	−23.46	226.94	
$ArPhSiH_2$	−43.45	203.8	
hexacoordinate			
$(Ar)_2SiHF$ (1)	−37.33	285.45	277.0
$(Ar)_2SiH_2$ (2)	−41.07	216.4	
$(Ar)_2SiHOMe$ (4)	−27.43	279.9	
$(Ar)_2SiHMe$ (5)	−26.79	235.8	
$(Ar)_2SiMePh$ (6)	−12.08		

[a] Np = naphthyl; Ar = 8-(dimethylamino)naphthyl.

Evidence of hexacoordination in solution is also clearly seen in the temperature-dependent changes in the ^{1}H NMR spectra. At low temperature, in all four cases, four different *N*-methyl signals and twelve aromatic proton signals from two different naphthyl groups were observed (Table II). This observation is in agreement with a dissymmetric structure in which the two NMe_2 groups are different with two diastereotopic methyls on each. Moreover the two naphthyl groups are also not equivalent and are diastereotopically related. The other NMR resonances characteristic of each compound are shown in Table II. For compounds 1 and 4, all the signals were assigned by homonuclear decoupling and NOE experiments. Structures similar to that shown in Figure 1 are the most probable (fluorine and methoxy groups are in the same position).

In the case of 6, at very low temperature, the NMR spectrum shows the appearance of another isomer, each of the two isomers having similar NMR features. The major isomer could have possibly the geometry 6A in which one nitrogen atom is opposite to the phenyl group (see Figure 2). This attribution is based on the X-ray structure of the pentacoordinated compound 7 in which the phenyl group is opposite to the NMe_2 group in contrast of the perpendicular position for the methyl group.[3,5]

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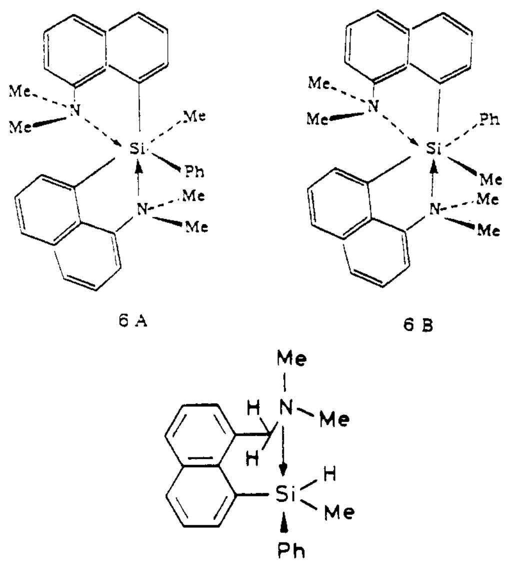

6 A

6 B

7

Figure 2. Possible isomeric forms for compound **6**.

Table II. ^1H Chemical Shift Data for Hexacoordinate Compounds at Low Temperature (in Solution in C_7D_8 with TMS as Internal Reference)

δ, ppm	1	4	5	6[a]	6[b]
NCH_3 (A)	1.58	1.44	1.95	0.83	1.18
NCH_3 (A′)	3.015	2.82	2.75	2.42	2.30
NCH_3 (B)	2.415	2.44	2.48	1.47	2.35
NCH_3 (B′)	2.87	2.76	2.90	1.96	1.69
Si-X[c]		3.38[e]	0.55 (d)[f]	1.06[f]	0.75
Si-H	5.89 (d)	5.69	5.64 (q)		
aromatic[d]					
C_2-H	6.69	6.66	6.76	6.72	
C_2'-H	8.02	8.21	7.99	7.88	
C_3-H	6.96	7.0	6.97	6.79	
C_3'-H	7.60	7.66			
C_4-H	7.61	7.72			
C_4'-H	7.45	7.99			
C_5-H	7.68	7.715			
C_5'-H	7.88	7.88			
C_6-H	7.53	7.41			
C_6'-H	7.43	7.60			
C_7-H	7.57	7.24			
C_7'-H	7.31	7.46			

[a] Chemical shifts for major isomer of **6**. [b] Chemical shifts for minor isomer of **6**. [c] ^{19}F chemical shift for **1** $\delta = -145$ ppm ($\delta_{CFCl_3} = 0$). [d] Not all the aromatic protons signals could be determined by irradiation in case of **5** and **6** owing to the proximity of the signals. [e] SiOMe. [f] SiMe.

The NMR spectra observed at 253 K for **1** and **4** show the existence of a pair of enantiomers in fluxional equilibrium. Selective irradiation of each proton site of the molecule shows a transfer of saturation occurring uniquely between pairs of equivalent sites: the two naphthyl groups are equivalent by exchange; the four methyl groups are equivalent in pairs by exchange and each methyl in signal A is equivalent to one methyl in signal B.

The variable-temperature signals lead to the same conclusions. For each product the four NMe signals coalesce to two NMe signals and the aromatic signals coalesce, also indicating two equivalent naphthyl groups.

These experimental observations are in agreement with a regular mechanism of isomerization taking place without bond breaking in which both the two naphthyl and the NMe_2 groups are successively in equivalent positions toward the functional groups. The two methyl groups of an amino group are never equivalent together. However because of this intramolecular isomerization, all methyl groups are equivalent by pairs from one NMe_2 group to the other one.

Scheme I. Possible Intermediates for Dissociative Isomerization of Hexacoordinated Silicon Compounds

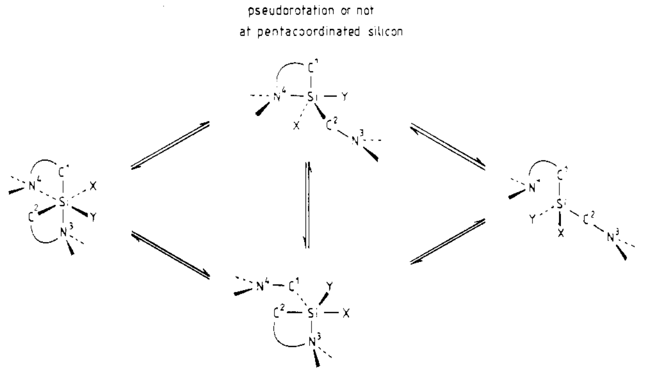

Table III. Free Energy of Activation for Isomerization of Hexacoordinate Compounds from Line-Shape Data[a]

compd	X	Y	$\Delta G^{\ddagger}$, kcal (at 300 K)
1	H	F	14.7
4	H	OMe	15.2
5	H	Me	9.3
6	Me	Ph	12.7

[a] These experimental values are accurate to within ±15%.

All the irregular processes involving Si←N bond scission can be ruled out. (I) Cleavage of two dative N→Si bonds would result in a symmetrical tetrahedral molecule: only a singlet from the NMe_2 groups and a single set of naphthyl signals in the NMR spectrum would be observed. (II) If only one of the dative N→Si bonds were to break, two mechanistic possibilities would ensue: the resulting pentacoordinate specie might or might not undergo facile ligand permutation before re-forming the bond (see Scheme I).[6] If the pentacoordinate intermediate was stereochemically rigid, the NMR spectrum would be expectecd to show two different naphthyl group signals and three different NMe signals, two of the latter arising from the diastereotopic NMe_2 group remaining coordinated to the silicon atom and third from the free ligand (relative intensities: 1:1:2). In the case of fluxionability of the pentacoordinated silicon atom due to the pseudorotation, two NMe_2 signals and two different naphthyl groups would be evident in the NMR spectrum; however, these two set of signals would be quite distinct and saturation transfer experiments would not show protons occupying alternative sites in the molecule, as experimentally observed.

For all four compounds the observation of only one set of naphthyl groups and two different NMe group environments at high temperature are in full agreement with an intramolecular nondissociative process. This isomerization process could be one of nondissociative pathways precedently described generally in the case of an ideal octahedral geometry (Bailar twist, Ray–Dutt twist, or Springers–Sievers twist));[7] Investigations with other models are necessary before a detailled description of the mechanism.

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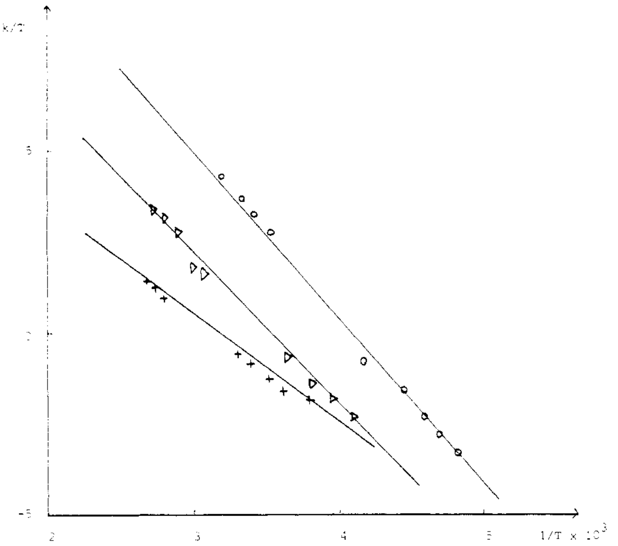

Figure 3. Eyring plot of data from line-shape analysis (compounds **1** (○), **5** (▽), and **6** (+)).

Over the temperature range, the study of exchange-broadened spectra allows the isomerization rate to be evaluated. From measurements of *k* at different temperatures (373–293 K) the free energy of activation was calculated to be as shown in Table III. The results suggest that a single mechanism is operative throughout the temperature range because the Eyring plots are linear (see Figure 3). The values of the energy of activation ($\Delta G^{\ddagger} < 15$ kcal·mol^{-1}) are similar for the four compounds showing little dependence on the substituents around the silicon atom. These values of $\Delta G^{\ddagger}$ are lower than the energies of activation observed in case of other fluxional octahedral nonmetal species.[8]

In conclusion our results show that the hexacoordinate dissymmetric geometry observed by X-ray analysis in the solid state is maintained in solution. Significantly hexacoordination occurs also when the silicon atom is bound only to carbon (compound **6**). These observations provide good support for the postulate of the participation of such structures as intermediates in the course of reactions involving nucleophilic activation at silicon, as proposed for the Michaël reactions and aldolization reactions of silyl enolates[9] or in group transfer polymerization.[10] Furthermore the fluxional behavior observed for both pentacoordinate[11] and hexacoordinate silicon compounds could be indicative of the difficulty in using chiral silicon compounds for inducing asymmetry in some organic reactions.[12]

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Additions and Corrections

John C. Cochran,* Lois E. Williams, Brian S. Bronk, Julie A. Calhoun, Julianne Fassberg, and Kimber G. Clark: Protodestannylation of Carbomethoxy-Substituted Vinylstannanes: Kinetics, Stereochemistry, and Mechanisms. **1989**, *8*, 804.

There are several typographical errors in the registry paragraph of the original paper. The following is the corrected version thereof.

$HC{\equiv}CCO_2Me$, 922-67-8; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; $EtO_2CC{\equiv}CCO_2Et$, 762-21-0; $HC{\equiv}CCO_2Et$, 623-47-2.