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INTRAMOLECULAR REARRANGEMENTS IN TRIS(TRIMETHYLSILYL)-CYCLOPENTADIENE*

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Summary

Clear-cut temperature dependences of line shapes and line intensities in NMR spectra recorded for tris(trimethylsilyl)cyclopentadiene (I) and for the deuterated analogue (II) demonstrate that metallotropic and prototropic intramolecular rearrangements occur in these compounds. Four possible migration routes for metallotropic rearrangements in compounds I and II have been considered. It has been shown that temperature dependences of PMR and $^{13}C—\{^1H\}$ NMR spectra for I and II and a Diels—Alder reaction of I with acetylenedicarboxylic ester may be explained only in terms of four successive 1,2 shifts of the metal.

A detailed description of dynamic processes in tris(trimethylsilyl)cyclopentadiene has been made on the basis of total line shape studies carried out for $^1H—\{^2H\}$ NMR spectra of II under exchange conditions. These spectra avoid complications from spin—coupling effects.

The effect of introduction of organometallic groups in the cyclopentadienyl ring on the metallotropic rearrangement is discussed. An attempt is made to extend the concept of relative migratory ability of metals so as to include cyclopentadienyl ligands.

Introduction

h^1-Cyclopentadienyl compounds of transition and non-transition metals are good models for the study of carbon—carbon metallotropic rearrangements. In recent years a joint attack has been made successfully on degenerate metallotropic rearrangements occurring in monometallated cyclopentadienes [1,2].

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For example, orbital symmetry conservation was verified in all cases, and it was established that the rearrangements proceed via successive 1,2-shifts of the organometallic groups (1,5-sigmatropic rearrangements). Theoretical calculations [3,4] showed that the rearrangements were governed essentially by σ—π conjugation of the metal—carbon bond with the cyclopentadienyl ring diene system. This effect is also reflected in the ionisation potentials of metallated cyclopentadienes, which are lower than that of the unsubstituted compound [5], while the Diels—Alder reactivity of the latter is greater [6].

The second substituent introduced in the cyclopentadienyl ring eliminates degeneration and the rearrangement becomes the proper carbon—carbon tautomeric equilibrium, involving a number of isomers. A detailed description of processes of this kind has never been reported, probably owing to the complexity of unravelling temperature dependent NMR spectra of dimetallated cyclopentadienes. Preliminary results, however, have been obtained [7-9]. It was shown that, as with monometallated compounds, the most stable isomer is that with substituents on position 5 of the ring. Nevertheless, the question as to what is the mechanism and how large are the energy parameters so far awaits answer.

This paper deals with an extensive study of intramolecular rearrangements in tris(trimethylsilyl)cyclopentadiene (I). New data on the mechanism, the kinetic and thermodynamic characteristics have been obtained, and the effect of introduction of $Si(CH_3)_3$ groups on the rate of metallotropic rearrangement is discussed.

PMR, ^1H—$\{^2H\}$ NMR, and ^{13}C NMR spectra of tris(trimethylsilyl)cyclopentadiene at low temperatures

A PMR spectrum of tris(trimethylsilyl)cyclopentadiene (I) recorded at —11°C is shown in Fig. 1a. At high field, the signals of the protons of six methyl groups attached to silicons in position 5 and of three methyls at position 2 of the ring appear. Olefin proton signals (H_1, H_3 and H_4; an AMX pattern) lie at lower fields. The intensity ratio for 2,5,5-tris(trimethylsilyl)cyclopentadiene (Ia) is 18/9/1/1/1.

Assignment of ring protons in the spectrum is easy (Table 1) and is based on the data obtained earlier for cyclopentadiene [10], monometallated [11] and dimetallated [7,8] cyclopentadienes. Like in compounds of the type $C_5H_5M(CH_3)_3$ and $C_5H_4M'(CH_3)_3M(CH_3)_3$ (M, M' = Si, Ge, Sn), the olefin H_3 signal lies downfield from the H_1 and H_4 signals, while the spin—spin couplings associated with the Ia ring protons differ insignificantly from those known for dimetallated cyclopentadienes. The H_3—H_4 coupling in the compound is, however, ca. 0.6 Hz lower than that in monometallated cyclopentadienes.

A PMR spectrum of the residual protons of a mixture of 2,5,5-tris(trimethylsilyl)cyclopentadienes-d_2 (II) containing deuterium atoms in the positions 1,3, or 1,4, or 3,4 of the ring was measured at —11°C under deuterium decoupling conditions. It contains three singlets at low field. The absence of multiplicity is due to low probability of two H atoms occurring in a molecule of II. The deuterium isotope effect on the proton chemical shifts is low and comparable with the instrumental error (see Table 1). The spectrum is characteristic in that the H_1 intensity is lower than that of H_3 or H_4. However, the

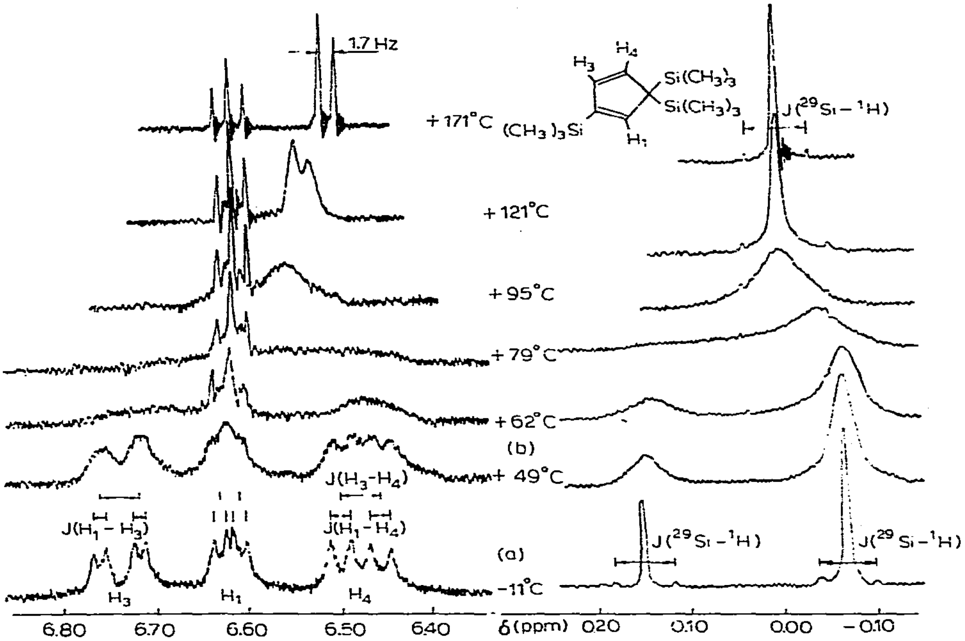
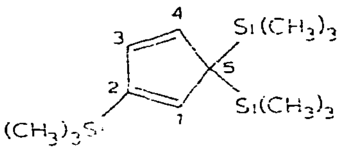


Fig. 1. 100.1 MHz PMR spectra of tris(trimethylsilyl)cyclopentadiene (I): (a) at the temperature of stereochemical rigidity; (b) at various temperatures.

TABLE 1

PMR DATA FOR 2,5,5-TRIS(TRIMETHYLSILYL)CYCLOPENTADIENE (Ia) AND 2,5,5-TRIS(TRIMETHYLSILYL)CYCLOPENTADIENE-d_2 (IIa)[a]



(Ia)

Compound	Chemical shifts (δ, ppm)					Spin—spin couplings, $J(H_i—H_j)$ (Hz)			T (°C)	Solvent
	H_1	H_3	H_4	CH_3^b	CH_3^c	$H_1—H_3$	$H_1—H_4$	$H_3—H_4$		
Ia	6.62	6.74	6.48	0.15	—0.07	1.41	2.22	4.44	—11	CS_2
	6.63	6.57	6.57	0.00	0.00	$J(H_{3,4}—H_1)$ =	1.79[d]		171	neat
IIa	6.63	6.74	6.46	0.16	—0.08	—	—	—	—10	CS_2
	6.63	6.56	6.56	0.00	0.00	—	—	—	172	decalin

[a] Chemical shifts are accurate to 0.01 ppm, spin—spin coupling to 0.05 Hz. [b] For Me_3Si on 2-position in the ring. [c] For Me_3Si on 5-position in the ring. [d] $J(H_{3,4}—H_1) = [J(H_1—H_3) — J(H_1—H_4)]/2$.

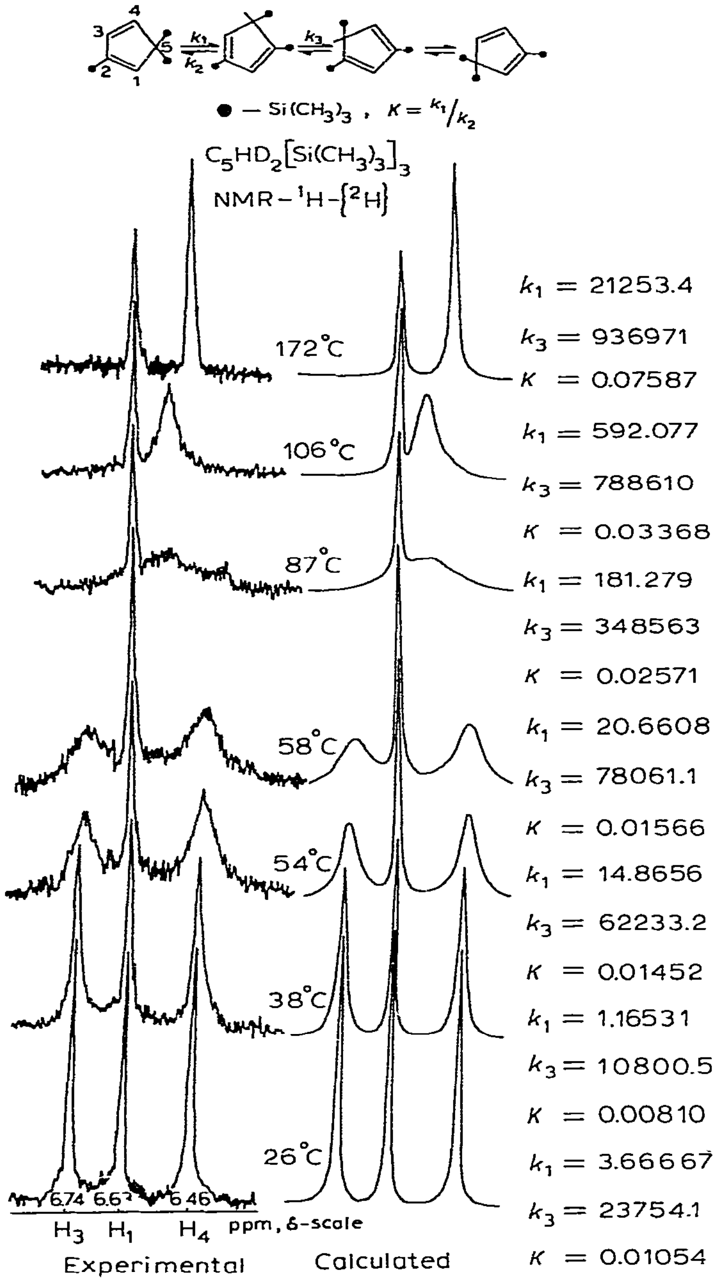


Fig. 2. Experimental ^{1}H— {^{2}H} NMR spectra of tris(trimethylsilyl)cyclopentadiene-d_2 (II) (left) and the calculated (right) pattern at various temperatures.

intensity ratio of 0.6/1/1 at this temperature is levelled at higher temperatures. This will be discussed in more detail below.

Figure 3a shows the ^{13}C—{^{1}H} NMR spectrum of I at room temperature. The assignment of carbon signals is based on (i) selective saturation of protons

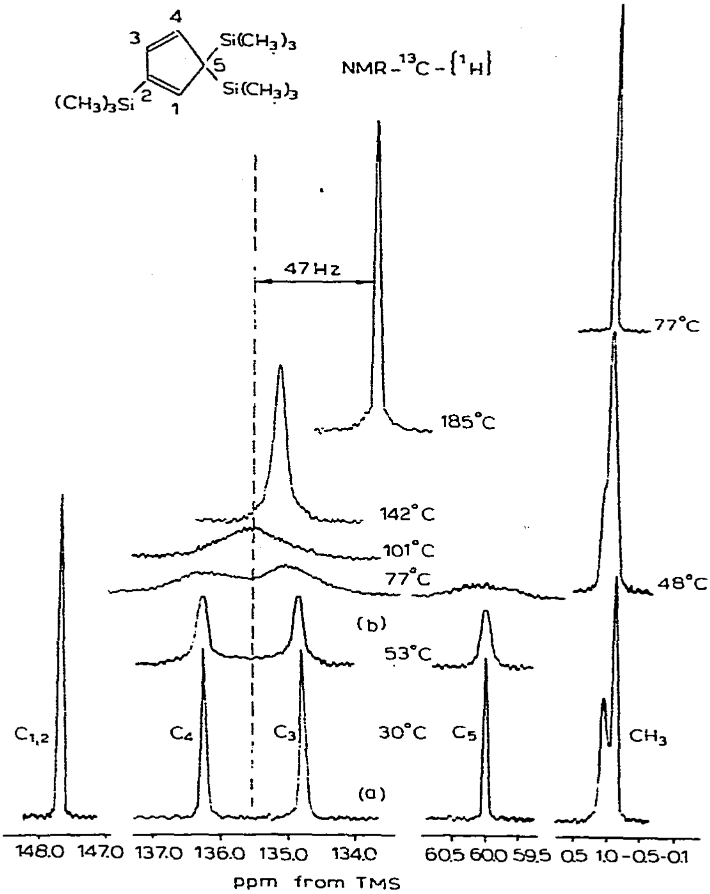


Fig. 3. 25.2 MHz ^{13}C—$\{^1$H$\}$ NMR-FT spectra of I: (a) at the temperature of stereochemical rigidity; (b) at various temperatures.

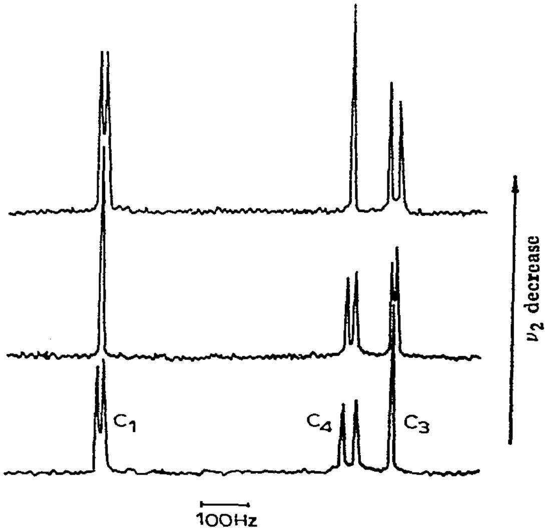


Fig. 4. ^{1}H selectively decoupled ^{13}C NMR spectra of olefinic carbons (C_1, C_3 and C_4) of I.

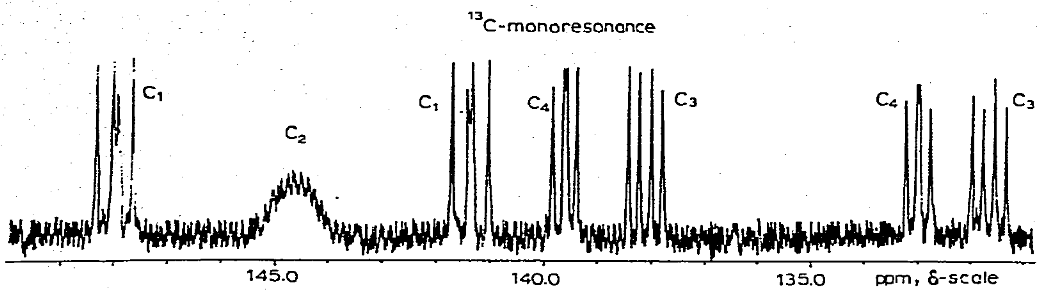


Fig. 5. Monoresonance ^{13}C NMR spectrum of ring carbons of I at room temperature.

[12,13] (Fig. 4), (ii) the ^{13}C monoresonance spectrum (Fig. 5)*, (iii) an additive approach based on the effect of the $Si(CH_3)_3$ groups on the shielding of ring carbons, proposed by us earlier [9].

The carbon chemical shifts (Table 2) lie in the same region as do those in 5-trimethylsilyl [14] and 5,5-bis(trimethylsilyl)cyclopentadiene [9]. In all these compounds, the ring C_4 signal lies downfield from C_3. Note a long-range spin—spin coupling (ca. 0.3 Hz) of methyl protons with the olefin carbon C_4, observable in a ^{13}C monoresonance spectrum of I. $^{2}J(C_4—H_3)$ is equal to $^{2}J(C_3—H_4)$ in I, as in 5,5-bis(trimethylsilyl)cyclopentadiene and unlike five-membered heterocycles studied by Weigert and Roberts [15].

Table 2 lists also the chemical shifts calculated through an additive scheme worked out for $Si(CH_3)_3$ as substituent in the cyclopentadienyl ligand. The experimental and calculated carbon chemical shifts were in good accord, so the approach was used in a further study of the system.

TABLE 2

CARBON CHEMICAL SHIFTS $J(^{13}C—^{1}H)$ IN 2,5,5-TRIS(TRIMETHYLSILYL)CYCLOPENTADIENE AND SPIN—SPIN COUPLING CONSTANTS[a]

See Table 1 for atom numbering

Chemical shifts (ppm vs. TMS)							
	C_1	C_2	C_3	C_4	C_5	CH_3^b	CH_3^c
Expt.	144.65	144.65	134.86	136.33	59.96	0.07	—0.14
Calcd.[d]	144.6	144.8	134.8	136.1	59.8	—	—
Spin—spin couplings $J(^{13}C_i—^{1}H_j)$ (Hz)							
H_1	164.0	[e]	10.9	6.5	[e]		
H_3	9.4	[e]	161.0	5.2	[e]		
H_4	7.6	[e]	5.2	166.0	[e]		

[a] Chemical shifts are measured at 25°C for neat Ia accurately to 0.05 ppm, the constants accurately to 0.1 Hz. [b] For carbons of Me_3Si on 2-position. [c] For carbons of Me_3Si on 5-position. [d] Calculated via an additive approach (see text). [e] The monoresonance ^{13}C spectrum of the tertiary carbons C_2 and C_5 was not analysed.

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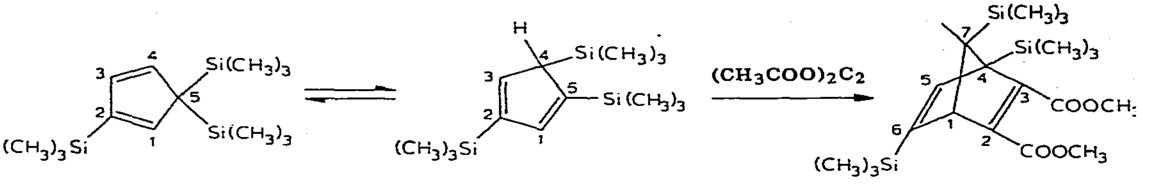
* The C_2 signal can be assigned only on the basis of the ^{13}C monoresonance spectrum since the C_1 and C_2 chemical shifts coincide.

^1H and ^{13}C NMR patterns for I and II measured at low temperatures demonstrate that tris(trimethylsilyl)cyclopentadiene exists essentially in the form of a 2,5,5-isomer (Ia). On the other hand, the effects discussed below suggest that a metallotropic and a prototropic intramolecular rearrangement occur in I and II, as in the case of dimetallated cyclopentadienes [7-9].

Reaction of I with acetylenedicarboxylic ester

A reaction of I with acetylenedicarboxylic ester in CCl_4 occurs at a higher temperature than that of bis(trimethylsilyl)cyclopentadiene with the same reagent [8], and leads to dimethyl 4,6,7-tris(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (III). The adduct structure corresponds to the 2,4,5-isomer (Table 3).

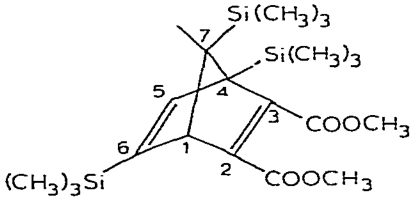


(Ia) (Ib) (III)

Thus the most stable, 2,5,5-isomer (Ia) is equilibrated with the 2,4,5-isomer (Ib), whose formation brings forth the metallotropic rearrangement. Note that the compound I resembles its 5,5-bis-analogue in that it has a decreased reactivity towards dienophiles.

TABLE 3

PMR DATA FOR ADDUCT III[a]



Chemical shifts (δ ppm)

H_1	H_5	H_7	CH_3^b	CH_3^c	CH_3^d	CH_3^e	CH_3^f
4.11	6.90	1.56	0.17	0.10	−0.04	3.56	3.59

Spin—spin couplings $J(H_i—H_j)$ (Hz)

H_1—H	H_1—H_7	H_3—H_7
0.8	1.0	

[a] Proton chemical shifts are accurate to 0.01 ppm, spin—spin couplings to 0.1 Hz; the spectrum was measured at room temperature for a solution of III in CCl_4. [b] Me on 2-position. [c] Me_3Si on 4-position. [d] Me_3Si on 7-position. [e] Carbomethoxy protons on 3-position. [f] Same on 2-position.

Temperature dependences of NMR spectra of I and II

The spectra of I and II display definite temperature dependences (Figs. 1b, 2b and 3b) that prove rearrangements to occur in the compounds. All the heating—cooling cycles are reversible. Temperature ranges of slow, intermediate, and fast exchanges are easily discernible.

At lower rates of the dynamic process (below 45° C) the $^1H—\{^2H\}$ NMR spectrum of II reveals gradual broadening of the H_3 and H_4 signals (Fig. 2). The broadening is at first symmetrical. The PMR H_3 and H_4 signals of I have different multiplicities $[J(H_1—H_3) < J(H_1—H_4)]$ and consequently the change of multiplicity is more pronounced with H_3, albeit the multiplet components are of equal widths (Fig. 1b).

Further heating leads to even stronger broadening of the H_3 and H_4 signals which simultaneously change their position. Both the effects are more pronounced with the lower-field H_3 signal, which is shifted upfield whereas the H_4 signal is shifted just slightly downfield at about 62°C.

The H_1 signal of II remains unaffected at the temperatures applied while its multiplet structure becomes more diffuse in the PMR spectrum of I above 45°C.

Above 80°C, the H_3 and H_4 signals coalesce and the broadened signal becomes more and more narrow and at the same time is shifted upfield (Figs. 6a and 6b). The PMR H_1 signal of I gradually transforms to a triplet and the ring

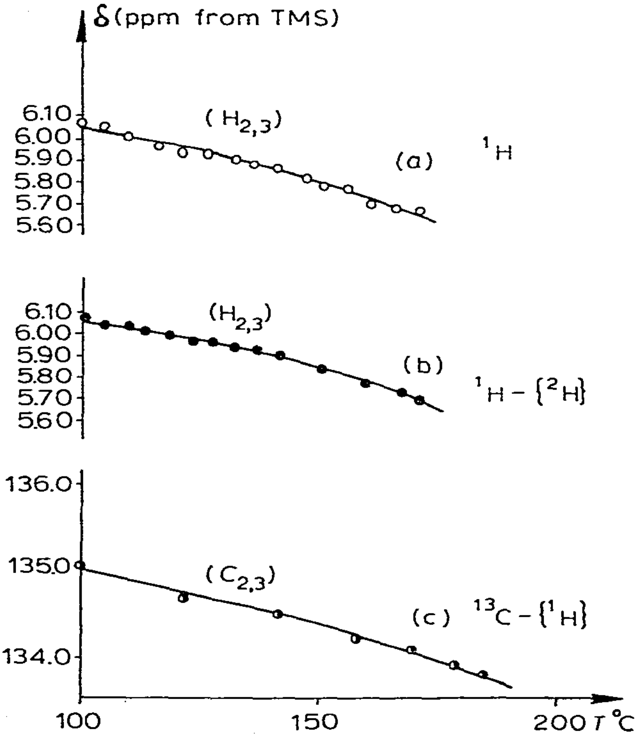


Fig. 6. Averaged ($H_{3,4}$ and $C_{3,4}$) chemical shifts at various temperatures.

protons give an A_2B spectrum under the fast exchange condition (at 170°C, Table 1).

In parallel with the changes discussed above, a broadening is observed at higher fields in the ^1H NMR spectra of I and II, followed by a collapse of the methyl proton signals (at 80°C). Heating to >80°C makes the averaged signal more narrow and shifts it slightly downfield.

The temperature dependence pattern obtained for a $^{13}C-\{^1H\}$ NMR spectrum of I is on the whole similar to the patterns described above. The first step is the broadening of the ring and methyl carbon signals (Fig. 3b). The temperature dependence of the signal of the quaternary carbon C_2 was studied under $^{13}C-\{^1H\}$ off-resonance conditions since the C_1 and C_2 chemical shifts coincided.

The broadening of the C_3 and C_4 signals is symmetrical up to 65°C, but a pronounced asymmetry is observed at 77°C, viz., the lowfield C_4 signal is broadened more strongly. At about 100°C these signals coalesce and the C_3 and C_4 averaged signal ($C_{3,4}$) becomes more and more narrow and is shifted upfield with an increase in temperature (Fig. 6c). Resonance frequencies of the carbons C_2 and C_5 differ markedly, therefore their averaged signal was not observed even at temperature as high as 185°C. The C_1 signal is practically insensitive to heating at the entire range studied.

Results, processing and discussion

(a) Metallotropic rearrangement pattern

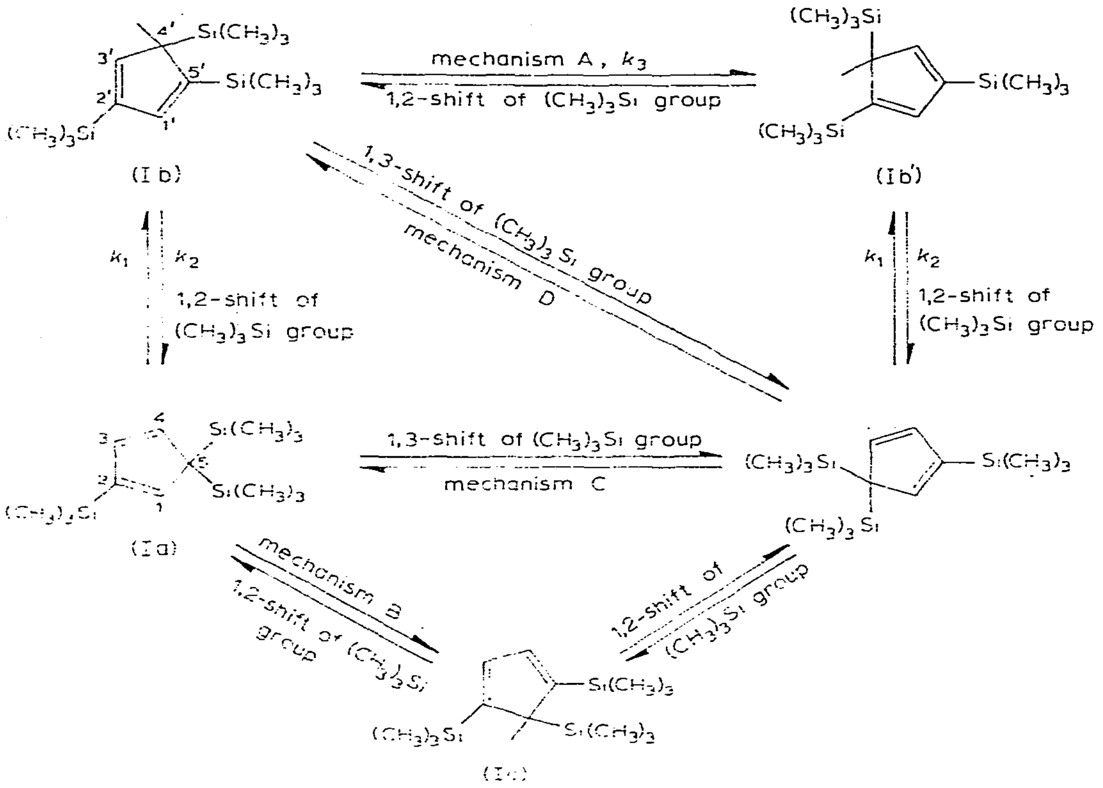
The widespread interest in metallotropic rearrangements stems from the question as to what is the mechanism and how high are the energy parameters of the process under study.

The temperature dependent NMR spectra measured for I and II, and also the Diels—Alder reaction carried out with I, evidence that the isomers Ia and Ib (and IIa and IIb) equilibrate. The content of Ib (or IIb) in the equilibrated mixture is low at low temperatures, as verified by the absence of their signals from the NMR spectra under these conditions. Consequently, the free energy $\Delta G^{\ddagger}_{300}$ of the equilibrium Ia $\rightleftharpoons$ Ib is somewhat higher than in the case of bis(trimethylsilyl)cyclopentadiene, whose less stable 2,5-isomer could be found in the PMR [8] and $^{13}C-\{^1H\}$ NMR [9] spectra at low temperatures. The content of Ib and/or IIb in the mixture increases with temperature but no resonance signals of the isomers are observed under these conditions either, since the parallel increase in the dynamic process rates broadens the signals and then makes them collapse with signals of the main isomers, Ia and IIa, respectively.

Pairwise broadening of the signals of H_3 and H_4 (C_3 and C_4), C_2 and C_5, and $Si(CH_3)_3$ groups shows us that the metallotropic rearrangement is finished by a transformation of Ia and IIa to the equivalent structures (accurately to position of the isotope label), so the process may be considered quasi-degenerate [16], similar to the metallotropic rearrangement in h^1-indenyl compounds [17]. All intermolecular mechanisms may be ruled out because there is no solvent effect on the rate of the dynamic process and resonance signals are broadened unsymmetrically at intermediate rates of exchange.

Four migration routes may be considered for the $Si(CH_3)_3$ group in tris(trimethylsilyl)cyclopentadiene (Scheme 1).

SCHEME 1



Mechanism A, a series of successive 1,2-shifts of the organometal group, is the most probable in terms of the earlier information on metallotropism in monometallated h^1-cyclopentadiene, which rearrange according to the orbital symmetry conservation rule via 1,2-shifts (1,5-sigmatropic rearrangements). The mechanism allows one to rationalise the non-degenerate equilibrium Ia $\rightleftharpoons$ Ib and the quasi-degenerate process Ia $\rightleftharpoons$ Ia′ from a single point of view.

The mechanism B, involving the intermediate Ic, does not agree with the temperature dependence observed. The averaged H_3 and H_4 (C_3 and C_4) signal should not have shifted upfield with temperature. On the other hand, the equilibrium Ia $\rightleftharpoons$ Ic should have led to a strong shift of $H_1(C_1)$, proved to be inexistent experimentally.

The Diels—Alder reaction does not fit with the mechanism either, because no 1,2,5-isomer of I was formed. The same considerations allow us to rule out mechanism C.

The last route to be discussed is a compound mechanism of the 1,2- and 1,3-shifts (D). This, however, would lead to a greater energy barrier than C, so it may be rejected as well.

Consequently, the temperature dependences observed for I and II may be explained only in terms of the mechanism A, and we will consider this mechanism in more detail.

We have noted already that the H_3 and H_4 (and/or C_3 and C_4) signals are broadened identically at lower exchange rates. This is possible only when the degenerate metallotropic rearrangement Ib ⇌ Ib′ has an energy of activation markedly lower than has the process Ia → Ib. Indeed, a metallotropic rearrangement in bis(trimethylsilyl)cyclopentadiene [9] involves a degenerate rearrangement between the 2,5- and 3,5-isomers which is faster than is the transformation of the 5,5- to the 2,5-isomer. Consequently, a good assumption is that at 45°C, when the lines start broadening in the spectra of I and II subject to the rearrangement Ia ⇌ Ib, the process Ib ⇌ Ib′ is so fast that signals of the nuclei H'_3 and H'_4, C'_3 and C'_4 of the Ib and Ib′ isomers are close to their collapse.

When we consider unsymmetrical broadening of the ^{1}H and ^{13}C NMR signals of I and II at intermediate rates of exchange we see that just the lower-field (H_3 and C_4, respectively) signal is broadened more strongly. This is similar to unsymmetrical broadening of the $^1H—^{199}Hg$ satellites in the PMR spectrum of C_5H_5HgCl [18] and the $^1H—^{117/119}Sn$ satellites in the spectra of $C_5H_5Sn(CH_3)_3$ [16] and $C_9H_7Sn(CH_3)_3$ [17]; the phenomenon is governed by the difference between resonance frequencies of the lines to be averaged. In our case, the lines in question are the averaged H'_3 and H'_4 (or C'_3 and C'_4) signal of Ib on the one hand, and $H_3(C_3)$ and $H_4(C_4)$ signals of Ia on the other. Naturally, the difference between the frequencies is greater for lower-field signals (H_3 and C_4) and these undergo the greater broadening.

Cotton [19] developed an elegant method for testing metallotropic rearrangement mechanisms. With tris(trimethylsilyl)cyclopentadiene, however, this does not work, while consideration of the PMR and ^{13}C NMR spectra separately leads to a contradiction. Probably, the criterion of prevalent broadening at the initial stages of exchange is applicable to degenerate rearrangements only.

No detailed description of a dynamic process is possible without reliable thermodynamic data. These will be discussed in the course of the following analysis of temperature dependences of the spectra of I and II.

(b) Equilibrium constants for Ia ⇌ IIb

The averaged chemical shifts $\delta(H^{obs}_{3,4})$ and $\delta(C^{obs}_{3,4})$ have been noted already as temperature-sensitive (Fig. 6) at faster exchange rates, and their magnitudes depend on the weight ratio of Ia and Ib at equilibrium. The equilibrium constant may be written as follows:

$$K = \frac{\langle\delta_{3,4}\rangle - \delta^{obs}_{3,4}}{\delta^{obs}_{3,4} - \delta_x}$$

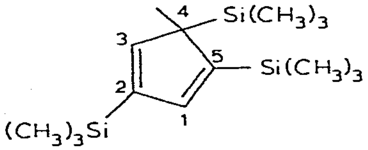
where $\langle\delta_{3,4}\rangle = (\delta_3 + \delta_4)/2$, $\delta_x = (\delta_{3'} + \delta_{4'})/2$, while δ_3, δ_4 and $\delta_{3'}$, $\delta_{4'}$ are the chemical shifts of protons (or carbons) of Ia and Ib, respectively, in the slow exchange limit.

It has been shown already that $\delta_{3'}$ and $\delta_{4'}$ cannot be found directly from the NMR spectra. We have used the optimization procedure MINIMAX-1 [7] written in ALGOL. The computations were made on a BESM-6 computer.

To find the Ia ⇌ Ib equilibrium constant from the temperature dependence of the averaged $C_{3,4}$ signal in the $^{13}C—\{^1H\}$ NMR spectrum of I, we have made a direct calculation based on the $\delta(C'_3)$ and $\delta(C'_4)$ values obtained via an additive

TABLE 4

CARBON CHEMICAL SHIFTS IN 2,4,5-TRIS-(TRIMETHYLSILYL)-CYCLOPENTADIENE, AS CALCULATED VIA AN ADDITIVE PATTERN OF $Si(CH_3)_3$ SUBSTITUTION IN THE CYCLOPENTADIENYL RING[a]



(I b)

Compound	C_1	C_2	C_3	C_4	C_5
Ib	144.1	149.6	143.9	59.4	148.3

[a] The additive scheme applied was described by us elsewhere [9].

scheme (see above; see also Table 4). Thermodynamic parameters obtained through the Arrhenius plot (see Table 5) via the optimization and direct calculations fit in satisfactorily, so the additive scheme applied may be considered reliable.

(c) *Ia → Ib metallotropic rearrangement rate*

Preliminary estimates. The transformation rate of Ia was estimated by using approximate formulae and $^1H-\{^2H\}$ NMR H_3 and H_4 signal widths for II and $^{13}C-\{^1H\}$ NMR C_3 and C_4 signal widths for I, at slow exchange at various temperatures. At fast exchange rates we employed the averaged $H_{3,4}$ (and $C_{3,4}$) signal

TABLE 5

THERMODYNAMIC CHARACTERISTICS OF THE Ia ⇌ Ib METALLOTROPIC EQUILIBRIUM IN TRIS(TRIMETHYLSILYL)CYCLOPENTADIENE

Experimental parameter	δ_0(ppm)	δ_x(ppm)[a]	ΔH (kcal/mol)	ΔS (cal/mol deg.)	Method
$\delta^{obs}(H_{3,4})$	6.639	5.621	4.05	3.95	^{1}H spectra of I, MINIMAX-1
$\delta^{obs}(H_{3,4})$	6.631	5.610	4.04	3.97	$^1H-\{^2H\}$ spectra of of II, MINIMAX-1
$\delta^{obs}(C_{3,4})$	135.85	102.8	4.06	3.92	$^{13}C-\{^1H\}$ spectra of I, MINIMAX-1
$\delta^{obs}(C_{3,4})$	135.55	101.5	4.1	3.8	$^{13}C-\{^1H\}$ spectra of I, additive scheme

[a] $\delta_x = (\delta_3' + \delta_4')/2$, where δ_3' and δ_4' are chemical shifts of olefinic carbons C_3 and C_4 (or H_3 and H_4 protons) in isomer Ib.

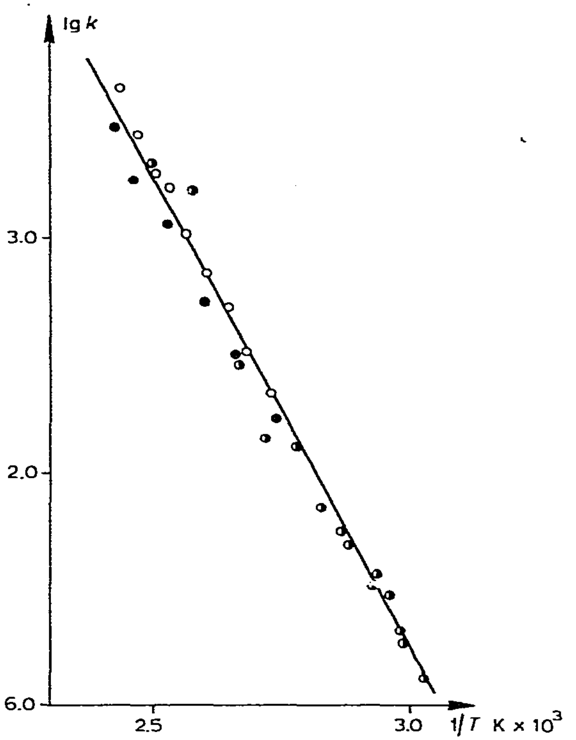


Fig. 7. Log k vs. $1/T$ for the metallotropic rearrangement Ia→Ib in tris(trimethylsilyl)cyclopentadiene: open circles, from PMR spectra ($Si(CH_3)_3$); half-filled circles, from $^1H—\{^2D\}$ ($H_{3,4}$); filled circles, from $^{13}C—\{^1H\}$NMR spectra ($C_{3,4}$ and $Si(CH_3)_3$).

width as a function of temperature*. Temperature dependences of the PMR and $^{13}C—\{^1H\}$ NMR $Si(CH_3)_3$ signals in I were also used. Figure 7 a plot of lg k_1 vs. $1/T$ summarises all the results obtained. The activation parameters obtained for Ia → Ib are E_a = 18.5 ± 0.6 kcal/mol and $\Delta G^{\ddagger}_{300}$ = 17.8 ± 0.2 kcal/mol. However good the correlation factor obtained, the activation parameters are only rough estimates since neglect of the equilibrium Ia $\rightleftharpoons$ Ib may lead to a considerable systematic error.

(d) *Analysis of line shapes in* $^1H—\{^2H\}$ *NMR spectra of II under exchange conditions*

The estimates obtained above are far from a complete pattern of the metallotropic rearrangement occurring in tris(trimethylsilyl)cyclopentadiene because they provide no information on the rearrangement Ib $\rightleftharpoons$ Ib′. No explanation is given either of the different intensities of NMR H_1, H_3 and H_4 signals of II at low temperatures. We have calculated the H_1, H_3 and H_4 line shapes in $^1H—\{^2H\}$ NMR spectra of II under exchange conditions.

Mechanism A has been selected already as a predominant pattern (see

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* Temperature dependences of PMR H_3 and H_4 signals of I cannot be used in the preliminary estimates because it would be difficult to account for spin—spin coupling under exchange conditions.

above), so K, k_1, k_2, k_3, as well as $\delta(H'_3)$ and $\delta(H'_4)$ are the unknown quantities. The quantities K, ΔH and ΔS for Ia $\rightleftharpoons$ Ib, and δ_x have already been found at a sufficient accuracy, while $\delta(H'_3)$ and $\delta(H'_4)$ may be estimated on the basis of the data reported for the $Si(CH_3)_3$ effect on the cyclopentadienyl proton shifts [8]. Also, $k_3 \gg k_1$ at any of the temperatures studied, while k_2 is a single-valued function of K and k_1.

The zero approximation for the degenerate rearrangement Ib $\rightleftharpoons$ Ib′ is $E_a = 14.5$ kcal/mol and $\Delta S = 0$, obtained earlier [8] for a degenerate rearrangement in 2,5-bis(trimethylsilyl)cyclopentadiene.

The line shape calculations were based on the multiposition exchange formalism introduced by McConnell [20]. The TOLISH (Total Line Shape) program written in ALGOL allowed us to calculate the spectra directly from the input parameters listed above. The computations were made on a BESM-6 computer and plotted on a CALCOMP display.

The starting parameters $\Delta H_i^{\ddagger}$, $\Delta S_i^{\ddagger}$ ($i = 1$ or 3), $\delta(H'_3)$ and $\delta(H'_4)$ were vary with a best fit criterion against the experimental spectra over the entire temperature range studied. The first steps have shown that a satisfactory agreement may be achieved only if $\Delta H_3^{\ddagger} \leqslant 12.0$ kcal/mol.

Besides, k_1 and k_3 cannot be found independently since they are interrelated by $k_{eff}^{-1} = k_1^{-1} + k_2^{-1} + k_3^{-1}$, where k_{eff} is the total effective rate constant for the quasi-degenerate process Ia $\rightleftharpoons$ Ia′.

The processing works only when the H_1, H_3 and H_4 intensity ratios vary with temperature as is shown in Fig. 8. The intensities are equalised at 426 K. The most probable explanation is that a metallotropic rearrangement is accompanied by a prototropic (deuterotropic) one. A reasonable pattern is given in Scheme 2. The metallotropic rearrangement transforms IIa to IIa′, the process being quite fast even at room temperature. However, it is quasi-degenerate and so cannot redistribute the proton intensities. Deuterium (proton) migration

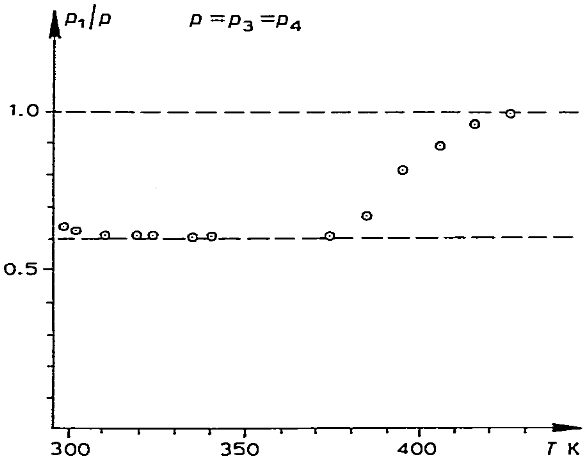
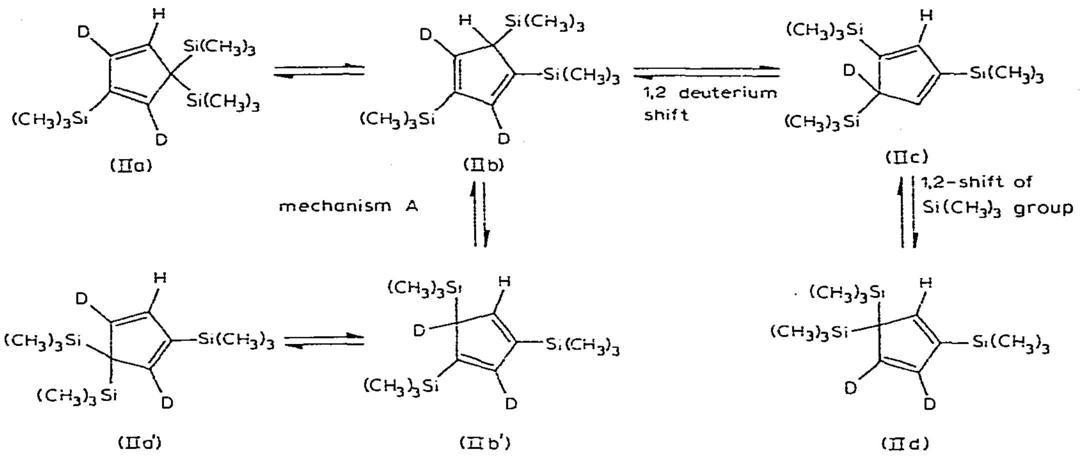


Fig. 8. Intensity ratios for olefinic absorptions in $^1H-\{^2H\}$ NMR spectra of II at various temperatures, obtained through the TOLISH procedure: p_1 is the H_1 contribution to the intensity; $p_3 = p_4$ are H_3 and H_4 contributions to the intensity.

SCHEME 2



leads to IId (Scheme 2) and it is just this migration that redistributes the intensities. The energy of activation of prototropic rearrangements occurring in metal cyclopentadienyls or cyclopentadiene itself is rather high, 22 to 24 kcal/mol [21, 22], which is why there is an inflection point in the intensity ratio vs. temperature curve: the IIa $\rightleftharpoons$ IId equilibration is sufficiently fast only at higher temperatures. Finally, the intensity vs. temperature dependence obtained allows us to estimate the difference between the free energies of IIA and IIc $\Delta(\Delta G^{\ddagger}_{300}) \approx 0.26$ kcal/mol.

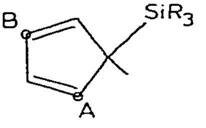
Theoretical and experimental spectra obtained with the best set of the parameters (Table 6) are shown in Fig. 3b.

(e) Discussion

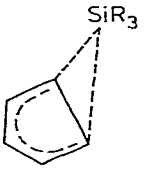
If we exclude the prototropic rearrangement and neglect the deuterium isotope effect on the kinetics we will come to the following pattern (Fig. 9) that reflects the free energy variation with the reaction coordinate in tris(trimethylsilyl)-cyclopentadiene.

Earlier [23] we calculated ground- and transition-state electron structures of $C_5H_5SiH_3$. These calculations may be now collated with the present data on the effect of $Si(CH_3)_3$ substitution in the cyclopentadienyl ring.

Negative charges on C_2 and the carbons forming the bond along which the rearrangement occurs are levelled in the transition state (TS) and are lower than in the ground state (GS) whereas negative charges built up on C_1 and C_3 increase markedly. Consequently, introducing an electron acceptor substituent in posi-



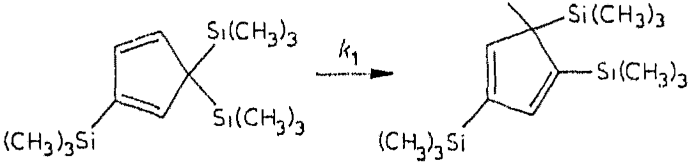
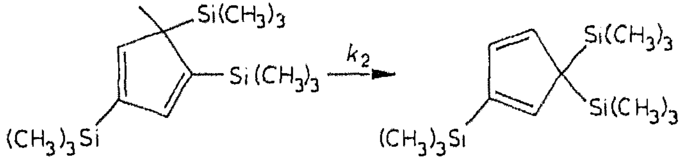
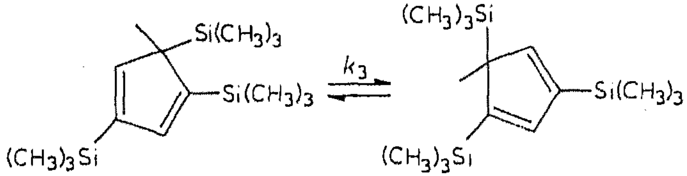
(GS)



(TS)

TABLE 6

CHARACTERICTICS OF THE METALLOTROPIC REARRANGEMENTS IN TRIS(TRIMETHYLSILYL)CYCLOPENTADIENE[a]

Process	E_a (kcal/mol)	$\Delta G^{\ddagger}_{300}$ (kcal/mol)	$\Delta S^{\ddagger}_{300}$ (cal/mol deg.)
	17.8 ± 0.3	17.5 ± 0.1	—0.9 ± 0.7
	14.1 ± 0.3	14.7 ± 0.1	—4.3 ± 0.7
	12.3 ± 0.3	12.0 ± 0.1	—1.2 ± 0.7

[a] Calculated using a TOLISH program, together with the experimental $^1H-\{^2H\}$ NMR spectra of II.

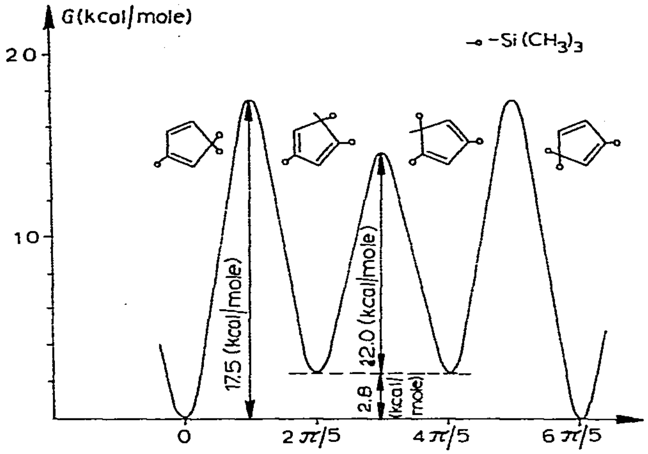


Fig. 9. Potential energy curve for the metallotropism in tris(trimethylsilyl)cyclopentadiene.

tion A or B of the ring should stabilise the transition state and accelerate the rearrangement. Just this effect results from an introduction of two $Si(CH_3)_3$ groups, because photoelectron spectra [24] and theoretical calculations [25,26] show that a $Si(CH_3)_3$ group in the vinyl position is a weak electron acceptor. Hence, the fact that the degenerate rearrangement Ib $\rightleftharpoons$ Ib′ in tris(trimethylsilyl)cyclopentadiene is faster than is the respective rearrangement in bis(trimethylsilyl)-cyclopentadiene has received its reasonable explanation.

Earlier, we studied [17] the temperature dependent PMR and CMR spectra of monometallated indenyl compounds and introduced a parameter to account for the relative ability of a ligand to facilitate metal migration, $r_a = -0.43/RT$ $[\Delta G^{\ddagger}_{M}(\text{ligand}) - \Delta G^{\ddagger}_{M}(\text{cyclopentadienyl})]$. This approach permits some predictions to be made for quasi-degenerate metallotropic rearrangements in trimetallated cyclopentadienes. A preliminary estimation made with 2,5-bis(trimethylsilyl)cyclopentadiene as ligand showed that the r_a factors for bis(trimethylsilyl)-(trimethylstannyl)cyclopentadiene* and tris(trimethylsilyl)cyclopentadiene were close to —1.9. On the basis of this factor we may predict 16 kcal/mol for the free energy of activation of the quasi-degenerate metallotropic rearrangement in bis(trimethylsilyl)(trimethylgermyl)cyclopentadiene.

Experimental

Tris(trimethylsilyl)cyclopentadiene (I)

It was obtained via a technique similar to that described by Jutzi [27]. A solution of butyllithium (0.045 mol) in hexane was added at 0°C to 5,5-bis(trimethylsilyl)cyclopentadiene (8 g, 0.038 mol) in 30 ml tetrahydrofuran. The mixture was stirred at room temperature for an hour, treated with a solution of $ClSi(CH_3)_3$ (5.4 g, 0.05 mol in 20 ml THF), heated to boiling of THF, and refluxed for 6h. The solvent was removed, the residue chromatographed on a

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* The free energy of activation $\Delta G^{\ddagger}_{300}$ for the quasi-degenerate rearrangement in this compound was measured by us to be 9.3 kcal/mol (unpublished results).

small alumina column, compound I was isolated by fractional distillation in vacuo, b.p. 67°C/2 Torr, yield 51%. Found: C, 59.68; H, 10.73; Si, 28.74. $C_{14}H_{30}Si_3$ calcd.: C, 59.63; H, 10.63; Si, 29.84%. Mass spectrum: parent ion M^+ at m/e of 282, $W_M = 6\%$ [5].

Tris(trimethylsilyl)cyclopentadiene-d_3 (II)

This was synthesised in the manner described above. The starting compound was bis(trimethylsilyl)cyclopentadiene-d_4, obtained from cyclopentadiene-d_6 [28]. The isotope composition of II (d_3 77.5, d_2 18.0, d_1 1.9%) was found from mass spectra. The yield of deuterated compound was somewhat lower than in the case of I.

Dimethyl 4,6,7-tris(trimethylsilyl)bicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylate (III)

Compound III was obtained via a technique described earlier [8] for a Diels—Alder reaction of bis(trimethylsilyl)cyclopentadiene with acetylenedicarboxylate as dienophile, but at a higher temperature. Found: C, 56.84; H, 8.64; Si, 19.72. $C_{20}H_{36}O_4Si_3$ calcd.: C, 56.56; H, 8.47; Si, 19.84%.

NMR spectra

The spectra were measured on a Varian XL-100-15 instrument. PMR spectra were recorded for neat samples of I and II*, and for the solutions in CS_2 and decalin. All samples were degassed and sealed. ^{13}C NMR spectra were measured for neat I in the Fourier transform mode. The temperature was controlled within ±1°C.

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* PMR spectra of II were measured under the double heteronuclear $^1H-\{^2H\}$ resonance conditions.

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