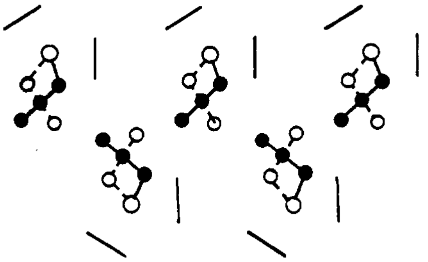
Organometallics 1991, *10*, 3739–3745

Chart II



molecules (a sort of clicking wave which propagates along the *a* axis as shown in Chart II[17]). This observation may be taken as indicating that a substantial lattice modification, perhaps an order–disorder phase transition above 300 K, is necessary to allow diene topomerization in 3.

The occurrence of order–disorder phase transitions seems to be a general feature of crystals made of structurally nonrigid neutral organometallic molecules. Besides those known to occur for ferrocene,[1f] transitions to plastic phases have been observed, for instance, in crystalline formylferrocene[14] and acetylferrocene[15] and in $(C_4H_4S)Cr(CO)_3$,[16] while the onset of reorientational motion of the arene fragments has been invoked to explain the behavior observed by ^{1}H spin–lattice NMR spectroscopy in crystalline $(1,2,3\text{-}C_6H_3Me_3)Cr(CO)_3$ and $(1,2,4,5\text{-}C_6H_2Me_4)Cr(CO)_3$.[1d]

Along this line of thinking, one may wish to speculate on the possibility of "predicting" the occurrence of phase transitions (or other lattice modifications) from a knowledge of the molecular assembly in the lattice and of the internal degrees of freedom of the molecules under investigation. It seems that crystals containing structurally nonrigid organometallic molecules are very likely to undergo *intermolecular* rearrangements as a function of the temperature. An increase in temperature (and the consequence loss of lattice cohesion) will tend to increase the motional freedom of the molecular fragments, particularly along low-energy intramolecular rearrangement pathways, up to a point beyond which the intramolecular modification will be able to "propagate" through the lattice, becoming an intermolecular rearrangement. The intermolecular pathways for processes of this kind can be seen as the result of the *combination* of lattice periodicity with intramolecular rearrangement pathways. On these premises, it should be clear that any hypothesis on solid-state intermolecular rearrangements and phase transition mechanisms must be based on an exact knowledge of the molecular organization in the crystal.

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[14] Daniel, M. F.; Leadbetter, A. J.; Mazid, M. A. *J. Chem. Soc., Faraday Trans. 2* 1981, *77*, 1837.

[15] Sato, K.; Katada, M.; Sano, H.; Konno, M. *Bull. Chem. Soc. Jpn.* 1984, *57*, 2361.

[16] Calvarin, G.; Berar, J. F.; Weigel, D.; Azokpota, C.; Pommier, C. *J. Solid State Chem.* 1978, *25*, 219.

[17] This simple model also necessitates that the molecules rotate slightly around their centers of mass in order to decrease the repulsive interactions between the methyl groups and the Cp ligands of next-neighboring molecules.

Synthesis, Structure, and Fluxional Behavior of 4-Sila-, 4-Germa-, and 4-Stanna-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacenes

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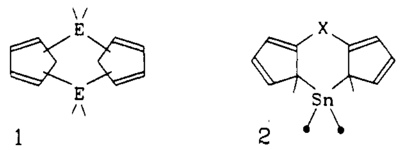
4-Elementa-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacenes were obtained as a result of interaction of dilithiated dicyclopentadienyldimethylmethane with dichlorodimethylsilane, -germane, and -stannane, and their ^{1}H and ^{13}C NMR spectra were studied in detail. Tin and germanium derivatives in solution were found to be equilibrium mixtures of syn and anti isomers with respect to the mutual orientation of their allylic hydrogens at C(3a) and C(4a). The interconversion of these isomers occurs because of the elementotropic rearrangements. The mechanism of the processes was ascertained by use of 2D ACCORDION experiments, and the kinetic parameters were determined by means of complete line-shape analyses of the dynamic NMR spectra. Prototropic rearrangements were observed for 4-sila-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacene.

Introduction

η^1-Cyclopentadienyl derivatives of the group IVA elements (Si, Ge, Sn, and Pb) are so-called fluxional compounds owing to the rapid intramolecular [1,5]-sigmatropic migration of the organometallic group over the cyclopentadienyl ring. Numerous experiments have been carried out to study such rearrangements.[1] These compounds including polymetalated cyclopentadienes have attracted recently the attention of synthetic chemists as the initial materials for the syntheses of various transition-metal derivatives of substituted cyclopentadienes.[2] Compounds

Scheme I



1 2

E = Si; Ge

X = CH_2; CMe_2; $SiMe_2$

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[1] Jutzi, P. *Chem. Rev.* 1986, *86*, 983.

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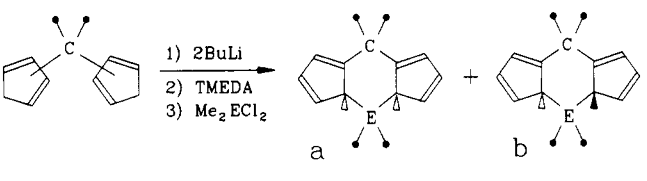
Table I. ^{13}C NMR Chemical Shifts for Compounds 3–6

	compound, δ, ppm					
carbon atom	**3a**	**4a**	**4b**	**5a**	**5b**	**6**
C(4a), C(3a)	49.57	49.37	50.58	50.48	53.78	49.99, 135.21
C(7a), C(8a)	160.22	161.38	163.27	161.33	162.45	155.94, 168.56
C(7), C(1)	122.55	121.62	122.12	119.92	119.68	122.82, 133.05
C(6), C(2)	129.55	127.93	128.48	123.39	123.84	129.66, 139.71
C(5), C(3)	130.14	130.06	130.56	127.66	128.60	130.69, 43.39
C(8)	39.73	39.55	39.33	38.91	39.04	39.21
CH_3(C)	33.49, 25.74	32.89, 26.07	30.60	31.48, 26.76	30.37	32.52, 27.22
CH_3(E)	−0.47, −14.70	0.09, −15.20	−3.19	−4.53, −19.61	−7.79	−1.15, −5.80

Scheme II



E = Si(3); Ge(4); Sn(5)

possessing the skeleton of 3a,4,4a,8-tetrahydro-*s*-indacene, with at least one of the bridges being a non-transition-metal atom, reveal both new synthetic opportunities and a particular kind of the dynamic behavior. Dimers of sila- and germafulvenes (**1**) were the first substances of this type reported[3-5] (Scheme I).

We were the first to isolate a series of 4-elementa-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacenes (**2**).[6] Since the NMR spectra of compounds **1** and **2** are temperature dependent, we concluded that metallotropic intramolecular rearrangements take place. Here we present a detailed study on the dynamic behavior of such *ansa*-dicyclopentadienyl derivatives of Si, Ge, and Sn.

Results and Discussion

The 4-elementa-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacenes (**3**–**5**) were obtained from dicyclopentadienyldimethylmethane by successive treatment with butyllithium, leading to the corresponding dilithium salt, and with Me_2ECl_2 (E = Si, Ge, Sn) in THF (Scheme II).

The yields of **3**–**5** were 50–70%. We have found 2 equiv of tetramethylethylenediamine (TMEDA) to increase significantly the yield of the products. The tin derivative was prepared earlier[6] without TMEDA and the yield reported was 25–30%. The influence of TMEDA on the yield of the products seems to be due to the strong solvation of Li^+ cation. This brings about an increase in the nucleophilic ability of the dilithiated dicyclopentadienyldimethylmethane.

Compounds **3**–**5** are colorless crystalline solids stable in an inert atmosphere but easily decomposed when exposed to air and moisture.

One might expect compounds **3**–**5** to give rise to different isomers with various size of the cycle, conformations, and stereochemical characteristics as a result of proto- and metallotropic rearrangements. But we have isolated the compound **3** as a single isomer **3a**. Its two allylic hydrogens at C(3a) and C(4a) are mutually syn oriented, methyl groups at carbon and silicon bridges being nonequivalent in pairs (for ^1H and ^{13}C NMR spectral data see the Experimental Section and Table I). The NMR spectra of the compound **4** indicate the formation of two isomers in the molar ratio 11:1. The dominant isomer **4a** has a structure analogous to that of **3a**. The minor isomer **4b** has the equivalent methyl groups at the bridging C and Ge atoms. It has a structure with allylic protons at C(3a) and C(4a) in the anti orientation with respect to each other. The broadening and coalescence of the signals of isomers **4a** and **4b** caused by the exchange between them were observed during the temperature increase. The NMR spectra of compound **5** at room temperature are averaged, owing to fast chemical exchange. At −90 °C one can observe the signals of two isomers **5a** and −5b in the molar ratio 2:1, analogous to **4a** and **4b**, respectively. The characteristic temperature dependence of spectra is observed over the range from −90 to +20 °C.

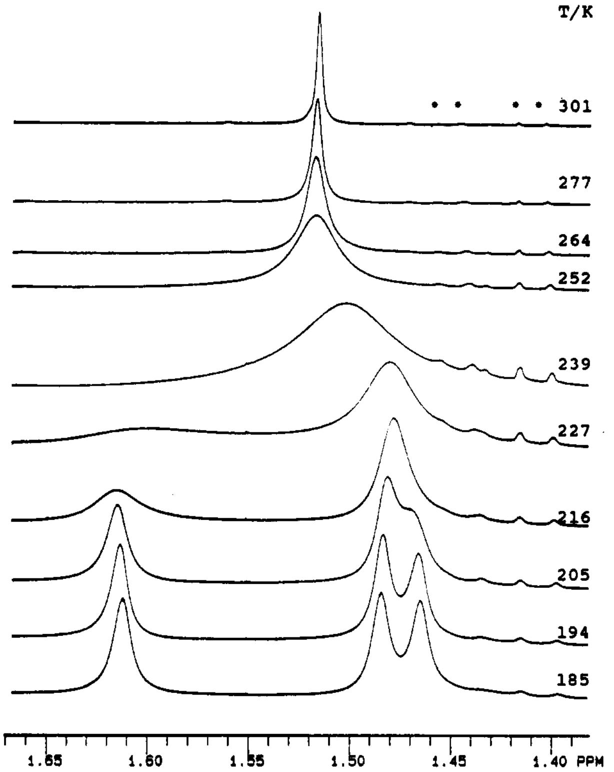


Figure 1. ^1H DNMR (400 MHz, THF-d_8) spectra of **5** for $(CH_3)_2C$ resonances. The signals of small impurities are marked by an asterisk.

It is evident from the data presented above that the content of the minor isomer **b** increases in the series **3**–**5** as 0%, 8%, and 33%. This phenomenon can be explained in general by taking into account the increase of the angular tension in **a** isomers with elongation of the E–C bonds on one hand and at the same time the relative stabilization of the twisted **b** isomers on the other.

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(2) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982.

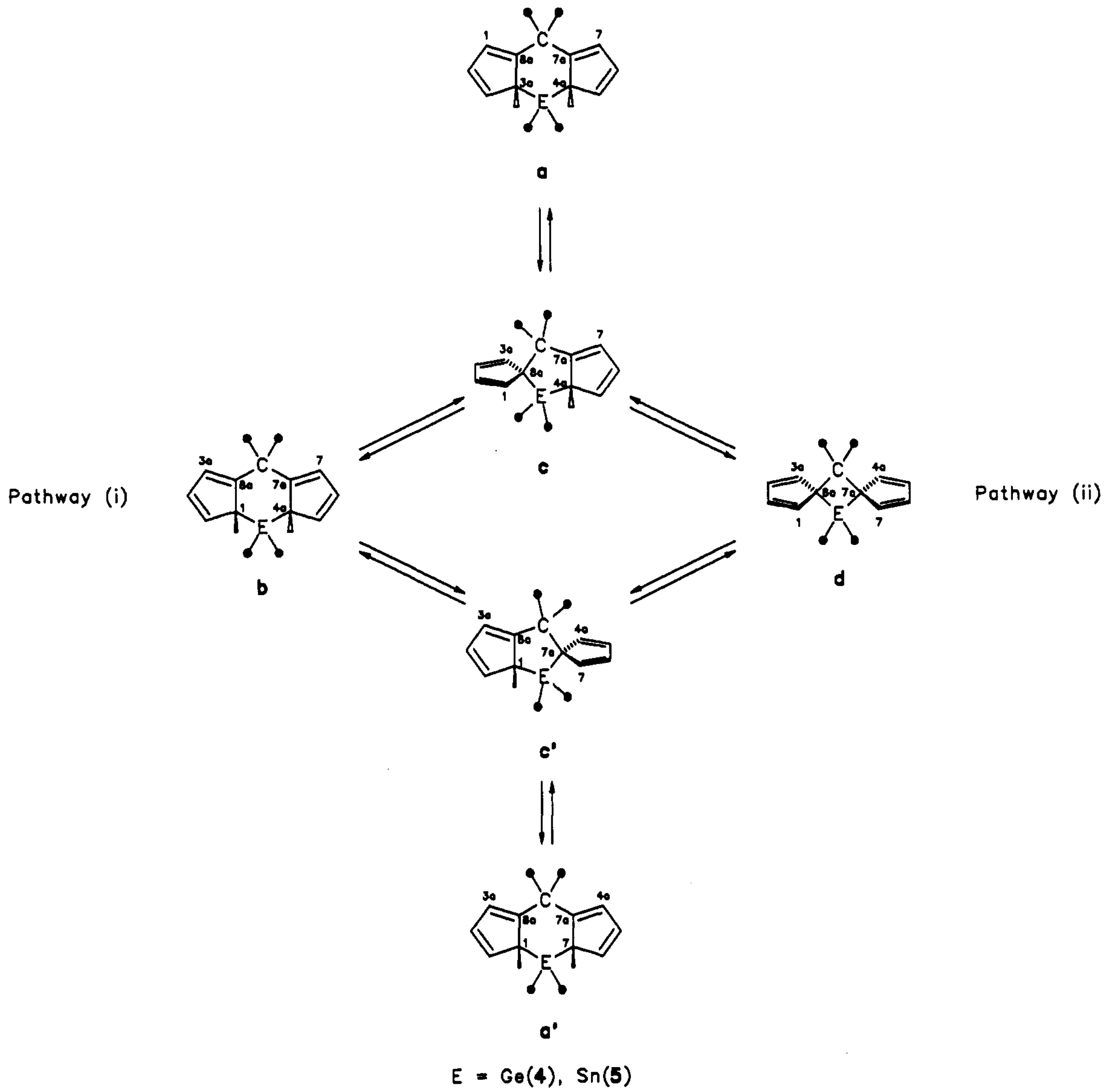
(3) Barton, T. J.; Burns, G. T.; Arnold, E. W.; Clardy, J. *Tetrahedron Lett.* **1982**, *22*, 7.

(4) Beletskaya, I. P.; Belsky, V. K.; Zemlyansky, N. N.; Borisova, I. V.; Kolosova, N. D. *Izv. Akad. Nauk UzSSR, Ser. Khim.* **1981**, 1184.

(5) Beletskaya, I. P.; Ustynyuk, Yu. A.; Zemlyansky, N. N.; Borisova, I. V.; Luzikov, Yu. N.; Kolosova, N. D. *Izv. Akad. Nauk UzSSR, Ser. Khim.* **1980**, 2668.

(6) Nifant'ev, I. E.; Shestakova, A. K.; Lemenovskii, D. A.; Slovokhotov, Yu. L.; Struchkov, Yu. T. *Metalloorg. Khim.* **1991**, *4*, 292.

Scheme III



The temperature dependence of the NMR spectra of the compounds **4** and **5** (see, for example, Figure 1) suggests the existence of elementotropic rearrangements leading to the interconversion of isomers **a** and **b**. It is accompanied by averaging of the signals of the nonequivalent methyl groups in the **a** isomers as a result of six-membered cycle inversion.

One can imagine two different pathways for such rearrangements (see Scheme III).

The first pathway (i) comprises two consecutive [1,5] shifts of the element's atom over one of the η^1-cyclopentadienyl rings and results in the formation of the intermediate **c** with a five-membered elementa-cycle after the first step and the minor isomer **b** after the second one. Two analogous shifts over the other η^1-cyclopentadienyl ring take place after that via the intermediate **c**′, which is structurally identical with **c**. Thus, if pathway i takes place, the minor isomer **b** turns out to be a necessary intermediate in the process leading to the averaging of the nonequivalent methyl groups in the dominant isomer **a**.

The second pathway (ii) supposes that two consecutive [1,5] shifts of the element atom take place step by step in both of the η^1-cyclopentadienyl rings. A four-membered cycle possessing intermediate **d** with a mirror symmetry plane arises in this case and methyl groups become equivalent in their pairs. If we assume the latter mechanism (ii) to be the actual one, then the interconversion between **a** and **b** and the averaging of the signals of the nonequivalent methyl groups in **a** must be considered as two independent processes.

The kinetic scheme of a multisite exchange can be revealed by means of NOESY spectroscopy[7] from the analysis of the cross-peaks' integral intensities plotted against the mixing time τ_m in the NOESY pulse sequence (see Experimental Section). This technique, however, has the limitations imposed by the relatively low sensitivity, especially in case of exchange between the less populated sites. The modified NOESY-ACCORDION technique[8] is much more sensitive. Initially it was proposed to calculate the chemical exchange matrix from the characteristic 2D signal shape analysis. But it might also be useful for pure qualitative purposes, especially because of the possibility of obtaining more intense cross-peaks than by the usual NOESY technique. The intensity ratio of the cross- and

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[7] Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

[8] Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, 1987; p 490.

Table II. Activation and Thermodynamic Parameters for Interconversions 4a ⇄ 4b and 5a ⇄ 5b

compd	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/(mol K)	$\Delta G^{\ddagger}_{298}$, kJ/mol	ΔH°, kJ/mol	ΔS°, J/(mol K)	ΔG°_{298}, kJ/mol
4	47.79 ± 1.96	-86.0 ± 5.7	73.42 ± 0.24	7.09 ± 1.94	8.9 ± 5.7	4.43 ± 0.24
5	42.98 ± 0.86	-21.5 ± 4.0	49.38 ± 0.25	3.62 ± 0.17	11.3 ± 0.6	0.25 ± 0.02

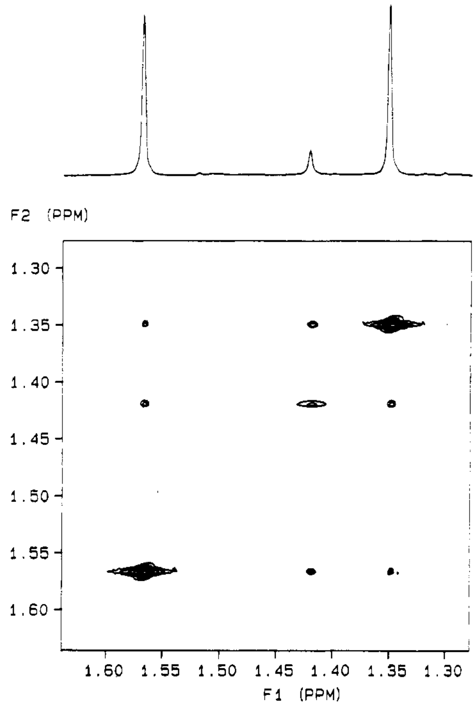

Figure 2. Contour plot of the ^{1}H 2D ACCORDION spectrum (400 MHz, toluene-d_8, 30 °C) of 4 in the $(CH_3)_2C$ region obtained with a 128 × 512 point time domain ($t_1 \times t_2$) data matrix zero-filled in the t_1 dimension to 512 before double-Fourier transformation. Sixteen transients for each t_1 increment and a 2-s delay between repetitions of the pulse sequence were used. The κ parameter (see the Experimental Section) was chosen to be 8, which corresponds to a variation of τ_m from 0 to 2.6 s. The 1D spectrum is shown along the upper edge of the contour plot.

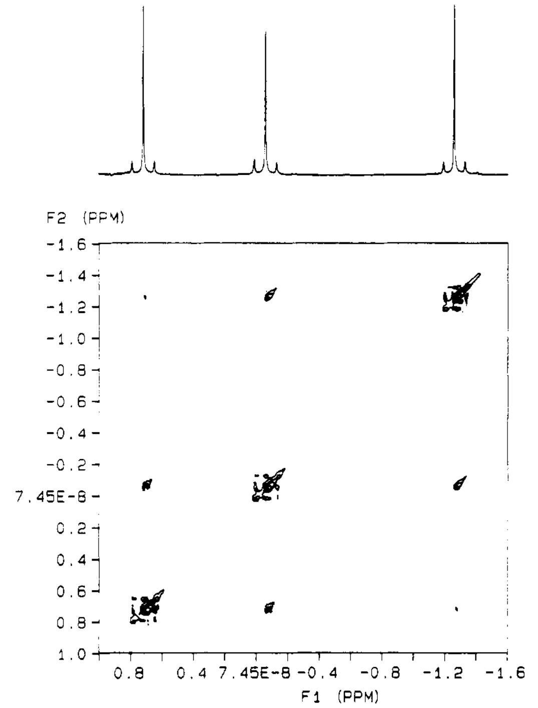

Figure 3. Contour plot of the ^{1}H 2D ACCORDION spectrum (400 MHz, THF-d_8, -90 °C) of 5 in the $(CH_3)_2Sn$ region obtained with a 256 × 1024 point time domain ($t_1 \times t_2$) data matrix zero-filled in the t_1 dimension to 1024 before double-Fourier transformation. Sixteen transients for each t_1 increment and a 1.3-s delay between repetitions of the pulse sequence were used. The κ parameter (see the Experimental Section) was chosen to be 20, which corresponds to variation of τ_m from 0 to 1.8 s. The 2D spectrum is symmetrized about the main diagonal. The 1D spectrum is shown along the upper edge of the contour plot.

auto-peaks in ACCORDION spectra may be applied as a characteristic parameter for the determination of the cross-peaks' order. As was established by numerical computer modeling of ACCORDION spectra,[9] the intensity of the first-order cross-peak should not differ significantly from the intensity of the auto-peak of a less populated site taking part in exchange, while the intensities of the high-order cross-peaks are sufficiently smaller than those of respective auto-peaks.

^{1}H ACCORDION spectra of 4 in the $C(CH_3)_2$ and 5 in the $Sn(CH_3)_2$ regions are presented in Figures 2 and 3. The intensities of the cross-peaks corresponding to exchange between isomers **a** and **b** do not differ substantially from those of the auto-peak of minor isomer, which are characteristic of the first-order cross-peaks. The cross-peaks between two nonequivalent methyl groups of **a** are significantly smaller then their auto-peaks and should be considered as second-order cross-peaks due to a two-step magnetization transfer. This means that isomer **b** is an intermediate in the interconversion of **a** and **a′**, and we should accept the first mechanism (i) as the actual one:

$$\mathbf{a} \rightleftarrows \mathbf{b} \rightleftarrows \mathbf{a}'$$

Having assumed this mechanism, the activation parameters of the rearrangements in 4 and 5 were calculated by means of the complete line-shape analysis of the ^{1}H DNMR spectra in the $C(CH_3)_2$ region (see Figure 1). The data obtained were processed by the computer program DISPARD (see the Experimental Section) for simultaneous optimization of both activation ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$) and thermodynamic (ΔH°, ΔS°, ΔG°) parameters.[10] The results are presented in Table II.

Scheme IV

3 6

The temperature dependence of the silicon derivative 3 NMR spectra is not observed in the range up to 100 °C, and this indicates the absence of any fast elementotropic shifts. A slight broadening of the signal is evident only at 100 °C. Nevertheless, at 80–100 °C one can observe a slow prototropic rearrangement in one of the cyclopentadienyl rings of 3 transforming it into 6 (Scheme IV).

Besides 6, there are several minor isomers occurring, but their entire content in the reaction mixture does not exceed 5%. The formation of 6 is reversible, and all the experiments result in an equilibrium mixture of 3 and 6 in the

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(9) Yarnykh, V. L.; Ustynyuk, Yu. A., manuscript in preparation.

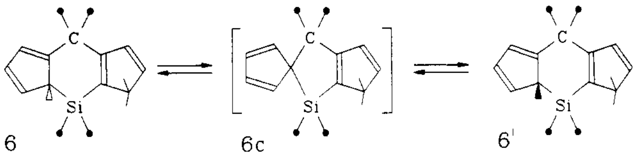
(10) Mstislavsky, V. I.; Sergeev, N. M. *Magn. Reson. Chem.*, in press.

Table III. Direct Spin-Coupling Constants ^{13}C–^{13}C for Compounds 3 and 6

carbon–carbon bond	compd, $^1J(^{13}C-^{13}C)$, Hz	
	3	**6**
C(4a)–C(7a), C(3a)–C(8a)	35.7	34.5, 52.5
C(4a)–C(5), C(3a)–C(3)	38.2	39.4, 32.4
C(7a)–C(7), C(8a)–C(1)	66.4	66.2, 47.7
C(7a)–C(8), C(8a)–C(8)	44.8	47.4, 43.8
C(7)–C(6), C(1)–C(2)	51.5	52.1, 66.7
C(6)–C(5), C(2)–C(3)	[a]	[a] 37.5
C(8)–CH_3	35.6, 36.0	33.3, 33.9

[a] Cannot be measured because of the signals are closely spased.

Scheme V



molar ratio of 3:2, approximately. The isomer **6** always occurs as a byproduct in the synthesis of **3**, but **3** can be easily separated from **6** by recrystallization.

The fact that **6** is the product of a proton shift in one of the cyclopentadienyl rings of **3** was ascertained by a NMR study of the equlibrium mixture of **3** and **6**. There are two signals in the ^1H NMR spectrum of **6** in the range of the allylic protons with intensities ratio 1:2, namely, an unresolved multiplet at 3.50 ppm and a multiplet centered at 2.81 ppm, representing the AB part of an ABXY spin system with a characteristic spin-coupling constant J_{AB} equal to 23.8 Hz and with small constants J_{AX}, J_{AY}, J_{BX}, and J_{BY} equal to 1.2–1.5 Hz. This spectral pattern is quite unambiguous and corresponds to the SiCH fragment in one of the cyclopentadienyl rings in **6** and to the CH_2 fragment, characterized by a large geminal spin coupling constant, in the other. The ^{13}C NMR spectrum of **6** (see Table I) corroborates the nonequivalence of the cyclopentadienyl rings. The localization of the CH_2 fragment in **6** as well as the assignment of the ^{13}C NMR signals for both **3** and **6** was performed by the elucidation of the C–C-connectivity on the basis of a measurement of direct ^{13}C–^{13}C coupling constants. The $^1J_{^{13}C-^{13}C}$ values for **3** and **6** measured by the ^{13}C NMR INADEQUATE technique (see the Experimental Section) are listed in Table III. The structure proposed for **6** corresponds to the carbon–carbon bond sequence derived from the ^{13}C NMR INADEQUATE experiment. As for the minor isomers present in the equlibrium mixture of **3** and **6**, their concentration is too small to obtain any reliable information on their structure. One can suggest only that they are the products of consecutive proton shifts in **6**.

In contrast to **3**, the ^1H NMR spectrum of **6** undergoes pronounced changes when the temperature increases. There are the averaging of the signals of the pseudoequatorial and pseudoaxial methyl groups on the one hand and of allylic proton at C(4a) and vinylic proton at C(7) on the other. At the same time the multiplet of the CH_2 fragment collapses, owing to the exchange between unequivalent protons at C(3), but does not shift. It is obvious that the only mechanism consistent with the observed dynamic behavior is the combination of two consecutive [1,5] shifts of the silicon atom over the ring not subjected previously to the prototropic rearrangement (Scheme V).

Since compound **6** occurs in an equilibrium mixture with **3**, it is interesting to elucidate the complete chemical exchange network in this system. In order to do that the ^1H NMR NOESY spectrum of the mixture of **3** and **6** in the $C(CH_3)_2$ region (see Figure 4) was obtained. The cross-peaks are observed for the signals of the nonequivalent methyl groups of **6** only, and they are absent between the signals of **3** and **6**, as well as between those of the nonequivalent methyl groups of **3**. These results lead to the conclusion that the rearrangement **6** ⇄ **6′** is an independent process not involving **3** and confirms the fact that there are no inner dynamics in **3**. As for the prototropic rearrangement **3** ⇄ **6**, its rate at room temperature is too small to be revealed by any NMR technique (rate constant less than 10^{-2} s^{-1}).

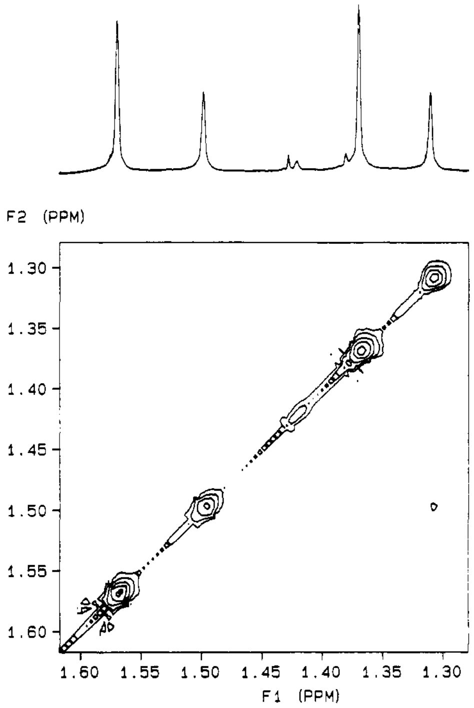


Figure 4. Contour plot of the ^1H 2D NOESY spectrum (400 MHz, toluene-d_8, 30 °C) of the equilibrium mixture of **3** and **6** in the $(CH_3)_2C$ region obtained with a 64 × 256 point time domain ($t_1 \times t_2$) data matrix zero-filled in the t_1 dimension to 256 before double-Fourier transformation. Sixteen transients for each t_1 increment, a 2-s delay between repetitions of the pulse sequence, and a mixing time τ_m = 0.2 s were used. The 2D spectrum is symmetrized about the main diagonal. The 1D spectrum is shown along the upper edge of the contour plot.

The independence of the dynamic behavior of **6** provides us with the possibility to determine the activation parameters of the rearrangement **6** ⇄ **6′** using ^1H DNMR spectra for the methyl resonances in the framework of a simple two-site exchange model. Since in the fast and medium exchange regions (more than 100 °C) the rearrangement **3** ⇄ **6** makes a significant contribution to the spectral pattern, we treated the DNMR spectra within the interval of a slow exchange (from −10 to 90 °C). The activation parameters were estimated by using the magnitudes of the exchange broadening for the signals of the methyl groups at the bridging Si atom (see the Experimental Section). The following values were obtained: $\Delta H^\ddagger = 64.7 \pm 1.8$ kJ/mol; $\Delta S^\ddagger = -32.2 \pm 2.3$ J/(mol K); $\Delta G^\ddagger(298) = 74.3 \pm 1.2$ kJ/mol.

We believe, that the distinct difference of the rates of exchange in **3** and **6** is caused by the different energies of the intermediates, which take part in the rearrangements. One should expect the compounds **3a** and **3c**, which must take part in the rearrangement of **3**, as in Scheme III, to possess sila-cycles of considerable angle strain, while the five-membered sila-cycle in the intermediate **6c** (see Scheme V) seems to be nearly planar and more stable, owing to the presence of the endocyclic double bond.

It is interesting to compare the activation parameters of the rearrangements in **4**, **5**, and **6** with those in the η^1-cyclopentadienyl derivatives of Si, Ge, and Sn.[11] One can easily admit that incorporation of the element-containing group to the six-membered cycle leads to a significant increase of the magnitude of the activation barrier for [1,5] shifts in **4**–**6** relative to those in compounds $C_5H_5EMe_3$ (E = Si, Ge, and Sn; $\Delta G^{\ddagger}(300)$ = 63.6, 56.1, and 29.7 kJ/mol, respectively[11]). There are steric limitations in both the transition states and the **c** intermediates participating in the rearrangements, which seems to be a reason for such an increase; electronic effects of the substituent both by element atom and by cyclopentadienyl ring influence only weaken activation parameters of this type.[1,11] The negative values of activation entropy of the rearrangements observed in the present work appear to be typical for the elementotropic rearrangements of all the group IVA element substituted cyclopentadienes (for instance, $\Delta S^{\ddagger}$ = −39, −66, and −13 J/(mol K) in $C_5H_5EMe_3$, E = Si, Ge, and Sn, respectively[11]). This may arise because of the decrease in the number of degrees of freedom in the transition states relative to the initial molecules (e.g., due to the increase of the rigidity of the transition states). The latter can be clearified, if one takes into account the fact that the rearrangements of **4**–**6** take place via the five-membered elementacycle containing the **c** intermediate with the more rigid and hindered structure. This makes the **c** intermediate and the transition state rather similar, the energy of intermediate being higher than that of the initial molecules.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of argon by means of conventional Schlenk techniques. Hexane was distilled from Na, THF from sodium benzophenone ketyl. Elemental analyses were performed in the analytical laboratory of the Moscow State University.

NMR Experiments. The NMR ^1H (400 MHz) and ^{13}C (100 MHz) spectra were recorded on a Varian VXR-400 spectrometer with digital resolution of 0.1 Hz (^1H) and 0.3 Hz (^{13}C) per point. The chemical shifts are referenced to the signals of residual protons and ^{13}C nuclei of the perdeuterated solvent. The ^{13}C INADEQUATE[12] and ^1H NOESY[7] NMR spectra were obtained by using the standard pulse sequences. The $J_{C\text{-}C}$ parameter value for the ^{13}C INADEQUATE (the average expected value of $^1J_{^{13}C\text{-}^{13}C}$ in the compound under investigation) was taken as 50 Hz. The pulse sequence ACCORDION[8]

$$90°\text{-}t_1\text{-}90°\text{-}\tau_m\text{-}90°\text{-}t_2$$

differing from the standard NOESY technique by the possibility of incrementing the mixing time $\tau_m = \kappa t_1$ was implemented in the present work. All the 2D NMR spectra were registered by using phase-sensitive techniques and are presented in the pure absorption mode. The temperature measurements in the DNMR experiments were performed with a precision of ±1 K and a temperature stabilization accuracy of ±0.5 K, using the temperature controller of the spectrometer calibrated with respect to standard samples of methanol and ethylene glycol.

DNMR Computations. The computation of both the activation and thermodynamic parameters of the equilibrium for compounds **4** and **5** was carried out on an IBM PC/AT computer on the basis of the complete line-shape analysis by the direct-search method with DISPARD[10] software. This method considers the complete series of measured spectra as the representation of the absorption function of two variables (frequency and temperature). The program DISPARD optimizes all parameters of the function simultaneously to fit the experimental and the calculated spectra. Among the parameters there are the free energies of activation $\Delta G^{\ddagger}(T_m)$ and equilibrium $\Delta G°(T_m)$ for the mean value of the temperature interval, $\Delta S^{\ddagger}$ and $\Delta S°$. For calculating enthalpies $\Delta H^{\ddagger}$ and $\Delta H°$, the expression

$$\Delta H = \Delta G(T_m) + T_m\Delta S \quad (1)$$

is used. Free energies $\Delta G^{\ddagger}(298)$ and $\Delta G°(298)$ are calculated according to the relation

$$\Delta G(T) = \Delta G(T_m) - (T - T_m)\Delta S \quad (2)$$

which is true for any temperature.

The program DISPARD also gives the possibility of optimizing the coefficients of temperature dependences of chemical shifts and relaxation-caused line widths within the second-order approach. These dependences, obtained from the series of spectra in the low-temperature region (if exchange broadening is negligibly small), were used for the line-shape analysis of the complete series of spectra.

Standard deviations for $\Delta G(T_m)$ and ΔS are determined with DISPARD by the usual procedure using a covariance matrix. Standard deviations for ΔH and $\Delta G(298)$ are obtained by using expressions 1 and 2

$$\sigma_{\Delta H}{}^2 = \sigma_{\Delta G_m}{}^2 + 2T_m \operatorname{cov}(\Delta G_m, \Delta S) + T_m{}^2\sigma_{\Delta G_m}{}^2 \quad (3)$$

and

$$\sigma_{\Delta G(T)}{}^2 = \sigma_{\Delta G_m}{}^2 - 2(T - T_m)\operatorname{cov}(\Delta G_m,\Delta S) + (T - T_m)^2\sigma_{\Delta G_m}{}^2 \quad (4)$$

where $\Delta G_m = \Delta G(T_m)$. In order to obtain confidence limits (Δ) of desired values, one should use Student's factor (**t**):

$$\Delta = \sigma\mathbf{t} \quad (5)$$

for number of degrees of freedom along the T axis (n)

$$n = N_T - n_a \quad (6)$$

where N_T is the number of temperature points and n_a is the number of all variable parameters. The number of temperature points used in the computations for **4** and **5** is 11 and 18, respectively. The value of n_a is equal to 4 because four parameters have been simultaneously optimized. The confidence limits for parameters given in Table II have been calculated by using Student's factor values for a confidence level of 0.05 in accordance with expression 5.

The rate constants for the rearrangement of **6** were computed with the use of the exchange broadening of lines (Δ_{ex}) in the slow exchange region as

$$k = \pi\Delta_{ex} \quad (7)$$

where $\Delta_{ex} = \Delta_{obs} - \Delta_0$, Δ_{obs} is the observed half-width of the line, and Δ_0 is the relaxation-caused half-width of the line.[13] The temperature dependence of the rate constants was treated conventionally by means of a linear regression analysis to establish Eyring's equation parameters.

Preparation of Dicyclopentadienyldimethylmethane. Freshly distilled cyclopentadiene, 66 g (1 mol), was added to a cooled (0 °C) mixture of 100 g of NaOH and 5 g of TEBA chloride in 500 mL of THF. Acetone (29 g, 0.5 mol) was added within 2 h under vigorous stirring at the same temperature. The resulting mixture was stirred for another 2 h and then was allowed to warm gradually to room temperature. The solution was decanted from the solid residue, washed till the washing waters react neutrally, and dried over Na_2SO_4, and the volatile components were removed in vacuo. The resulting oil was distilled; the fraction 54–55 °C (0.1 Torr) was collected (49 g, yield 58%). The ^1H NMR spectrum

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(12) Bax, A.; Freeman, R.; Kempsell, S. R. *J. Am. Chem. Soc.* 1980, *102*, 4849.

(13) Günther, H. *NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1973; p 248.

agrees with that reported earlier.[14]

Preparation of 3a,4,4a,8-Tetrahydro-4,4,8,8-tetramethyl-4-sila-*s*-indacene (3). To a solution of 47 g (0.27 mol) of dicyclopentadienyldimethylmethane in 500 mL of THF at −20 °C, 27 mL of 2.0 N hexane solution of *n*-butyllithium (0.54 mol) was added under stirring at −20 °C. The mixture was allowed to warm to room temperature, TMEDA (62.6 g, 0.54 mol) was added, and the mixture was cooled to −50 °C. A solution of 34.9 g (0.27 mol) of dichlorodimethylsilane in 200 mL of THF was added dropwise within 3 h. Stirring was continued for another 1 h at −50 °C. After warming to room temperature, the mixture was decanted from the solid residue, the solvents were removed in vacuo, and the resulting oil was distilled. The fraction at 80–82 °C (0.1 Torr) was collected (the yield of resultant **3**, **6**, and minor isomers was up to 52%). The major isomer **3** was isolated after recrystallization from pentane (17 g, 25%). ^{1}H NMR (toluene-d_8, 26 °C): δ −1.06 (s, 3 H, CH_3Si), 0.25 (s, 3 H, CH_3Si), 1.37 (s, 3 H, CH_3C), 1.57 (s, 3 H, CH_3C), 3.40 (m, 2 H, H–C(3a),C(4a)), 6.19–6.21 (m, 2 H, Cp), 6.22–6.25 (m, 2 H, Cp), 6.32–6.36 (m, 2 H, Cp); $^{13}C\{^1H\}$ NMR (dioxane-d_8), 26 °C, see Table I. Anal. Calcd for $C_{15}H_{20}Si$: C, 78.91; H, 8.83. Found: C, 79.01; H, 9.46.

Thermolysis of 3. The solution of **3** in toluene-d_8 was heated at 100 °C for 2 h in an NMR tube. The additional signals of **6** appeared in the NMR spectrum. When the resulting solution was heated some time more, the ratio of **3** and **6** (about 3:2) remained the same. The fraction of isomers different from **3** and **6** is less than 5% of the total amount of substance. Compound **6**: ^{1}H NMR (toluene-d_8, 26 °C) δ −0.43 (s, 3 H, CH_3Si), 0.26 (s, 3 H, CH_3Si), 1.32 (s, 3 H, CH_3C), 1.50 (s, 3 H, CH_3C), 2.72–2.89 (AB part of ABXY spin system, $J_{AB} = 23.8$ Hz, $J_{AX} \approx J_{AY} \approx J_{BX} \approx J_{BY} \approx 1.2$–1.5 Hz, 2 H, $H_2C(3)$), 3.50 (m, 1 H, HC(4a)), 6.37–6.39 (m, 1 H, Cp), 6.43–6.46 (m, 1 H, Cp), 6.55–6.63 (3 overlapping mult, 3 H, Cp); $^{13}C\{^1H\}$ NMR (dioxane-d_8, 26 °C), see Table I.

Preparation of 4-Germa-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacene (4). The synthesis is analogous to that described above for **3**. From 23 g (0.13 mol) of dicyclopentadienyldimethylmethane, 27 g (0.09 mol) of **4** was obtained (bp 86–91 °C (0.1 Torr), yield 71%). ^{1}H NMR (toluene-d_8, 26 °C): isomer **4a** δ −0.97 (s, 3 H, CH_3Ge), 0.43 (s, 3 H, CH_3Ge), 1.35 (s, 3 H, CH_3C), 1.57 (s, 3 H, CH_3C), 3.54 (m, 2 H, H–C(3a),C(4a)), 6.18–6.23 (2 overlapping m, 4 H, Cp), 6.28–6.32 (m, 2 H, Cp); isomer **4b** δ −0.08 (s, 6 H, $(CH_3)_2Ge$), 1.42 (s, 6 H, $(CH_3)_2C$), 3.08 (m, 2 H, H–C(3a),C(4a)), 6.1–6.5 (3 m overlapping with signals of **4a**, 6 H, Cp). $^{13}C\{^1H\}$ NMR (THF-d_8, 26 °C), see Table I. Anal. Calcd for $C_{15}H_{20}Ge$: C, 66.04; H, 7.38. Found: C, 65.92; H, 7.31.

Preparation of 3a,4,4a,8-Tetrahydro-4,4,8,8-tetramethyl-4-stanna-*s*-indacene (5). The synthesis is analogous to that described above for **3**. From 47 g (0.27 mol) of dicyclopentadienyldimethylmethane, 47 g (0.15 mol) of **5** was obtained (bp 100–105 °C (0.1 Torr), yield 57%). ^{1}H NMR (THF-d_8, 26 °C) δ −0.1 (br s, 6 H), 1.52 (s, 6 H), 5.2 (br m, 4 H), 6.21 (t, J = 1.2 Hz, 4 H). ^{1}H NMR (THF-d_8, −90 °C): isomer **5a** δ −1.26 (s, 3 H, CH_3Sn, $^2J_{1}H_{-^{119}Sn} = 54.9$ Hz), 0.74 (s, 3 H, CH_3Sn, $^2J_{^1H-^{119}Sn} = 56.5$ Hz), 1.49 (s, 3 H, CH_3C), 1.62 (s, 3 H, CH_3C), 4.46 (m, 2 H, H–C(3a),C(4a), $^2J_{^1H-^{119}Sn} = 98.9$ Hz), 6.0–6.4 (overlapping br mult, 6 H, Cp); isomer **5b** δ −0.04 (s, 6 H, $(CH_3)_2Sn$, $^2J_{^1H^{111}Sn} = 56.5$ Hz), 1.46 (s, 6 H, $(CH_3)_2C$), 3.77 (m, 2 H, H–C(3a),C(4a), $^2J_{^1H-^{119}Sn} = 95.5$ Hz), 6.0–6.4 (overlapping br mult, 6 H, Cp). $^{13}C\{^1H\}$ NMR (THF-d_8, 26 °C) δ −8.96 (br), 30.95, 40.38, 127.26, 163.00. $^{13}C\{^1H\}$ NMR (THF-d_8, −90 °C), see Table I.

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Registry No. *cis*-**3**, 135734-11-1; *cis*-**4**, 135734-12-2; *trans*-**4**, 135734-14-4; *cis*-**5**, 134767-15-0; *trans*-**5**, 135734-15-5; **6**, 135734-13-3; dicyclopentadienyldimethylmethane, 134459-15-7; cyclopentadiene, 542-92-7; dichlorodimethylsilane, 75-78-5; dimethyldichlorogermane, 1529-48-2; dimethyldichlorostannane, 753-73-1.

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Low Quantum Yields of $Cr(CO)_6$ Substitution in Fluorocarbon Solvent: Evidence That Metal–Fluorocarbon Interactions Are Very Weak

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The relative heats of CO photosubstitution on $Cr(CO)_6$ by cyclohexane, benzene, and 1,2-dichloroethane (as ligands) in perfluorocarbon solvents and in neat ligand have been determined by photoacoustic calorimetry. From these results and the quantum yield of CO substitution in neat ligand (0.67, 0.67, and 0.62, respectively), the quantum yield in perfluorodecalin was found to be 0.3. These results are confirmed by conventional actinometry. The low quantum yield in perfluorodecalin can be attributed to its weaker coordination of $Cr(CO)_5$. The quantum yield is independent of wavelength (254, 302, and 337 nm) in perfluorodecalin, indicating that the low quantum yield does not result from more efficient vibrational relaxation. The $Cr(CO)_5$ generated by photolysis of $Cr(CO)_6$ can recombine with photodissociated CO still in the solvent cage, and the relative strong coordination of cyclohexane, benzene, or 1,2-dichloroethane inhibits recombination of CO in the solvent cage, so that CO is forced to escape the cage. The results suggest a weak coordination of a fluorocarbon allows more cage CO to recombine, thus reducing the overall quantum yield of substitution. It is concluded that more efficient cage recombination of CO in a fluorocarbon solvent is primarily responsible for the lower quantum yield of substitution.

Introduction

There has been great interest in the interaction of $M(CO)_5$ (M = Cr, Mo, W) fragments with inert compounds. Early studies with matrix isolation techniques demonstrated that methane stereospecifically binds to $Cr(CO)_5$ at an octahedral site and that the Cr–methane interaction has the characteristics of a chemical bond.[1] This finding is supported by flash photolysis studies which demonstrate

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