Mechanisms and kinetics of the elementotropic rearrangements of tetrahydro-4,4,8,8-tetramethyl-4,8-disila-*sym*-indacene

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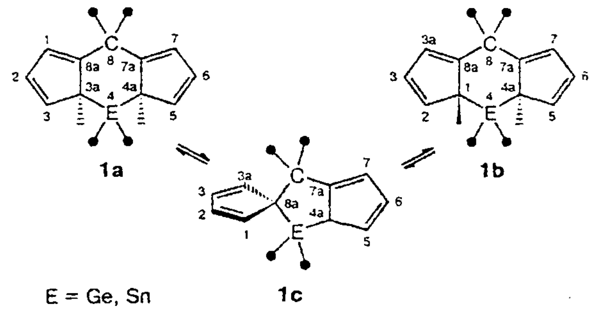
The dynamic stereochemistry of silatropic rearrangements of tetrahydro-4,4,8,8-tetramethyl-4,8-disila-*sym*-indacene (dimer of 6,6-dimethyl-6-silafulvene), which exists in solution as an equilibrium mixture of two interconverting isomers, was studied. The mechanisms and complete kinetic scheme of rearrangements were established using ^{1}H, ^{13}C, and ^{29}Si 2D quantitative EXSY NMR spectroscopy. It was found that the interconversion and degenerate rearrangements of the observed isomers proceed *via* two concurrent pathways due to the formation of different intermediates. The activation parameters of the rearrangements were determined by means of total lineshape analysis of dynamic NMR (DNMR) spectra.

Key words: dimer of 6,6-dimethyl-6-silafulvene; tetrahydro-4,4,8,8-tetramethyl-4,8-disila-*sym*-indacene; elementotropic rearrangements; mechanism; dynamic stereochemistry; activation parameters; quantitative 2D EXSY NMR spectroscopy; dynamic NMR (DNMR).

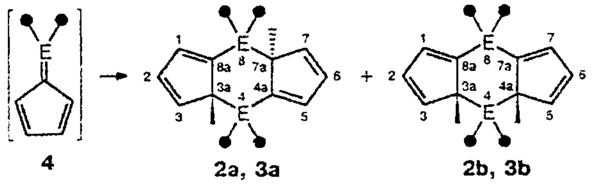
Intramolecular [1,5]-sigmatropic shifts of the organoelement groups in the η^1-cyclopentadienyl derivatives of transition and main group elements are a class of molecular dynamic processes that has been long and intensively studied.[1,2] From this viewpoint, mono-, di-, and trisubstituted cyclopentadienes and -indenes have most comprehensively been studied up to now. The dynamics of 4,8-disubstituted 3a,4,4a,8-tetrahydro-4-elementa-*sym*-indacenes[3,4] (**1**) has a specific character. The 4-sila-, -germa- and -stanna derivatives of (**1**) have been synthesized and studied in detail previously.[4] In these molecules, possible migrations of the bridging atom of the element are restricted to three sites: C(1)/(7), C(8a)/(7a), and C(3a)/(4a). In this case, the tin and germanium derivatives exist in solution as equilibrium mixtures of interconverting isomers **1a** and **1b** (Scheme 1). The use of 2D exchange ACCORDION NMR spectroscopy and a specially developed procedure for quantitative processing of the spectra[5] made it possible to reveal the mechanisms and to calculate the kinetic and thermodynamic parameters of the rearrangements of compounds **1** (E = Ge, Sn).[4,5]

Scheme 1



Much more complex elementotropic equilibria occur for tetrahydro-4,4,8,8-tetraalkyl-4,8-dielementa-*sym*-indacenes. The first representatives of this class of cyclopentadienyl compounds, tetrahydro-4,4,8,8-tetramethyl-4,8-disila-*sym*-indacene (**2**) and tetrahydro-4,4,8,8-tetraethyl-4,8-digerma-*sym*-indacene (**3**), were obtained in attempting to synthesize the corresponding 6,6-dialkyl-6-elementafulvenes (**4**).[6–9] However, compounds **4** appeared to be extremely unstable and reactive and dimerize instantly in an individual state[6–12] (Scheme 2). Nevertheless, their formation as short-lived

Scheme 2



4 **2a, 3a** **2b, 3b**

E = Si (**2**), Ge (**3**)

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intermediates was confirmed by reactions with trapping agents.[10—12]

According to the NMR data, 4,8-dielementa derivatives 2 and 3 exist in solutions as equilibrium mixtures of two interconverting isomers (similarly to compounds of type 1), differing from **1a** and **1b** in the positions of the allylic protons. In both cases, isomers **a** of the structure of 3a,4,7a,8-tetrahydro-4,4,8,8-tetraalkyl-4,8-dielementa-*sym*-indacenes with the *anti*-orientation of the H(3a) and H(7a) atoms are thermodynamically more stable than isomers **b** (3a,4,4a,8-tetrahydro-4,4,8,8-tetraalkyl-4,8-dielementa-*sym*-indacenes with the *syn*-orientation of the H(3a) and H(4a) atoms). At room temperature, the **a**/**b** ratios for compounds 2 and 3 are ~2 : 1 and 12 : 1, respectively. The structure of isolated isomer **2a** was established by X-ray analysis.[13] The variable-temperature NMR spectra of compounds 2 and 3 indicate the interconversion of isomers **a** and **b** as well as the possibility of their degenerate rearrangements. The mechanisms of these processes have not been studied in more detail because of the complexity and variety of pathways of rearrangements due to migration of two atoms of the element in two cyclopentadienyl fragments.

Recently, compounds of types 1—3 have drawn attention as potential ligands for synthesizing mononuclear and binuclear complexes of transition metals,[14—20] which are of interest as promising catalysts. Ligands analogous to compounds 1—3 and differing from them in the type of bridging group[18,19] or in the substituents in the cyclopentadienyl rings[15,20] have been synthesized. Temperature dependences of the NMR spectra of most compounds of this class indicate elementotropic tautomerism; in this case the stereochemistry of the rearrangements becomes much more complicated as the symmetry of the ligand is lowered. For example, a recently synthesized analog of compound 2 in which one methyl group is replaced by a phenyl group[19] exists (according to the NMR data) as a mixture of five interconverting stereoisomers. It should be noted that despite the efficient synthetic application of compounds of types 1—3, their dynamic stereochemistry has been studied in few works.[3—5,14] The molecular dynamics of type 2 disilicon derivatives has been investigated only in one paper[14] dedicated to studying the dynamic behavior of the monoanion 5 obtained by deprotonation of one of the cyclopentadienyl rings of 2. Of special note is the fact that the dynamic stereochemistry of 5 is in essence a simplified model of the rearrangements of 2, since [1,5]-sigmatropic shifts of the silicon atoms in compound 5 are possible only in the one cyclopentadienyl ring that does not undergo deprotonation. The knowledge of mechanisms and activation parameters of the elementotropic rearrangements in such compounds is of importance for predicting their reactivity and synthetic applications. Previously,[21] we performed a quantum-chemical study of possible pathways for rearrangements of compound 2. In this work, the results of experimental study and analysis of the 1D and 2D dynamic NMR (DNMR) spectra of this compound are presented.

Results and Discussion

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of a mixture of isomers **2a** and **2b** (see Experimental) and their relative content are in good agreement with the published data.[6—9,14] Since the assignment of the signals of the methyl groups in the ^{1}H NMR spectra and that of the signals of the cyclopentadienyl rings in the ^{13}C NMR spectra for both isomers of compound 2 is of fundamental importance for studying the mechanisms of the elementotropic rearrangements by 2D EXSY NMR spectroscopy, this question has been studied in detail. It should be noted that no assignment of the signals of the methyl groups has been performed in previous works, and the assignment of the signals of the cyclopentadienyl rings[14] is controversial.

Because the six-membered heterocycle in isomer **2a** has a chair-like conformation,[13] the high-field (at δ −0.45) and the low-field (at δ 0.41) signals in its ^{1}H NMR spectrum can be assigned to the axial and the equatorial methyl groups, respectively (analogously to the cyclohexane systems). Four signals (at δ −1.27, 0.28, 0.33, and 0.46) correspond to isomer **2b** with nonequivalent silicon atoms. The assignment of the most high-field signal (at δ −1.27) is obvious, because its high-field shift can be due to shielding effect of the cyclopentadienyl rings, which is possible only in the case when the methyl group has a pseudoaxial orientation at the silicon atom that occupies the allylic position in both rings. Other signals of the methyl groups of compound **2b** were assigned using the ^{29}Si—^{1}H 2D HETCOR NMR spectrum. The ^{1}H signal at δ −1.27 in the HETCOR spectrum is related to the low-field ^{29}Si signal (at δ 4.63), which, hence, corresponds to the diallylic silicon atom (Si(4)). The proton signal at δ 0.28, corresponding to the methyl group in the pseudo-equatorial orientation, is also related to this ^{29}Si signal. The second ^{29}Si signal of isomer **2b** (at δ −19.43), corresponding to the Si(8) atom, is related to the pair of ^{1}H signals at δ 0.33 and 0.46. Analogously to isomer **2a**, the higher and lower field signals of this pair can be assigned to the methyl groups in pseudoaxial and pseudoequatorial orientations, respectively. The assignment of the ^{29}Si signals coincides with the data[14] based on the values of the ^{29}Si chemical shifts.

The signals of the cyclopentadienyl rings in the ^{13}C NMR spectra were assigned using the additive scheme,[22,23] which predicts well chemical shifts in polyelementsubstituted cyclopentadienes and indenes.[22—24] The calculated values of chemical shifts for compounds **2a** and **2b** (see Experimental) differ slightly from their experimental values. It should be noted that our assignments differ from those reported in[14] for the signal pairs C(2)/C(6) and C(3)/C(7) for compound **2a** and C(2)/C(6) and C(3)/C(5) for compound **2b**. The assignments of the remaining signals are identical. Taking into account that the use of additive schemes gives only approximate results when assigning close signals, we can not make the unambiguous statement that our assignment is correct. At the same time, the assignment based on the values of the ^{1}H—^{1}H spin-spin coupling constants of the cyclopentadienyl protons[14] is doubtful since the values of the corresponding spin-spin coupling constants are not characteristic of polyelementa-substituted cyclopentadienes. As will be shown below, the indicated discrepancy has no effect on the interpretation of the exchange pattern in the cyclopentadienyl rings.

As was mentioned above, temperature dependences of the ^{1}H and ^{13}C NMR spectra of compound **2** (Fig. 1) have been repeatedly considered in the literature[8,9,14] at a qualitative level. They indicate a complex sequence of elementotropic rearrangements. The observed averaging of the signals of all methyl groups (Fig. 1) indicates the occurrence of rearrangement **2a** $\rightleftharpoons$ **2b**, which suggests the participation of intermediate **2c** with the five-membered silacycle (Scheme 3). At the same time, more complex mechanisms of rearrangements of **2a** and **2b** are also possible. They can involve unobservable structures **2d**, **2e**, and **2f** as intermediates (their formation from isomers **2a** and **2b** *via* the key intermediate **2c** is shown in Scheme 3). The relative energies of all isomers of compound **2** were estimated previously on the basis of the MO LCAO SCF calculations (in the INDO approximation using the Gordon parametrization) with full geometry optimization:[21]

Isomer	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
E/kJ mol^{-1}	0.0	3.4	29.4	14.7	23.1	130.5

These data allow one to exclude all processes with participation of intermediate **2f** with the four-membered silacycle from further consideration, since its relative energy is not only considerably higher than those of other isomers, but also exceeds all obtained activation barriers (Table 1).

Table 1. Activation parameters of the rearrangements of compound **2** and thermodynamic parameters of the **2a** $\rightleftharpoons$ **2b** equilibrium

Rearrangement	$\Delta H^{\ne}$ (ΔH°)	$\Delta G^{\ne}(298)$ (ΔG°)(298)	$\Delta S^{\ne}$ (ΔS°)
	/kJ mol^{-1}		/J (mol K)$^{-1}$
2a $\rightleftharpoons$ **2a´**	61.7±0.6	67.9±0.1	−21.0±1.9
2a $\rightleftharpoons$ **2b**	63.5±4.4 (1.1±0.7)	76.9±04 (2.5±0.1)	−44.9±13.8 (−4.6±2.2)
2a $\rightleftharpoons$ **2b´**	89.6±4.3	79.4±0.6	34.1±12.7
2b $\rightleftharpoons$ **2b´**	—	>105	—

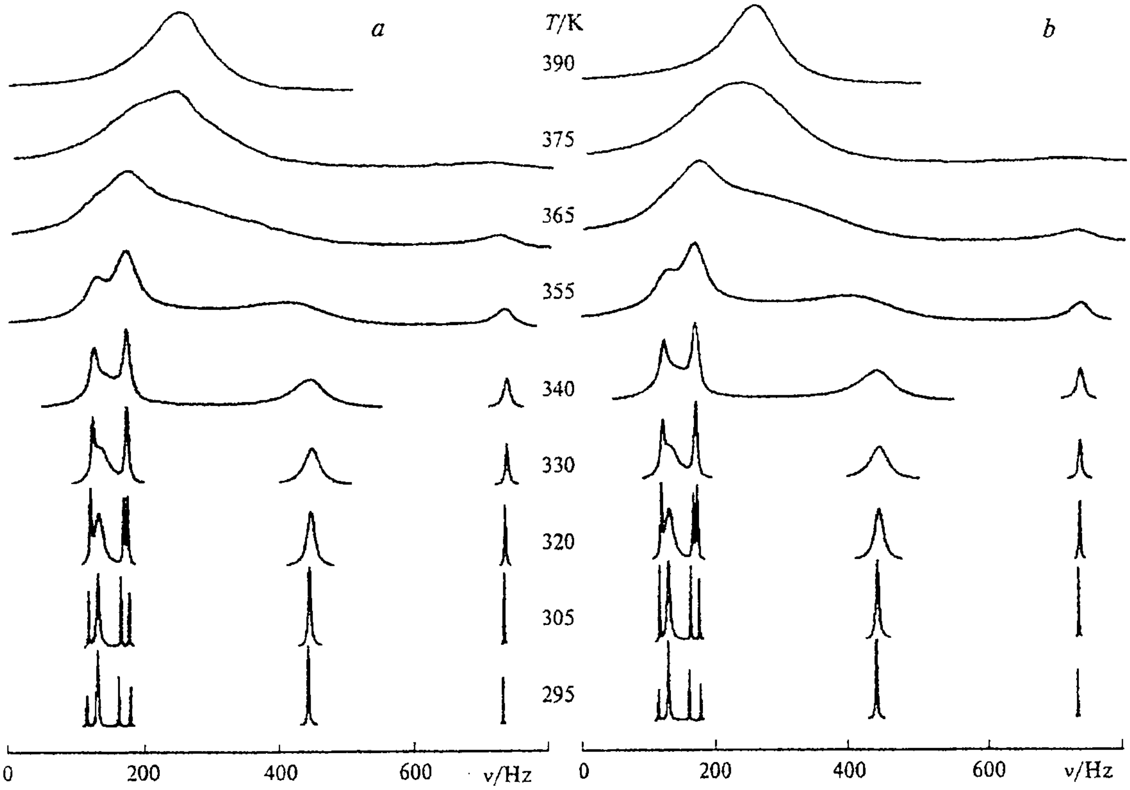
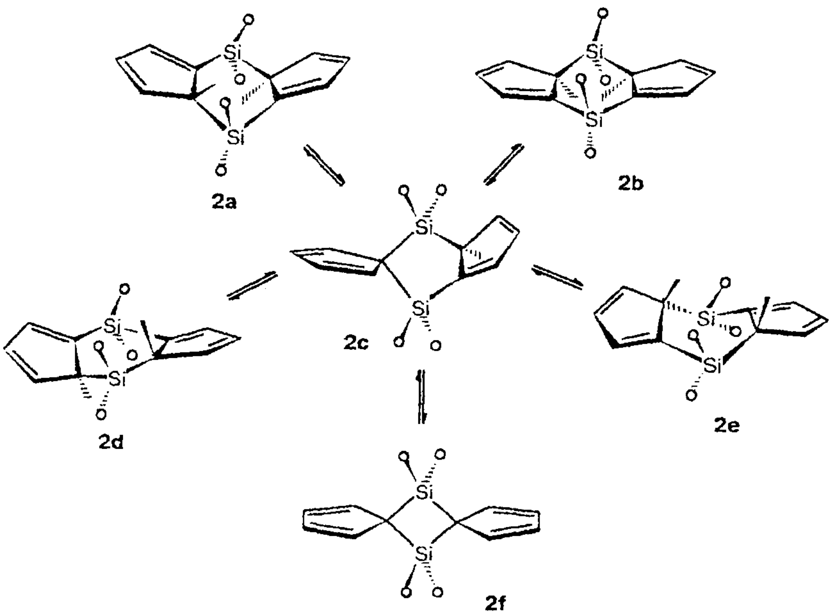


Fig. 1. ^{1}H DNMR spectra of compound **2** in the region of the signals of the methyl groups: *a* — experimental, *b* — calculated using the optimized activation and thermodynamic parameters (Table 1).

Scheme 3



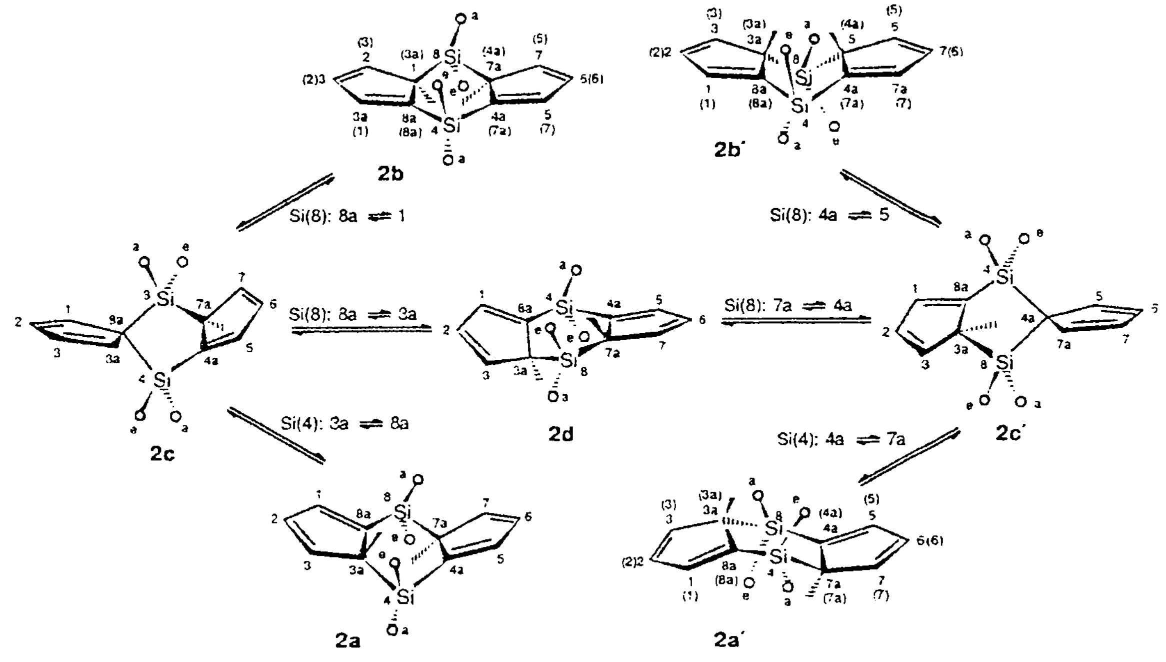
Note that as to intermediates with four-membered heterocycles, there is an analogy between compound **2** and compounds of type **1**, since (as was established previously[4]) these intermediates cannot participate in rearrangements.

The fact that broadening of the signals of the methyl groups for isomer **2a** in the regions of low and intermediate exchange is much larger than that of the corresponding signals of **2b** has attracted particular attention to detailed consideration of DNMR spectra of compound **2** (Fig. 1). This type of temperature dependence indicates a degenerate rearrangement of isomer **2a**, resulting in the exchange of its nonequivalent methyl groups. This process requires participation of one of the two intermediates, **2d** or **2e** (Schemes 4 and 5). All possible pathways of rearrangements of compound **2** with participation of intermediates **2d** and **2e** and an indication of the directions of the [1,5]-sigmatropic shifts of the silicon atoms at each stage are shown in Schemes 4 and 5. Isomer **2a** is considered as the initial point of the pathways. Numbering of the atoms and notations of the orientations of methyl groups are common for all structures and correspond to those initially labeled for **2a**. For isomers **2a'**, **2b**, and **2b'** (the end points of the pathways), notations of the atoms corresponding to nomenclature, are given in parentheses. The existence of intermediates **2d** and **2e** makes it possible to conclude that interconversion of isomers **2a** and **2b** can proceed *via* different pathways resulting in different stereochemical results (Schemes 4 and 5). If the **2a** $\rightleftharpoons$ **2b** rearrangement proceeds without participation of **2d** or **2e** (only *via* intermediate **2c**) (Schemes 3, 4, and 5), then the mutual exchange of the methyl groups of isomer **2a** in the axial orientation with those of isomer **2b** in the pseudoaxial orientation and, correspondingly, of the methyl groups of isomer **2a** in the equatorial orientation with those of isomer **2b** in the pseudoequatorial orientation, should be observed. Thus, this rearrangement can be considered as interconversion of **2a** and **2b** with retention of the spatial configuration of the six-membered silacycle. The alternative pathways of **2a** $\rightleftharpoons$ **2b'** interconversion, involving intermediates **2d** and **2e** (Schemes 4 and 5), result in the exchange of the methyl groups of **2a** in axial orientations with those of **2b** in pseudoequatorial orientations as well as in that of the methyl groups of **2a** in equatorial orientations with those of **2b** in pseudoaxial orientations. Therefore, from the viewpoint of the stereochemical result, such processes can be considered as interconversions with inversion of the six-membered cycle. The complete kinetic scheme of the dynamic processes in compound **2** can thus include any of the equilibria considered or any of their combinations.

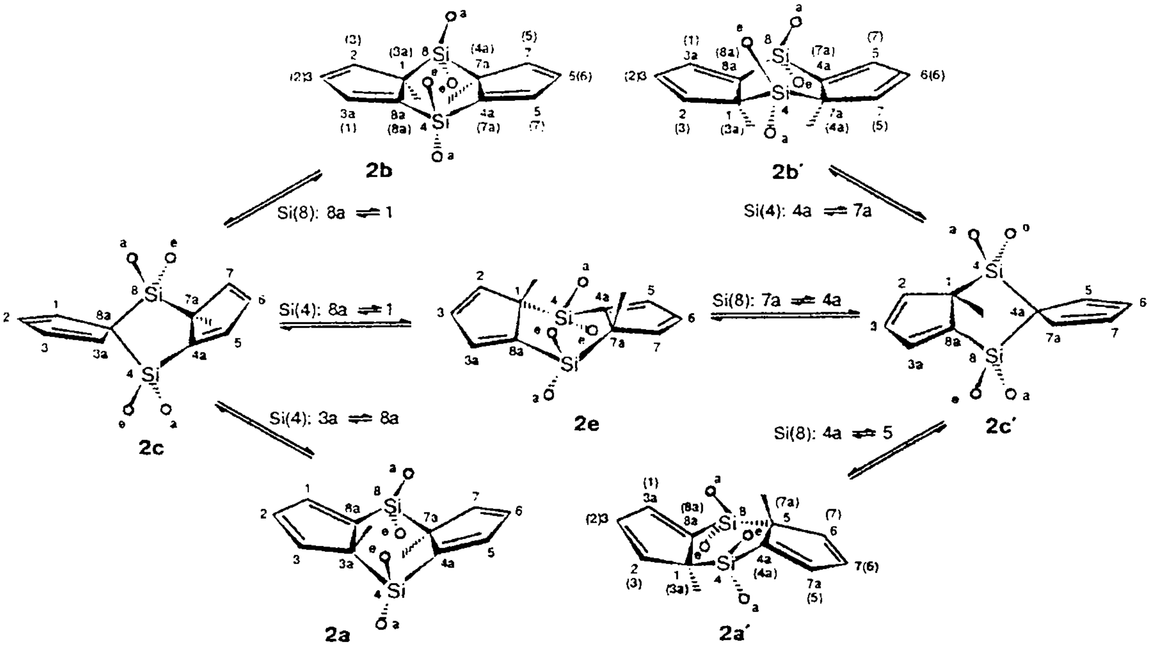
The mechanisms of rearrangements of **2** were established using quantitative 2D EXSY NMR spectroscopy.[25—28] This method makes it possible to calculate the rate constants for exchange between the magnetic environments from the measured integrated intensities of the peaks of the 2D EXSY NMR spectrum and is currently the most universal and informative approach for studying multisite chemical exchange.[26—28] Calculations were carried out using the original EXSYCALC computer program based on an algorithm described in the literature.[28]

The cross-peaks observed in the ^{1}H EXSY NMR spectrum of a mixture of isomers **2a** and **2b** in the region

Scheme 4



Scheme 5



of the signals of methyl groups (Fig. 2) indicate that exchange processes of various types occur. The most intense cross-peaks between the signals of the methyl groups of isomer **2a** confirm its degenerate rearrangement. The less intense cross-peaks observed between the signals of isomers **2a** and **2b** are evidence for their interconversion. At the same time, the intensities of the cross-peaks between the signals of the methyl groups of isomer **2b** are negligible and may be due to the transfer of magnetization as a result of a multistage process (second or higher order cross-peaks) or cross-relaxation. Processing the matrix of the integrated intensities I^{Me} of the ^{1}H EXSY NMR spectrum taking into account the vector of the relative populations of the magnetic envi-

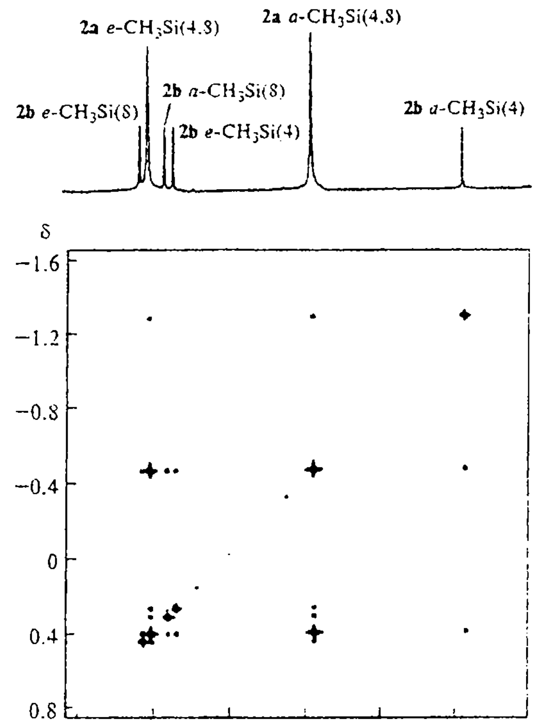


Fig. 2. ^{1}H 2D EXSY NMR spectrum of compound 2 at 25 °C in the region of the signals of the methyl groups obtained with a 1024×256 real point time domain data matrix, a relaxation delay of 4.0 s, and τ_m = 0.4 s; 16 transients for each t_1 increment were recorded.

ronments $\mathbf{P}^{\mathrm{Me}}$ using the EXSYCALC program gives the kinetic and relaxation matrix $\mathbf{L}^{\mathrm{Me}}$,

$$\mathbf{I}^{\mathrm{Me}} = \begin{bmatrix} 153.2 & 10.8 & 1.8 & 0.6 & 8.5 & 0.4 \\ 10.8 & 80.0 & 8.1 & 11.0 & 81.0 & 7.0 \\ 1.8 & 8.1 & 151.5 & 3.0 & 11.1 & 1.0 \\ 0.6 & 11.0 & 3.0 & 156.6 & 8.8 & 1.9 \\ 8.5 & 81.0 & 11.1 & 8.8 & 93.1 & 11.0 \\ 0.4 & 7.0 & 1.0 & 1.9 & 11.0 & 150.0 \end{bmatrix}; \quad \mathbf{P}^{\mathrm{Me}} = \begin{bmatrix} 0.075 \\ 0.350 \\ 0.075 \\ 0.075 \\ 0.350 \\ 0.075 \end{bmatrix};$$

$$\mathbf{L}^{\mathrm{Me}} = \begin{bmatrix} 19.05 & 0.412 & 0.025 & 0.004 & 0.188 & 0.002 \\ 0.088 & 10.70 & 0.040 & 0.088 & 4.318 & 0.028 \\ 0.025 & 0.188 & 19.02 & 0.044 & 0.397 & 0.011 \\ 0.004 & 0.409 & 0.044 & 19.10 & 0.191 & 0.026 \\ 0.040 & 4.318 & 0.085 & 0.041 & 11.40 & 0.091 \\ 0.002 & 0.131 & 0.011 & 0.026 & 0.424 & 19.00 \end{bmatrix} \pm$$

$$\pm \begin{bmatrix} - & 0.079 & 0.017 & 0.016 & 0.072 & 0.017 \\ 0.017 & - & 0.016 & 0.017 & 0.799 & 0.017 \\ 0.017 & 0.075 & - & 0.017 & 0.075 & 0.017 \\ 0.016 & 0.079 & 0.017 & - & 0.072 & 0.017 \\ 0.015 & 0.799 & 0.016 & 0.015 & - & 0.016 \\ 0.017 & 0.077 & 0.017 & 0.017 & 0.075 & - \end{bmatrix}, \qquad (1)$$

which makes it possible to quantitatively characterize the rearrangements. Note that matrices $\mathbf{I}^{\mathrm{Me}}$ and $\mathbf{L}^{\mathrm{Me}}$ are presented in the traditional mathematical form (the principal diagonal is directed from the upper left corner to the right lower corner), which corresponds to the EXSY spectrum turned 90° clockwise relative to the conventional representation. It should also be noted that the true values of the diagonal elements L_{ii} of the kinetic and relaxation matrix can not be obtained by the calculation procedure used and therefore the values of the spin-lattice relaxation times T_{1i} also can not be calculated.[28] At the same time, this approach does not result in a loss of the kinetic information contained in the off-diagonal elements $L_{ij} = k_{ji}$. For this reason, no errors for the diagonal matrix elements $\mathbf{L}^{\mathrm{Me}}$ were calculated.

An examination of matrix $\mathbf{L}^{\mathrm{Me}}$ (1) shows that the degenerate rearrangement of isomer **2a** is the fastest exchange process in the system under study and its rate constant ($k^{i}{}_{\mathbf{a}}$) is characterized by the matrix elements

$$L^{\mathrm{Me}}_{25} = L^{\mathrm{Me}}_{52} = k^{i}_{\mathbf{a}} = 4.32 \pm 0.80 \text{ s}^{-1}. \qquad (2)$$

Interconversion of isomers **2a** and **2b** is characterized by two groups of significantly differing rate constants, which confirms the above assumption that this process proceeds *via* different mechanisms. In this case, keeping in mind the above assignment of the signals of methyl groups, one can conclude that the matrix elements

$$L^{\mathrm{Me}}_{21} \cong L^{\mathrm{Me}}_{24} \cong L^{\mathrm{Me}}_{53} \cong L^{\mathrm{Me}}_{56} = 1/2k_{\mathbf{ab}} = 0.088 \pm 0.017 \text{ s}^{-1}. \qquad (3)$$

and

$$L^{\mathrm{Me}}_{12} \cong L^{\mathrm{Me}}_{42} \cong L^{\mathrm{Me}}_{35} \cong L^{\mathrm{Me}}_{65} = k_{\mathbf{ba}} = 0.411 \pm 0.077 \text{ s}^{-1} \qquad (4)$$

correspond to the rate constants for the direct and reverse interconversion of **2a** and **2b** ($k_{\mathbf{ab}}$ and $k_{\mathbf{ba}}$, respectively) with retention of the configuration of the six-membered cycle, while the matrix elements

$$L^{\mathrm{Me}}_{23} \cong L^{\mathrm{Me}}_{26} \cong L^{\mathrm{Me}}_{51} \cong L^{\mathrm{Me}}_{54} = 1/2k^{i}{}_{\mathbf{ab}} = 0.037 \pm 0.016 \text{ s}^{-1} \qquad (5)$$

and

$$L^{\mathrm{Me}}_{32} \cong L^{\mathrm{Me}}_{62} \cong L^{\mathrm{Me}}_{15} \cong L^{\mathrm{Me}}_{45} = k^{i}{}_{\mathbf{ba}} = 0.175 \pm 0.074 \text{ s}^{-1} \qquad (6)$$

characterize interconversion of **2a** and **2b** with the inversion of the configuration (the rate constants $k^{i}{}_{\mathbf{ab}}$ and $k^{i}{}_{\mathbf{ba}}$, respectively).

The calculations show that the exchange processes in isomer **2b** are characterized by rate constants whose values are close to zero within the limits of experimental error. In this case, it should be noted that it is theoretically possible for three stereochemically different degenerate rearrangements for compound **2b** to occur. Rearrangement with exchange of the pseudoaxial and pseudoequatorial methyl groups but without exchange of the nonequivalent silicon Si(4) and Si(8) atoms can proceed *via* intermediate **2d** (Scheme 4) and is characterized by the matrix elements $L^{\mathrm{Me}}{}_{13}$, and $L^{\mathrm{Me}}{}_{46}$ and those symmetric to both of them about the principal diagonal. However, the fact that the rate constant of this process differs from zero (0.025±0.017 s^{-1}) does not prove that it occurs, since the nonzero values of the corresponding matrix elements may be due to the cross-relaxation caused by the spatial closeness of the methyl

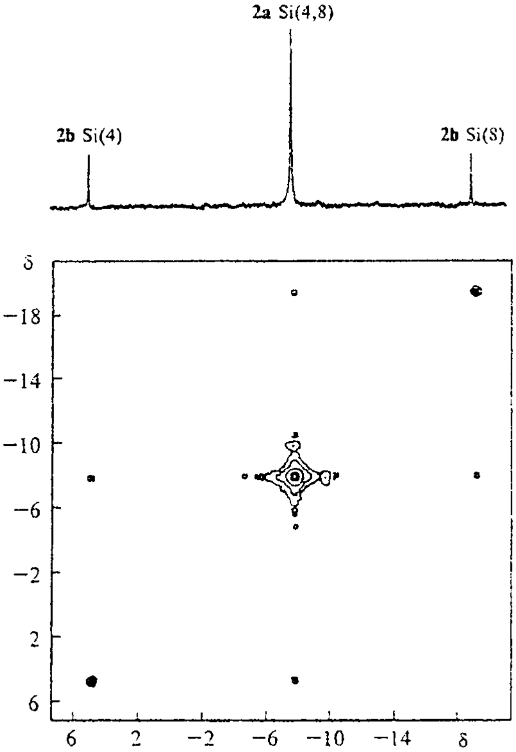


Fig. 3. ^{29}Si—{^{1}H} 2D EXSY NMR spectrum of compound 2 at 25 °C obtained with a 512×128 real point time domain data matrix, a relaxation delay of 38.0 s, and τ_m = 0.8 s; 16 transients for each t_1 increment were recorded.

groups at the same silicon atom. The second rearrangement with simultaneous exchange of the silicon atoms and the methyl groups in the pseudoaxial orientation and those in the pseudoequatorial orientation (matrix elements L^{Me}_{16} and L^{Me}_{34} and those symmetric to both of them about the principal diagonal) can proceed *via* formation of intermediate **2e** (Scheme 5). The rate constant of this process, which is characterized by the matrix element L^{Me}_{16}, is equal to zero. The relatively large value of the matrix element L^{Me}_{34} is caused by the error of integration due to the close position of the corresponding signals in the spectrum. The third rearrangement with the exchange of the silicon atoms and retention of the spatial orientation of the methyl groups can only proceed *via* the intermediate formation of isomer **2a** according to the scheme **2b** $\rightleftharpoons$ **2c** $\rightleftharpoons$ **2a** $\rightleftharpoons$ **2c** $\rightleftharpoons$ **2b′** and is therefore a second-order process. Its rate constant (matrix elements L^{Me}_{14}, and L^{Me}_{36} and those symmetric to both of them about the principal diagonal) is equal to zero within the limits of experimental error. The absence of exchange of the nonequivalent silicon atoms in isomer **2b** is additionally confirmed by the ^{29}Si 2D EXSY NMR spectrum (Fig. 3), which exhibits no cross-peaks between the signals of the silicon atoms of **2b**.

To establish the mechanisms of the rearrangements of **2** unambiguously, it is necessary to determine the relative contributions of intermediates **2d** and **2e**. A study of the exchange of the cyclopentadienyl carbon atoms provides the additional information required for this determination. Let us consider the stereochemical results of the degenerate rearrangement of isomer **2a** *via* different pathways (Schemes 4 and 5). If Scheme 4 is realized, the Si(4) atom migrates from the C(3a) atom to the C(8a) atom at the first step, and then migration of the Si(8) atom from the C(8a) atom to the C(3a) atom with the formation of intermediate **2d** occurs. Two analogous shifts in the second cyclopentadienyl fragment (C(7a)→C(4a) and C(4a)→C(7a) for the Si(8) and Si(4) atoms, respectively) transform intermediate **2d** into molecule **2a′**, in which the exchange of axial and equatorial methyl groups occurs. No exchange of the positions in the cyclopentadienyl rings occurs as a result of this rearrangement. The second pathway (Scheme 5) includes the sequence of shifts of the Si(4) atom in one cyclopentadienyl ring (from the C(3a) atom to the C(8a) atom and then from the C(8a) atom to the C(1) atom) with the formation of intermediate **2e**, followed by an analogous sequence of shifts for the Si(8) atom in the second ring (Si(8): C(7a)→C(4a)→C(5)), resulting in isomer **2a′**. As a result of this rearrangement, pairwise exchange between positions C(3a)/(7a) $\rightleftharpoons$ C(1)/(5) and C(2)/(6) $\rightleftharpoons$ C(3)/(7) in both cyclopentadienyl fragments occurs. The rate of this exchange should be equal to the rate of the exchange of the methyl groups. At the same time, positions C(8a) and C(4a) are not involved in exchange in this case. Having denoted the rate constant for exchange of the cyclopentadienyl carbon atoms with k_a^{Cp}, we can conclude that the following equality should be valid if the rearrangement proceeds according to the mechanism shown in Scheme 4

$$k_a^{Cp} = 0, \qquad (7)$$

while for Scheme 5 the following relation should be valid

$$k_a^{Cp} = k_a^{i}. \qquad (8)$$

Thus, the ratio of the rate constants for the exchange of nonequivalent methyl groups and cyclopentadienyl carbon atoms in the case of the degenerate rearrangement of **2a** makes it possible to conclude that intermediates **2d** and **2e** participate in the rearrangements of **2**.

An analogous consideration of the plausible pathways of the interconversion of isomers **2a** and **2b** (Schemes 4 and 5) shows that exchange of the cyclopentadienyl magnetic sites proceeds identically irrespective of the mechanism of interconversion (with or without inversion of the six-membered cycle) or the intermediates, **2d** or **2e**, involved in the process. In this case, the rate constants for the pairwise exchange of all cyclopentadienyl positions (k_{ab}^{Cp} and k_{ba}^{Cp}), except for C(8a)/(4a) for isomer **2a** and C(8a)/(7a) for isomer **2b**, should be equal to each other and satisfy the relations

$$k_{\mathbf{ab}}{}^{\mathrm{Cp}} = (k_{\mathbf{ab}} + k^{\mathrm{i}}{}_{\mathbf{ab}})/2, \tag{9}$$

$$k_{\mathbf{ba}}{}^{\mathrm{Cp}} = (k_{\mathbf{ba}} + k^{\mathrm{i}}{}_{\mathbf{ba}})/2. \tag{10}$$

Equations (9) and (10) provide a convenient procedure for verifying the agreement between the kinetic data on the exchange of the methyl groups and the cyclopentadienyl carbon atoms obtained in different experiments.

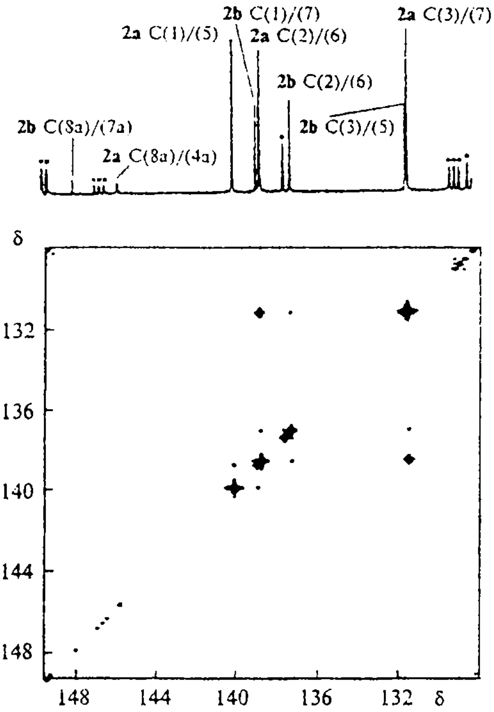


Fig. 4. ^{13}C—{^{1}H} 2D EXSY NMR spectrum of compound **2** at 25 °C in the region of the signals of the cyclopentadienyl rings obtained with a 2048×512 real point time domain data matrix, a relaxation delay of 3.8 s, and τ_m = 0.5 s; 16 transients for each t_1 increment were recorded. Signals of deuterated solvent are denoted by an asterisk.

The ^{13}C—{^{1}H} 2D EXSY NMR spectrum (Fig. 4), recorded at the same temperature (25 °C) as the ^{1}H EXSY spectrum discussed above, was used for quantitative studies of the kinetics of the exchange of cyclopentadienyl carbon atoms in **2**. As follows from the above theoretical consideration, the necessary rate constants $k_{\mathbf{a}}{}^{\mathrm{Cp}}$, $k_{\mathbf{ab}}{}^{\mathrm{Cp}}$, and $k_{\mathbf{ba}}{}^{\mathrm{Cp}}$ can be determined from the complete matrix of the exchange of the C(2)/(6) and C(3)/(7) signals of isomer **2a** and the C(2)/(6) and C(3)/(5) signals of isomer **2b**. In this case, the above-mentioned ambiguity in the assignment of the signals of pairs C(2)/C(6) and C(3)/C(7) for **2a** and C(2)/C(6) and C(3)/C(5) for **2b** can not result in an incorrect interpretation of the exchange pattern, since for all four signals pairwise exchange is possible only between each other. Using the matrix of the integrated intensities $\mathbf{I}^{\mathrm{Cp}}$ and the vector of the relative populations $\mathbf{P}^{\mathrm{Cp}}$, constructed using the experimental data (see Experimental), we calculated the kinetic and relaxation matrix $\mathbf{L}^{\mathrm{Cp}}$ for a given group of signals:

$$\mathbf{I}^{\mathrm{Cp}} = \begin{bmatrix} 135.8 & 12.6 & 12.6 & 72.5 \\ 12.6 & 79.0. & 2.6 & 12.6 \\ 12.6 & 2.6 & 79.0 & 12.6 \\ 72.5 & 12.6 & 12.6 & 135.8 \end{bmatrix}; \quad \mathbf{P}^{\mathrm{Cp}} = \begin{bmatrix} 0.35 \\ 0.15 \\ 0.15 \\ 0.35 \end{bmatrix};$$

$$\mathbf{L}^{\mathrm{Cp}} = \begin{bmatrix} 11.57 & 0.128 & 0.128 & 1.173 \\ 0.299 & 12.51 & 0.046 & 0.299 \\ 0.299 & 0.046 & 12.51 & 0.299 \\ 1.173 & 0.128 & 0.128 & 11.57 \end{bmatrix} \pm \begin{bmatrix} - & 0.173 & 0.073 & 0.156 \\ 0.171 & - & 0.120 & 0.171 \\ 0.171 & 0.120 & - & 0.171 \\ 0.156 & 0.073 & 0.073 & - \end{bmatrix} \tag{11}$$

The numerical values of its elements

$$L_{12}^{\mathrm{Cp}} = L_{13}^{\mathrm{Cp}} = L_{42}^{\mathrm{Cp}} = L_{43}^{\mathrm{Cp}} = k_{\mathbf{ab}}^{\mathrm{Cp}} = 0.13\pm0.07\ \mathrm{s}^{-1} \tag{12}$$

and

$$L_{21}^{\mathrm{Cp}} = L_{31}^{\mathrm{Cp}} = L_{24}^{\mathrm{Cp}} = L_{34}^{\mathrm{Cp}} = k_{\mathbf{ba}}^{\mathrm{Cp}} = 0.30\pm0.17\ \mathrm{s}^{-1}, \tag{13}$$

which describe the interconversion of **2a** and **2b**, are in good agreement with the values obtained from relationships (3)—(6)

$$(k_{\mathbf{ab}} + k^{\mathrm{i}}{}_{\mathbf{ab}})/2 = 0.125\ \mathrm{s}^{-1} \tag{14}$$

and

$$(k_{\mathbf{ba}} + k^{\mathrm{i}}{}_{\mathbf{ba}})/2 = 0.293\ \mathrm{s}^{-1}, \tag{15}$$

which, according to expressions (9) and (10), confirms the reliability of the obtained kinetic data.

It should be particularly emphasized that the value of the rate constant for the exchange of the cyclopentadienyl carbon atoms in isomer **2a**, $k_{\mathbf{a}}{}^{\mathrm{Cp}}$, characterized by the matrix elements

$$L_{14}^{\mathrm{Cp}} = L_{41}^{\mathrm{Cp}} = k_{\mathbf{a}}^{\mathrm{Cp}} = 1.17\pm0.16\ \mathrm{s}^{-1}, \tag{16}$$

differs significantly from both zero and the rate constant for the exchange of axial and equatorial methyl groups in this isomer, $k^{\mathrm{i}}{}_{\mathbf{a}}$ (relationship (2)). Moreover, the observed difference is so large that it can not be explained either by the error of integration or by the cross-relaxation contribution to the intensity of the cross-peaks in the ^{1}H EXSY spectrum. The obtained ratio of the rate constants $k_{\mathbf{a}}{}^{\mathrm{Cp}}$ and $k^{\mathrm{i}}{}_{\mathbf{a}}$ can only be explained by the concurrent degenerate rearrangement of isomer **2a** (Schemes 4 and 5) *via* both pathways considered above. Taking into account expressions (7) and (8), on the basis of numerical values (2) and (16) we can estimate the values of the rate constants for different pathways of the degenerate rearrangement of **2a**: *via* intermediate **2d** (k^{i}_{a}(**d**)) (see Scheme 4)

$$k^{i}_{a}(\mathbf{d}) = k^{i}_{a} - k_{a}^{Cp} = 3.15\pm0.96\ \mathrm{s}^{-1} \quad (17)$$

and *via* intermediate **2e** (k^{i}_{a}(**e**)) (see Scheme 5)

$$k^{i}_{a}(\mathbf{e}) = k_{a}^{Cp} = 1.17\pm0.16\ \mathrm{s}^{-1}. \quad (18)$$

The obtained values indicate that the pathway *via* intermediate **2d** makes the major contribution to the rate of the observed process. Thus, the results obtained unambiguously prove that both unobservable isomeric structures **2d** and **2e** participate in the rearrangements of compound 2 as intermediates.

In the framework of the established kinetic scheme we determined the activation parameters of the rearrangements of compound 2 (see Table 1) using total-lineshape analysis of the DNMR spectra in the temperature interval from −10 to +117 °C. The calculations for the signals of the methyl groups in the ^{1}H spectrum were performed using the DISPARD computer program.[29] Good agreement between the experimental and calculated spectra obtained using optimized parameters was achieved (see Fig. 1). The following exchange processes discussed above (Schemes 4 and 5) were taken into account:

1) degenerate rearrangement **2a** $\rightleftharpoons$ **2a**′;

2) interconversion **2a** $\rightleftharpoons$ **2b** with retention of the configuration of the six-membered silacycle;

3) interconversion **2a** $\rightleftharpoons$ **2b**′ with inversion of the six-membered silacycle;

4) degenerate rearrangement **2b** $\rightleftharpoons$ **2b**′ followed by pairwise exchange of pseudoaxial and pseudoequatorial methyl groups without exchange of nonequivalent silicon atoms; and

5) degenerate rearrangement **2b** $\rightleftharpoons$ **2b**′ with simultaneous exchange of the methyl groups of different orientation and the silicon atoms.

The two last processes, the presence of which was not confirmed by the 2D EXSY NMR data, were taken into account in calculations since, in principle, their manifestation at higher temperatures (according to Schemes 4 and 5) can not be ruled out. However, the results obtained show that these rearrangements make no contribution to the lineshape in the studied temperature interval due to very high activation barriers, for which we only succeeded in estimating their lower bounds (see Table 1).

As a whole, the values of the activation parameters of the rearrangements of compound 2 are in good agreement with the published data for various mono-and polysilylsubstituted cyclopentadienyl compounds.[1,2,4,14] In this case, an increase in the energy of activation of the [1,5]-sigmatropic shift of the silicon atoms over those of mono- and disilylcyclopentadienes[2] is observed for compound 2; this is due to the incorporation of the silicon atoms into the six-membered cycle. Previously, we found an analogous effect for the series of compounds **1**.[4] It is interesting to note that unlike 2, no dynamics caused by elementotropic rearrangements is observed at all for the type **1** silicon derivative.[4] This fact shows that replacement of one of the bridging $Si(CH_3)_2$ groups in molecule **2** by a $C(CH_3)_2$ group results in a sharp increase in the activation barriers to rearrangements, which is likely associated with increasing strains in the five-membered cycle in the type **1c** and **2c** intermediates and in the transition states.

In conclusion, the marked differences in the activation barriers to different rearrangements of isomers of compound **2** (Table 1) should be emphasized. They are likely due to the different energies of activation of the [1,5]-sigmatropic shifts of silicon atoms Si(4) and Si(8) to the C(1) and C(3a) sites in intermediate **2c**, which transform it into structures **2a**, **2b**, **2d**, and **2e** (Scheme 3). A more detailed explanation of this phenomenon must be based on the results of quantum-chemical calculations of transition states for each conversion, which are currently in progress.

Experimental

NMR spectra and preprocessing. The ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (79 MHz) NMR spectra were recorded on a Varian VXR-400 spectrometer in toluene-d_8 with a digital resolution of 0.1 (^{1}H) or 0.3 (^{13}C and ^{29}Si) Hz per point. Chemical shifts were measured relative to $SiMe_4$. The 2D EXSY and HETCOR spectra were recorded using standard pulse sequences. The EXSY spectra were obtained in the absolute value mode and symmetrized about the principal diagonal.

To construct the $\mathbf{I}_H$ (1) and $\mathbf{I}_C$ (11) matrices, volume integration of the signals of the 2D spectra was performed using the standard software of the spectrometer with preliminary determination of the limits of integration from the cross-sections yielding the maximum contribution to the intensities of the signals. Taking into account the closeness of the C(3)/(7) signal of **2a** and the C(3)/(5) signal of **2b** as well as of the C(2)/(6) signal of **2a** and the C(1)/(7) signal of **2b** in the ^{13}C EXSY spectrum (Fig. 4), the integrated intensities of the diagonal peaks C(2)/(6) and C(3)/(7) of **2a** were assumed to be equal to the integrated intensity of the separately located C(1)/(5) signal of this isomer, while the integrated intensities of both diagonal peaks C(2)/(6) and C(3)/(5) of **2b** were assumed to be equal to the integrated intensity of its easily integrated diagonal peak C(2)/(6). The intensities of the corresponding signals in the 1D spectrum were obtained analogously. The intensities of all cross-peaks corresponding to the interconversion of isomers **2a** and **2b** were assumed to be equal to the intensity of the separately integrated cross-peak due to exchange between C(2)/(6) of **2a** and C(2)/(6) of **2b**. The true intensity of the cross-peaks corresponding to the exchange of the C(2)/(6) and C(3)/(7) signals of **2a** was determined as the difference between the measured value corresponding to the superposition of the cross-peaks corresponding to C(2)/(6)**2a** $\rightleftharpoons$ C(3)/(7)**2a** exchange and C(2)/(6)**2a** $\rightleftharpoons$ C(3)/(5)**2b** exchange and the intensity of the cross-peaks for the C(2)/(6) signal of **2a** and the C(2)/(6) signal of **2b**. The integrated intensity of the cross-peaks for signals C(2)/(6) and C(3)/(5) of isomer **2b** was calculated analogously, by subtracting the intensity of the cross-peak between the C(2)/(6) signal of **2a** and the C(2)/(6) signal of **2b** from the measured intensity of the cross-peak between the

Table 2. Spin-lattice relaxation times (T_1) of the cyclopentadienyl ^{13}C nuclei of isomers **2**

2a		**2b**	
Atom	T_1/s	Atom	T_1/s
C(8a)/(4a)	17.9±0.7	C(8a)/(7a)	18.9±0.4
C(1)/(5)	2.6±0.2	C(1)/(7)	2.6±0.1
C(2)/(6)	2.9±0.1	C(2)/(6)	3.1±0.1
C(3)/(7)	2.9±0.1	C(3)/(5)	2.9±0.1

C(2)/(6) signal of **2b** and the C(3)/(7) signal of **2a**. The obtained value lies within the limits of the error of integration (see below). The assumptions made are valid if the exchange processes are identical and the values of the spin-lattice relaxation times T_1 are close for the magnetic environments in each of the isomers **2a** and **2b** considered when constructing matrix $\mathbf{I}_C$ (11). The fulfillment of the first condition follows from the above stereochemical analysis. The T_1 values (Table 2) measured by the "inversion—recovery" technique satisfy the second requirement.

Calculations and software. To calculate the rate constants for multisite exchange from the data of 2D EXSY NMR spectroscopy, we used the method of direct calculation of the kinetic and relaxation matrix **L** from the matrix of the integrated intensities **I** of the 2D EXSY spectrum based on the solution of the matrix equation

$$\mathbf{I} = M_0\mathbf{P}\exp(\mathbf{L}\tau_m), \tag{19}$$

where **P** is the column-vector of the relative populations of the exchanging magnetic environments p_i, determined by integrating the 1D spectrum; M_0 is the total magnetization of nuclear spins of the system; τ_m is the mixing time.[28] The elements of matrix **L** in the absence of cross-relaxation are defined by the expressions:

$$L_{ij} = k_{ji},\ i \neq j,$$

$$L_{ii} = -1/T_{1i} - \sum_{j \neq i} k_{ij}, \tag{20}$$

where k_{ij} is the rate constant for exchange from site i to site j, and T_{1i} is the spin-lattice relaxation time at site i. Solution of Eq. (19) in the form

$$\mathbf{L} = \frac{1}{\tau_m} \cdot \ln \mathbf{B} = \frac{\mathbf{X} \cdot (\ln \mathbf{Z}) \cdot \mathbf{X}^{-1}}{\tau_m}, \tag{21}$$

where

$$\mathbf{B} = M_0 \cdot \mathbf{I} \cdot \mathbf{P}^{-1}, \tag{22}$$

Z is the diagonal matrix of eigenvalues, **X** is the matrix of eigenvectors of matrix **B**, such that

$$\mathbf{Z} = \mathbf{X}^{-1} \cdot \mathbf{B} \cdot \mathbf{X}, \tag{23}$$

gives the desired matrix **L**. Since there is no information on the M_0 value, the calculations were performed by assuming $M_0 = 1$. Such an approach results in matrix **L**'; its diagonal elements differ from the diagonal elements of the true matrix **L** by an arbitrary constant while the off-diagonal elements are identical to those of matrix **L**.[28]

The rate constants for exchange were calculated using the EXSYCALC computer program, which solves Eqs. (21)—(23) and calculates the errors of the obtained values. The program is written in TURBO PASCAL. Input data are the number of exchanging sites, the relative populations of each site, the integrated intensities of signals of the experimental EXSY spectrum, and the mixing time at which the spectrum was recorded. The Jacobi algorithm was used to diagonalize the asymmetric (in the general case) real matrix **B** (Eq. (23)). Spectral noise and error of integration were assumed to be the source of errors, and their contributions to the integrated intensity of the signal ((ΔI^N) and (δI), respectively) were taken into account when calculating errors of calculated rate constants.[28] The first contribution was estimated by repeated (15—20 values) integration of different spectral regions containing no signals, within the same limits and at the same scale as those used for integrating the signals. The largest of the obtained values was taken as the ΔI^N estimate. It is equal to 1.1 and 4.6 for the ^{1}H and ^{13}C EXSY spectra, respectively (using the same relative units as for the elements of matrices $\mathbf{I}_H$ and $\mathbf{I}_C$), and corresponds to "signal/noise" ratios of 140 and 30 for the most intense signals in each of the spectra, respectively. The error of integration was estimated by averaging the results of the individual measurements of the volume integrals for each signal for small variations of the limits of integration; it is equal to 2% and 3% for the ^{1}H and ^{13}C EXSY NMR spectra, respectively. The total error of measuring the integrated intensity of the signal I_{ij} (ΔI_{ij}) was determined from the expression

$$\Delta I_{ij} = \Delta I^N + \delta I \cdot I_{ij}. \tag{24}$$

The errors of the linearly independent rate constants (k_{ij}, where i = 1,..,n − 1; j = i + 1,..,n) were calculated from the equation

$$\sigma\mathbf{K} = \mathbf{D} \cdot \Delta\mathbf{I}^2 \cdot \mathbf{D}^T, \tag{25}$$

where $\sigma\mathbf{K}$ is the dispersion-covariance matrix of independent rate constants whose diagonal elements are equal to Δk^2_{ij}, $\Delta\mathbf{I}^2$ is the diagonal matrix of squares of deviations of the independent integrated intensities ΔI^2_{ij} (i = 1,..,n; j = i,..,n), **D** is the matrix of partial derivatives of all independent rate constants with respect to all independent integrated intensities, and $\mathbf{D}^T$ is the transpose of matrix **D**.[27,28] The errors for the rest of the rate constants were determined from the relationships

$$p_i \cdot \Delta k_{ij} = p_j \cdot \Delta k_{ji}. \tag{26}$$

Total-lineshape analysis of the DNMR spectra was performed by the DISPARD program, which works according to an algorithm of the direct search of the activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$) and thermodynamic parameters of the **2a** $\rightleftharpoons$ **2b** equilibrium (ΔH°, ΔS°, ΔG°) and makes it possible to simultaneously optimize all parameters using the temperature-dependent spectra taken altogether.[29] Temperature dependences of the chemical shifts and the spectral line widths in the absence of exchange were preliminarily approximated by quadratic functions in the temperature interval from −60 to −5 °C. The dependences obtained were extrapolated to the temperature range in which the search for the activation and thermodynamic parameters was performed. Eighteen temperature points were used in the calculations. The R-factor value (R) was used for determining the degree of fitting between the experimental and calculated spectra. The best R value obtained for the total number of the spectra was 0.099.

Compound 2 was synthesized according to the procedure described in Ref. 8. The obtained fraction (b.p. 110—115 °C (0.1 Torr)) was isolated by recrystallization from pentane.

^{1}H NMR (toluene-d_8, 25 °C, δ), **2a**: −0.45 (s, 6 H, *a*-CH_3Si), 0.41 (s, 6 H, *e*-CH_3Si), 3.42 (unresolved multiplet, 2 H, H—C(3a)/(7a)), 6.5—6.8 (several unresolved multiplets, 6 H, H—Cp); **2b**: −1.27 (s, 3 H, *a*-$CH_3Si(4)$), 0.28 (s, 3 H, *e*-$CH_3Si(4)$), 0.33 (s, 3 H, *a*-$CH_3Si(8)$), 0.46 (s, 3 H, *e*-$CH_3Si(8)$), 3.55 (unresolved multiplet, 2 H, H—C(3a)/(4a)), 6.5—6.8 (several unresolved multiplets, 6 H, H—Cp); ^{13}C—{^{1}H} **2a**: −6.94, −2.93 (CH_3), 57.38 (C(3a)/(7a)), 131.18 (C(3)/(7)), 138.53 (C(2)/(6)), 139.85 (C(1)/(5)), 145.52 (C(8a)/(4a)); **2b**: −15.39, −5.31, 0.43, 1.00 (CH_3), 55.55 (C(3a)/(4a)), 131.27 (C(3)/(5)), 137.04 (C(2)/(6)), 138.71 (C(1)/(7)), 147.73 (C(8a)/(7a)); ^{29}Si—{^{1}H} **2a**: −8.00; **2b**: −19.43 (Si(8)), 4.63 (Si(4)).

The ^{13}C(Cp) chemical shifts calculated according to the additive scheme:[22,23] 56.4 (C(3a)), 134.7 (C(3)), 136.9 (C(2)), 141.2 (C(1)), and 148.6 (C(8a)).

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