Stereodynamics of Neutral Six-coordinate Silicon Chelates: Evidence for Two Non-dissociative Rate Processes

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A DNMR spectroscopic study of the stereodynamics of novel neutral six-coordinate silicon chelates reveals two distinct ligand site exchange processes, both of which are intramolecular non-dissociative.
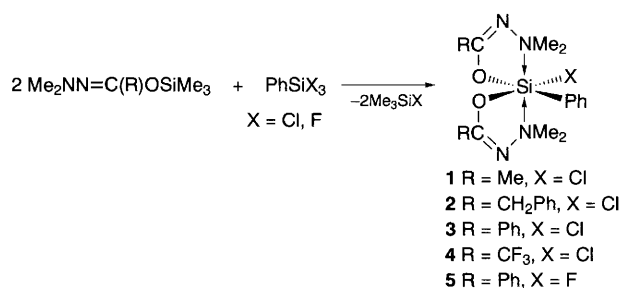
Hypervalent silicon complexes are known for their relative stereochemical non-rigidity and ease of ligand permutation.[1] Both inter- and intra-molecular ligand exchange processes have been reported, primarily in five-coordinate silicon compounds[2] and more recently also in six-coordinate complexes.[3] We now report on the observation of *two* apparently independent, simultaneous *intramolecular* rate processes in a series of novel neutral six-coordinate silicon complexes 1–5.

Complexes 1–5 are readily prepared according to Scheme 1.[4] The octahedral geometry of 1–5 has been tentatively confirmed by an X-ray crystallographic determination of a complex 6 analogous to 3, with Me and Cl as monodentate ligands,[5] and by the typical high-field ^{29}Si NMR chemical shifts (ranging between δ −128.8 and −132.7 for 1–4, and δ −148.3 for 5, compared with δ −121.7 for 6) characteristic of six-coordination in silicon.[6] The similarity of NMR spectra of all complexes assures their structural analogy with 6.

The ^{1}H and ^{13}C NMR spectra of 1–5 are temperature dependent, characteristic of kinetic changes occurring at the so-called 'NMR timescale'. At the slow exchange limit temperatures for 1–5 the spectra show the presence of only *one diastereoisomer* in solution, out of the possible six octahedral diastereoisomers (Fig. 1). At this temperature the N-methyl groups are all diastereotopic and display four singlets, typical of C_1 symmetry and in accord with the crystallographic structure for 6. Interestingly, two distinct and separate rate processes are

observed associated with the exchange and coalescence of signals from diastereotopic groups: the four N-methyls first coalesce to two singlets upon increase of temperature, and these coalesce to one singlet upon further increase of temperature (Fig. 1, Table 1). In addition, coalescence of C-methyl groups is observed in 1 simultaneously with the first coalescence of N-methyls (both in ^{1}H and ^{13}C NMR spectra), indicating that the lower of the two activation barriers brings about exchange of the chelate cycles. Fig. 1 also shows that coalescence of the *ortho* protons of the Si–Ph group occurs, simultaneously with C- and N-methyl coalescence, indicating restricted rotation about the Si–C bond.

Of the multitude of possible mechanisms for ligand exchange and ligand site exchange, including dissociative and non-dissociative processes, the evidence suggests that dissociative exchange may be ruled out. The most likely dissociation processes are Si–Cl ionic dissociation and cleavage of one of the
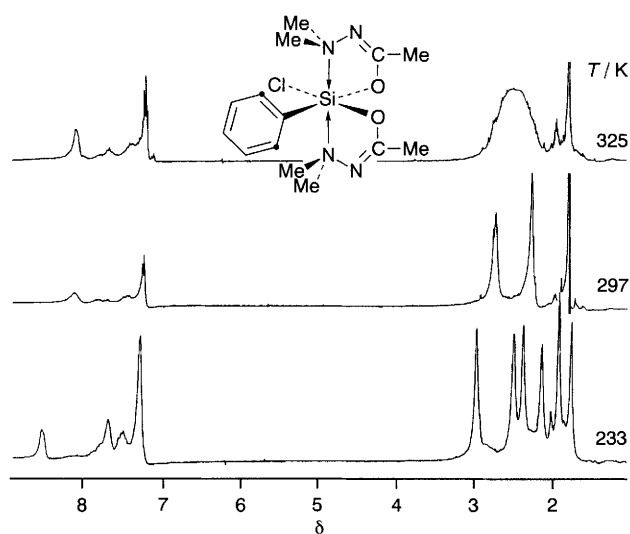

Fig. 1 Variable-temperature ^{1}H NMR spectra for 1 in (CD$_3$)$_2$CO solution

Scheme 1

$$2\ Me_2NN=C(R)OSiMe_3\ +\ PhSiX_3 \xrightarrow[-2Me_3SiX]{} $$

X = Cl, F

1 R = Me, X = Cl
2 R = CH$_2$Ph, X = Cl
3 R = Ph, X = Cl
4 R = CF$_3$, X = Cl
5 R = Ph, X = F

Table 1 ^{1}H NMR data and activation free energies for complexes 1–5[a]

Compound	X	R	T/K		δ(N-Me)					δ(R)		$\Delta G^{\ddagger}$/kJ mol^{-1}
1	Cl	Me	233	2.16		2.38		2.49		2.97	1.79	1.93	
			297		2.29				2.73		1.85		51.5 ± 1.0
			327				2.49				1.85		66.1 ± 1.0
2	Cl	CH$_2$Ph	190	1.97		2.19		2.37		2.80	3.22^{b,c}	3.33^{b,d}	
			297		2.23				2.56		3.28^{b,e}		51.5 ± 1.0
			325				2.40				3.28		66.5 ± 1.0
3	Cl	Ph	265	2.40		2.59		2.92		3.34			
			290		2.50				3.13				57.7 ± 1.0
			315				2.81						62.8 ± 1.0
4	Cl	CF$_3$	290	2.30		2.62		2.63		3.15			
			330				2.72^f						66.1, 68.2 ± 1.0^f
5	F	Ph	297	2.24		2.64		2.71		3.21			
			330				2.65^f						66.5, 68.2 ± 1.0^f

[a] Complexes 1–3 in (CD$_3$)$_2$CO solutions, 4 and 5 in CDCl$_3$ solutions, at 200 MHz. [b] AB-quartets centred at given δ values. [c] Δv_{AB} = 58 Hz, J_{AB} = 14 Hz. [d] Δv_{AB} = 19 Hz, J_{AB} = 14 Hz. [e] Δv_{AB} = 27 Hz, J_{AB} = 14 Hz. [f] The two rate processes were not fully resolved and rate constants and $\Delta G^{\ddagger}$ values were obtained from computer simulated spectra.

Si–N dative bonds, followed by rearrangement and recombination. Examination of the ^{29}Si NMR spectra for **5** shows that the large one-bond coupling constant $J(^{29}Si-^{19}F) = 271$ Hz does *not* collapse upon heating to temperatures well above the N-methyl coalescence temperature, and hence no Si–F bond cleavage takes place during this site-exchange process.

It might be argued that the lack of Si–F dissociation in **5** is no proof of similar behaviour of the Si–Cl bonds in **1–4**. However, the fact that **5** behaves very similarly to **1–4** in all other stereodynamic aspects (two activation barriers, similar coalescence temperatures, comparable NMR spectra) excludes the possibility that **5** undergoes exchange by a substantially different mechanism. It therefore follows that in **1–4** also the stereodynamic processes do not involve Si–Cl bond dissociation.

The alternative dissociation process, that of the Si–N dative bond, is ruled out by the results of DNMR experiments with **2**: in **2** the prochiral benzyl groups give rise, at the slow exchange limit temperature, to two AB-quartets representing the four diastereotopic methylene protons. When the temperature is raised two consecutive rate processes are observed, as in the other complexes, whereby first the two AB-quartets coalesce to one, followed by further coalescence of the remaining quartet to a singlet. These two exchanges take place *simultaneously* with the coalescence phenomena observed for the N-methyl signals, and must hence result from the same exchange reactions; if geminal N-methyl exchange were to take place *via* Si–N bond cleavage followed by rotation about the N–N bond, this process *cannot* cause *simultaneous* coalescence of the methylene-quartet. It must therefore be concluded that the common reaction responsible for coalescence of N-methyl and benzyl-methylene signals, respectively, does *not* involve Si–N bond cleavage.

The evidence thus definitely leads to the conclusion that site-exchange occurs by a non-dissociative topomerization process.
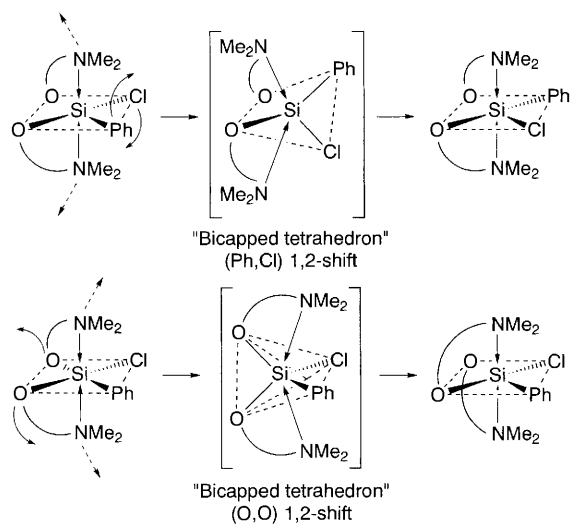

Fig. 2 Ligand site exchange mechanism by 1,2-shift *via* a bicapped tetrahedral intermediate. The two topomerizations responsible for two exchange barriers are shown.

The most likely mechanism which accounts for these observations is a 1,2-shift of adjacent ligands, through a 'bicapped tetrahedron' intermediate or transition state (Fig. 2).[7] Such structures have been reported as *stable* geometries for other six-coordinate silicon chelates in the solid state.[8]

An alternative mechanism has been proposed by a referee, whereby 1,2-shift occurs *non-symmetrically*, *i.e.* with only one of the Si–N dative bonds extending, and a transition state which resembles a five-coordinate more than a bicapped tetrahedral geometry. These two mechanisms are indistinguishable experimentally, and the arguments for the latter are (*a*) it would be easier (lower barrier) to cleave or extend one Si–N bond than two; (*b*) the resulting nearly trigonal-bipyramidal intermediate is likely to topomerize *via* a 1,2-shift. The main argument in favour of the bicapped tetrahedron (symmetrical) exchange is the discovery of stable structures of this kind.

The two barriers are assigned to (O,O)- and (Ph,X)-shifts, which differ slightly in nature and hence in activation energies. Each of these shifts effects a topomerization (*i.e.* ligand site exchange within the same diastereoisomeric structure). The combination of both shifts results in complete scrambling and site exchange of all N-methyl singlets (as well as methylene protons in **2**), and hence accounts for the appearance of only one singlet at fast exchange temperature.

Work is underway to fully characterize the exchange mechanism.

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