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Communications

Crystal Structure and Unambiguous Assignment of Two Ligand Exchange Barriers in Neutral Pentacoordinate Silicon Complexes: Correlation of ^{29}Si and ^{15}N Chemical Shifts and Si–N Cleavage Barriers

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Summary: The first assignment of both consecutive ligand exchange processes, Si–N cleavage and pseudorotation, in a series of neutral pentacoordinate silicon complexes with a single halogen ligand (monofunctional silanes) is described. The first crystal structure for a N–Si chelate with a ClSiC_2ON coordination center was determined. A remarkable linear correlation was found between Si–N cleavage barriers and the corresponding coordinative ^{29}Si and ^{15}N chemical shifts.

One of the most intriguing properties of hypervalent silicon complexes is their stereochemical nonrigidity.^{1,2} Several different mechanistic pathways, mostly intra-

molecular^{3–5} but also intermolecular,⁶ are possible in pentacoordinate complexes and may account for the observed ligand exchange phenomena. The present communication attempts to further clarify the process of ligand site exchange in pentacoordinate silicon complexes.

In previous studies on neutral pentacoordinate N–Si chelate complexes two intramolecular ligand exchange processes were identified: Si–N cleavage and pseudorotation.⁴ Both were measured and reported for complexes with two or three halogen ligands attached to silicon, in which interchange of axial and equatorial ligands could be monitored. In complexes with a single halogen ligand, however, discrimination and exact assignment of both barriers have not been reported.

We now report the first observation of both ligand exchange processes and their assignment to Si–N cleavage and pseudorotation for pentacoordinate complexes with a single halogen ligand.

The synthetic route shown in eq 1 afforded **1–8** in

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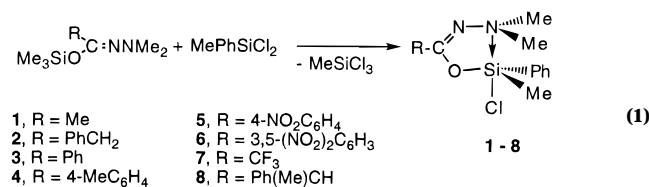
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Table 1. ^{29}Si and ^{15}N NMR Data and Barriers for Ligand Exchange in **1–8**

compd	R	$\delta(^{29}\text{Si})$, ppm	$\Delta_1(^{29}\text{Si})$, ^a ppm	$\Delta_2(^{29}\text{Si})$, ^b ppm	$\delta(^{15}\text{N})$, ^c ppm	$\Delta(^{15}\text{N})$, ^d ppm	ΔG^* , kcal mol ⁻¹
1	Me	-32.8	-51.9	-48.7	66.5	7.6	10.9
2	PhCH ₂	-31.8	-52.1	-47.7	66.4	7.5	11.0
3	Ph	-29.0	-47.8	-44.9	66.8	6.6	10.6
4	4-Me-C ₆ H ₄	-30.0	-48.2	-45.9			10.7
5	4-NO ₂ -C ₆ H ₄	-23.0	-44.5	-38.9			9.4
6	3,5-(NO ₂) ₂ -C ₆ H ₃	-14.7	-38.5	-30.6	68.2	3.7	8.9
7	CF ₃	-3.2	-30.0	-19.1	64.7	2.4	<7
8	PhMeCH	-33.8	-54.2	-49.7	65.7, 66.4	7.8, 5.7	11.4

^a Coordinative shift, defined by $\Delta_1(^{29}\text{Si}) = \delta(^{29}\text{Si}(\text{pentacoordinate})) - \delta(^{29}\text{Si}(\text{precursor, Me}_3\text{SiO}(\text{R})\text{C}=\text{NNMe}_2))$. ^b Coordinative shift, defined by $\Delta_2(^{29}\text{Si}) = \delta(^{29}\text{Si}(\text{pentacoordinate})) - \delta(^{29}\text{Si}((E)\text{-Me}_2\text{ClSiO}(\text{Me})\text{C}=\text{NNMe}_2))$. ^c ^{15}N shift for the NMe₂ group, relative to external NH₄Cl. ^d Coordinative shift, defined by $\Delta(^{15}\text{N}) = \delta(^{15}\text{N}(\text{pentacoordinate})) - \delta(^{15}\text{N}(\text{precursor, Me}_3\text{SiO}(\text{R})\text{C}=\text{NNMe}_2))$.

high yields⁷ and is a convenient way to obtain complexes with a chiral silicon center.⁸



Neutral complexes with the general ligand framework ClSiC₂ON have not previously been reported in the solid state. The crystal structure for complex **1** is depicted in Figure 1, featuring a slightly distorted trigonal-bipyramidal geometry. The Si–N and Si–Cl bond lengths were found to be equal (2.216 Å) and are characteristic of pentacoordination at silicon. The other bond lengths to silicon were as follows: Si–O, 1.703 Å; Si–Me, 1.863 Å; Si–Ph, 1.854 Å. The N–Si–Cl angle equals 166.7°. The silicon atom deviated by 0.121 Å from the equatorial plane toward the Cl atom.

The solution structure of the complexes was determined on the basis of the ^{29}Si chemical shifts. Table 1 lists the ^{29}Si shifts of **1–8**, along with the corresponding coordinative shifts ($\Delta_1(^{29}\text{Si})$), the chemical shift differences with respect to the tetracoordinate precursor trimethylsilylated hydrazides,^{8b} and $\Delta_2(^{29}\text{Si})$, the corresponding differences with respect to (*E*)-Me₂ClSiO(Me)C=NNMe₂ ($\delta(^{29}\text{Si})$ 15.9 ppm⁸).⁹ The large upfield shifts of **1–8** are evidence for their pentacoordinate nature in solution.¹⁰ Interestingly, the ^{29}Si shifts are highly sensitive to the remote group R on the chelate cycle. Additional evidence for pentacoordination comes from the substantial temperature dependence of the ^{29}Si chemical shifts for **1–8**, which change upfield upon

(7) Compounds **1–8** were prepared by mixing equimolar quantities of the O-trimethylsilylated *N,N*-dimethylhydrazides with PhMeSiCl₂ in toluene or chloroform solution under an inert atmosphere, at ambient temperature, for 8–12 h, followed by recrystallization from hexane. Yields range between 50 and 70%. **1–8** had ¹H, ¹³C, and ²⁹Si NMR spectra compatible with their structures. Anal. Calcd for **3** (mp 91–93 °C), C₁₆H₁₉ClN₂OSi: C, 60.27; H, 6.01; Cl, 11.12; N, 8.78; Si, 8.81. Found: C, 59.11; H, 6.11; Cl, 10.97; N, 8.51; Si, 8.95. The extreme moisture sensitivity prevented elemental analyses for the other compounds, which were characterized by spectral analogy.

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(9) Ideally, the comparison of ^{29}Si chemical shifts should be made with the exact tetracoordinate precursor: MePhClSiO(R)C=NNMe₂. However, these spontaneously form the pentacoordinate complexes **1–8**. $\Delta_1(^{29}\text{Si})$ and $\Delta_2(^{29}\text{Si})$ represent comparisons with the nearest available tetracoordinate analogs.

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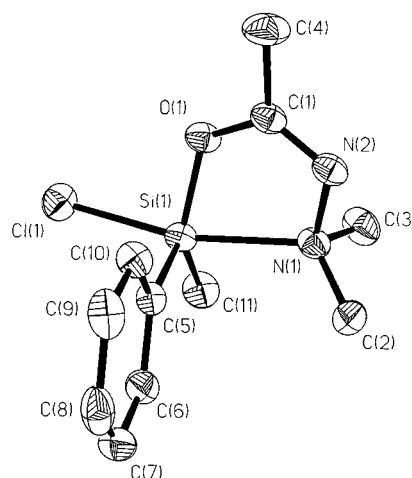


Figure 1. Crystal structure for **1**. The complete data can be found in the Supporting Information.

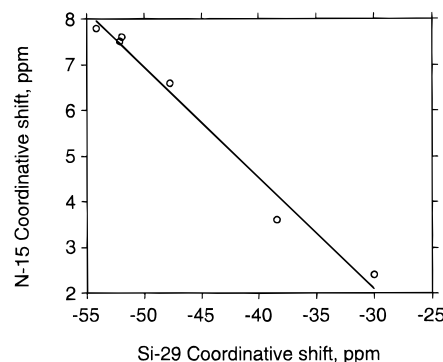


Figure 2. Linear correlation of ^{15}N and ^{29}Si coordinative chemical shifts ($\Delta(^{15}\text{N})$ vs $\Delta_1(^{29}\text{Si})$) for **1–8**.

cooling and downfield upon increase of temperature but remain within the pentacoordination range at all temperatures. For example, $\delta(^{29}\text{Si})$ for **8** changes from -33.8 ppm at 300 K to -39.0 ppm at 243 K (CD₂Cl₂) and from -34.7 to -28.2 ppm in C₆D₅NO₂ solution upon heating from 300 to 363 K.

In Table 1 are also included ^{15}N NMR chemical shifts and coordinative shifts of the dimethylamino nitrogens for several complexes. As in the ^{29}Si case, these shifts depend on the remote ligand R, although to a lesser extent. This dependence on R is also reflected in a linear correlation between ^{15}N and ^{29}Si chemical shifts (Figure 2). Since both Si and N are involved in the coordination, it is not surprising that changes in coordination affect both chemical shifts in a similar manner.

At ambient temperatures complexes **1–7** display a singlet for both *N*-methyl groups. However, upon cooling of the samples these singlets split into two singlets

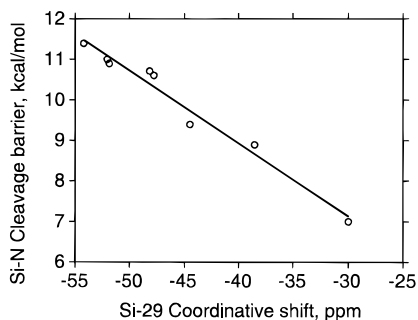


Figure 3. Linear correlation of *N*-methyl exchange barriers for **1–8** and coordinative ^{29}Si chemical shifts ($\Delta_{\text{I}}(^{29}\text{Si})$) at 300K.

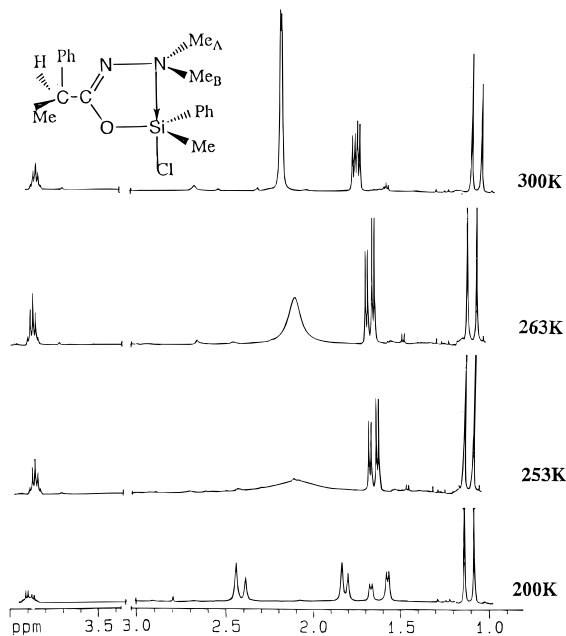


Figure 4. Variable (low)-temperature 500 MHz ^1H NMR spectra of **8** (high-field part) in CD_2Cl_2 solution.

in each case, as a result of “freezing out” of the exchange process. A linear correlation was found between the activation free energies for *N*-methyl exchange and the corresponding coordinative ^{29}Si chemical shifts (Table 1, Figure 3).

While the observation of *N*-methyl coalescence is evidence that ligand exchange takes place on the NMR time scale, no clue is provided by this experiment, for compounds **1–7**, as to the exact mechanism by which exchange is effected. For this purpose compound **8** was prepared, in which a second chiral center was introduced through the ligand.

As expected for **8**, two diastereomers are present in solution at the slow-exchange-limit temperature, due to the different relative configurations at the two chiral centers. This is evident from the doubling¹¹ of all signals in the ^1H (Figure 4), ^{13}C , and ^{29}Si NMR spectra. The equilibrium ratio of the diastereomers is 4:5. At this temperature (200 K), the *N*-methyl groups appear as four singlets. As the temperature is gradually increased, the four *N*-methyl singlets first coalesce into two singlets, while no significant changes in other signals are observed. Thus, a separate *N*-methyl interchange process is observed, while the two diastereomers are stable and do not exchange. The only plausible mechanism which can account for this obser-

vation is the exchange of *N*-methyls via Si–N bond cleavage, followed by rotation about the N–N bond and reclosure of the chelate ring, without concomitant epimerization at the silicon chiral center. Cleavage of the Si–N dative bond leaves behind a tetracoordinate silicon atom, which, under normal conditions, cannot undergo inversion of configuration. Reclosure of the Si–N bond might, in principle, occur after rotation about the Si–O bond at a different position relative to the broken bond and lead to epimerization at silicon. However, reclosure evidently takes place only apical to the chloro ligand, such that the configuration at silicon is retained.

As Table 1 and Figure 3 show, the barrier found for Si–N bond cleavage in **8** falls within the range of barriers measured for **1–7**. It is therefore concluded that, by analogy, also in **1–7** the observed barriers are due to the same process, i.e. Si–N bond cleavage. We may now interpret the linear correlation on the basis of this assignment: since the process observed by coalescence of *N*-methyl signals is Si–N cleavage, the higher barriers are the result of stronger Si–N coordination. Stronger coordination is associated with a more pentacoordinate character of the silicon complex, which, in turn, is manifested in a shift of the ^{29}Si signal to higher field.¹² Therefore, both the Si–N cleavage barriers, as well as the ^{29}Si chemical shifts, measure the degree of pentacoordination at silicon and are linearly related.

Since no pseudorotation was observed at temperatures accessible in CD_2Cl_2 solution, the high-temperature NMR spectra for **8** were measured in $\text{C}_6\text{D}_5\text{NO}_2$ solution. Increase of temperature brings about a second exchange process, in which all the signal pairs of the two diastereomers coalesce; i.e., epimerization at the silicon chiral center becomes rapid relative to the NMR time scale, resulting in the observation of a single isomer.¹³ This epimerization process, which presumably occurs by a pseudorotation reaction, is found to have a remarkably high activation barrier ($\Delta G^\ddagger = 18.7 \pm 0.2$ kcal mol⁻¹, based on the coalescence temperature of the Si–Me group; $T_c = 380 \pm 1$ K).¹⁴ Previously reported barriers for pseudorotation in N–Si pentacoordinate silicon chelates with two electronegative ligands (F, MeO, or Cl) range between 9 and 12 kcal mol⁻¹ and are comparable to those measured for acyclic silicate complexes.^{4a,d} The high barriers for exchange of *N*-methyl groups in monofunctional silanes (those with

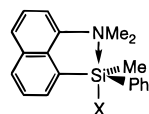
(11) Spectral assignment of the ^1H NMR spectrum of **8** in CD_2Cl_2 (Figure 4) for two diastereomers at 200 K is as follows (δ , ppm): major isomer, 1.15 (s, 3H, SiMe), 1.59 (d, 3H, C–Me, $J = 6.9$ Hz), 1.85 (s, 3H, N–Me_A), 2.46 (s, 3H, N–Me_B), 3.94 (q, 1H, CH–Me, $J = 6.9$ Hz); minor isomer, 1.09 (s, 3H, SiMe), 1.68 (d, 3H, C–Me, $J = 7.0$ Hz), 1.82 (s, 3H, N–Me_A), 2.41 (s, 3H, N–Me_B), 3.89 (q, 1H, CH–Me, $J = 7.0$ Hz).

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(13) One reviewer suggested that epimerization might actually take place at the carbon center at this temperature. We have initiated experiments aimed at a definite assignment of the epimerization process, which will be reported elsewhere. We thank the reviewer for this comment.

(14) (a) It has been shown previously that for simple coalescence cases the barriers determined at the coalescence temperature by $k_c = 2.2\Delta\nu$ are reliable: Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656. (b) Since the equilibrium constant between diastereomers is close to 1, the activation barriers for the forward and reverse reactions fall within the experimental error.

only one electronegative ligand; **9**), $\Delta G^* > 20 \text{ kcal mol}^{-1}$, were attributed to N–Si bond cleavage.^{4d,e}



9, X = Cl, F, OMe

Our results suggest that the high barrier in **8** is *not* associated with Si–N cleavage, since this process was definitely assigned at lower temperature. The higher barrier process was found to be independent of concentration within a 10-fold range and is therefore an intramolecular Si-epimerization, most likely a Berry pseudorotation. The relatively high barrier for this process in **8**, a “monofunctional” complex, may result from one of the following reasons. (a) During the Berry pseudorotation processes, the electronegative Cl ligand is forced out of the apical position and replaced by the less electronegative carbon ligand. This less stable arrangement may account for the higher barrier.¹⁵ This situation is not observed in complexes with two elec-

tronegative ligands, which can interchange between apical and equatorial positions.^{4d} (b) The second possible cause for the high barrier may be due to forcing the chelate ring into two equatorial positions, generating considerable ring strain. This step is required if complete inversion of configuration at the silicon center occurs.

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Supporting Information Available: Data for the crystallographic structure determination of **1**, including tables of structural refinement details, positional and thermal parameters, and bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

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