

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF METAL CYCLOPENTADIENYLS

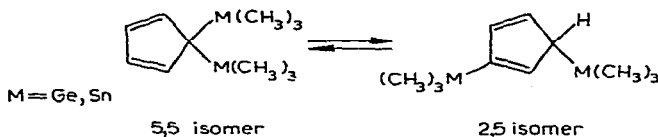
X*. PROTON MAGNETIC RESONANCE SPECTRA OF, AND DYNAMIC BEHAVIOUR IN, BIS(TRIMETHYLSILYL)CYCLOPENTADIENE**

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SUMMARY

The PMR spectra of bis(trimethylsilyl)cyclopentadiene (I) have been studied at -30° to $+220^{\circ}$ indicating that (I) is a mixture of the 5,5-(Ia), 2,5-(Ib), 1,4-(Ic), and 1,3-(Id) isomers, the ratio being 132/3.6/2.2/1 at -30° . The structures have been proved using INDOR and spin-decoupling techniques and through Diels-Alder reactions with dienophiles or metallation with an aminostannane. (Ib) has been shown to exhibit a degenerate metallotropic rearrangement which proceeds via the 1,2 shift of the 5-positioned $(\text{CH}_3)_3\text{Si}$ group (E_a 14.5 ± 1.8 kcal/mole, $\Delta S^{\ddagger} -1.5 \pm 4$ e.u.). The interconversion of (Ia) and (Ib) proceeds via the 1,3 shift of the $(\text{CH}_3)_3\text{Si}$ group. The methyl chemical shifts have been processed using a MINIMAX 1 program to yield the thermodynamic characteristics of the (Ia) \rightleftharpoons (Ib) metallotropic tautomeric equilibrium, *i.e.* ΔH 2.73 kcal/mole and ΔS 4.99 e.u. The values of the activation parameters have been obtained for the metallotropic rearrangement of (Ib) into (Ia) (E_a 15.8 ± 1.0 kcal/mole, $\Delta S^{\ddagger} -4.7 \pm 4$ e.u.) and (Ia) into (Ib) (E_a 18.6 ± 1.0 kcal/mole, $\Delta S^{\ddagger} 0.3 \pm 4$ e.u.). Above $+120^{\circ}$ (Ic) \rightleftharpoons (Ib) \rightleftharpoons (Id) hydrogen migration has been observed, the process being fast relative to the NMR time scale. The activation energy has been estimated as 21 kcal/mole for the rearrangement of (Ic) to (Ib).

In an earlier communication¹ it was shown that bis(trimethylgermyl)- and bis(trimethylstannyl)cyclopentadienes undergo a metallotropic rearrangement involving the 5,5 and 2,5 isomers.



* For Part IX see ref. 1.

** Reported in part at the 5th International Conference on Organometallic Chemistry, Moscow, August 1971, see ref. 2.

This is an example of non-degenerate carbon-carbon metallotropism, the 5,5 isomers being thermodynamically more favourable. At lower temperatures, the equilibrium lies well to the left, but on increasing the temperature the concentration of the 2,5 isomer increases, the rearrangement rate increases and the rearrangement becomes a fast process relative to the NMR time scale. For this reason it has proved impossible to observe any signals associated with the 2,5 isomer.

The temperature dependence has however been analysed spectroscopically for bis(trimethylgermyl)cyclopentadiene, to give the thermodynamic characteristics of the equilibrium (ΔH 4.6 kcal/mole, ΔS 11.5 e.u., ref. 1).

In this present communication a detailed study of the PMR spectra and chemical reactions of bis(trimethylsilyl)cyclopentadiene (I) are reported, this compound being one of the most convenient for the study of rearrangements of the type mentioned above. In this particular system more of the 2,5 isomer is present while the rearrangement is slower, so that a more detailed analysis of the dynamic processes occurring in the system is possible.

EXPERIMENTAL

Bis(trimethylsilyl)cyclopentadiene (I) and bis(trimethylsilyl)(trimethylstannyl)cyclopentadiene (II) were synthesised according to the procedure described earlier³, b.p. for (I) 45°/3 mmHg, for (II) 102°/4 mmHg*.

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

Freshly distilled (I) (0.42 g, 3 mmole) and dimethyl acetylenedicarboxylate (0.43 g, 3 mmole) were dissolved in 20 ml CCl₄ and left at 20° for 24 h (the reaction took two hours when carried out at 140° in xylene). The solvent was removed under reduced pressure and the residual oil was fractionated *in vacuo*. The fraction with b.p. 120–121°/3 mmHg gave a white crystalline solid when stored at room temperature for one day, m.p. 36–38°. (Found: C, 57.83; H, 8.08; Si, 16.08. C₁₇H₂₈O₄Si₂ calcd.: C, 57.91; H, 8.01; Si, 15.93 %.)

5,7-Bis(trimethylsilyl)-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-ene (IV)

Tetracyanoethylene (0.25 g, 2 mmole) was added to freshly distilled (I) (0.42 g, 2 mmole) dissolved in 20 ml of CH₂Cl₂ or C₆H₆. The mixture was kept at room temperature until the tetracyanoethylene had dissolved entirely and then for a further 24 h. The solvent was removed *in vacuo*, the residual yellow oil treated with 3 ml hexane to give white crystals, yield 0.63 g (94%). (Found: C, 60.68; H, 6.64. C₁₇H₂₂N₄Si₂ calcd.: C, 60.31; H, 6.55 %.)

Spectra were measured on HA-100D (Varian, 100 MHz) and JNM-C-60HL (JEOL, 60 MHz) instruments. The adducts were studied as solutions in CCl₄ (III) or CDCl₃ (IV) using cyclohexane as internal standard. Samples of (I) were either neat liquids or solutions in toluene-*d*₈ or decalin. Internal standards were cyclopentane (for the solution in C₆D₅CD₃), cyclohexane and benzene (for the neat sample), or hexamethyldisiloxane (for the solution in C₆D₅CD₃ and decalin). Concentrations were of the order of 1% *v/v*. Internal lock and frequency sweep were used throughout.

* Compounds (I) and (II) have also been synthesised by Abel and Moorhouse using a similar method⁴.

The temperature was controlled accurately to $\pm 1^\circ$. All chemical shifts are in δ -scale. Chemical shifts of the standards were taken as δ (HMDS*) 0.05, δ (C_6H_{12}) 1.42 and δ (C_5H_{10}) 1.50 ppm. A Muirhead D-890-B audiofrequency oscillator was used with the double-resonance experiments.

RESULTS AND DISCUSSIONS

1. PMR spectra of bis(trimethylsilyl)cyclopentadiene dissolved in $C_6D_5CD_3$

Figure 1 shows the spectrum of (I) recorded at 100 MHz for the solution in $C_6D_5CD_3$, as well as the fragments recorded at lower sweep rate and sweep width. The overall spectrum, Fig. 1a, demonstrates that the most intense signals are the singlet

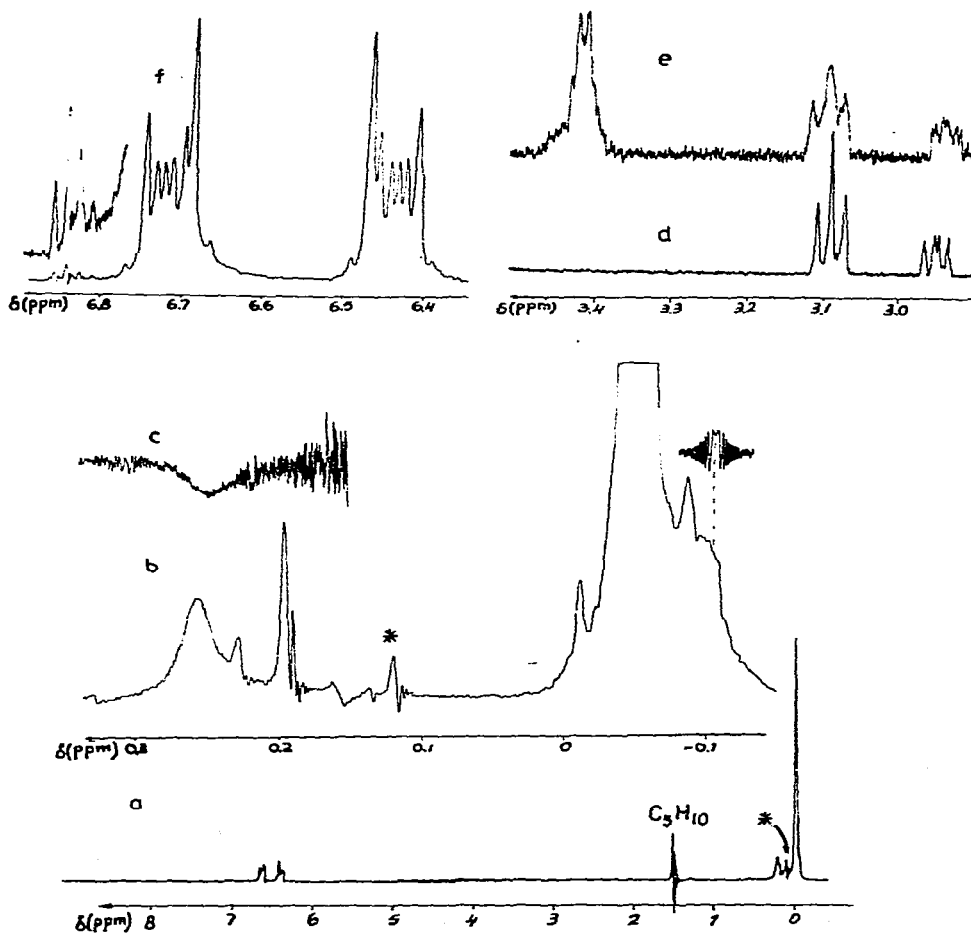
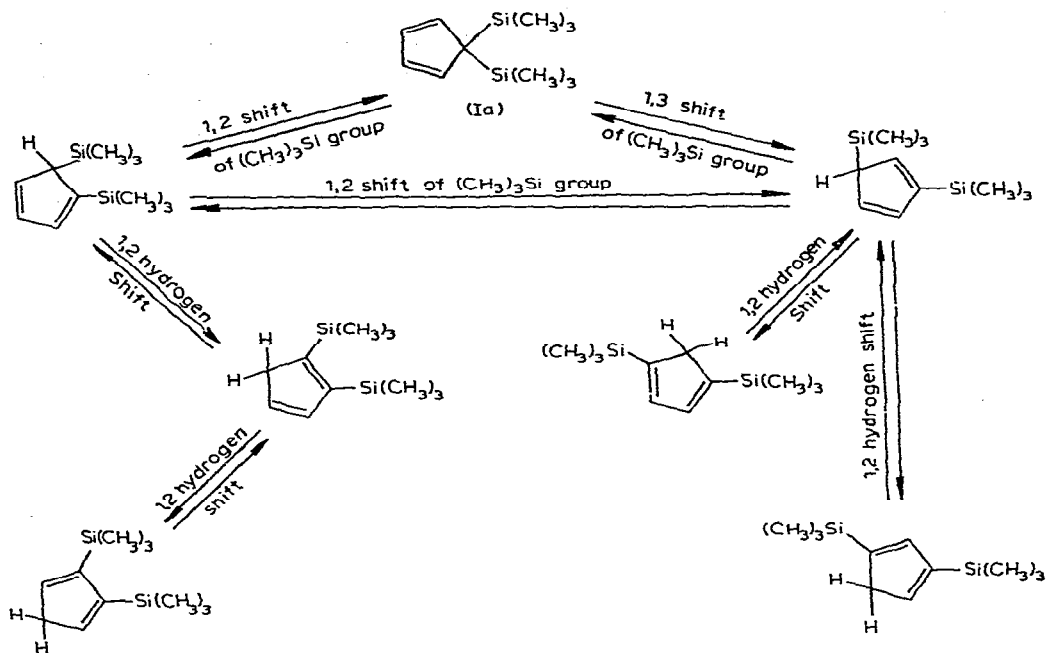


Fig. 1. PMR spectra of bis(trimethylsilyl)cyclopentadiene (100 MHz, toluene- d_8 solution). a, Overall spectrum at $+30^\circ$; b, methyl signals at $+30^\circ$; c, INDOR spectrum, while monitoring the signal at -0.107 ppm; d, methyne and methylene signals at -30° ; e, same for $+30^\circ$; f, olefine protons at $+30^\circ$. Asterisk indicates the signal of internal hexamethyldisiloxane.

* HMDS = hexamethyldisiloxane.

at -0.037 ppm at higher fields and the symmetrical AA'BB' multiplet at lower fields. The integral intensity ratio is 9/1/1 for these signals. For (I), in general, seven isomers may exist whose interconversion would occur through trimethylsilyl or hydrogen migrations, see Scheme 1.

SCHEME 1



The spectrum demonstrates unambiguously that (I) exists mainly as the 5,5 isomer (Ia)*, the higher-field signal being related to two trimethylsilyl groups which are in the allylic position. This assignment follows from the magnitude of the chemical shift. The signal has satellites due to spin-spin coupling involving the ²⁹Si isotope (natural abundance, 4.71%). $J(^{29}\text{Si}-^1\text{H})$ 6.60 ± 0.05 Hz. The AA'BB' spectrum (Fig. 1b) may be assigned to the two pairs of olefin protons in the ring. The spectrum has been analysed using a YaMR-1 program⁶ to give $\delta(\text{AA}')$ 6.712, $\delta(\text{BB}')$ 6.433 ppm; $J(\text{AB}) = J(\text{A}'\text{B}')$ 4.4, $J(\text{AB}') = J(\text{A}'\text{B})$ 1.2, $J(\text{AA}') = J(\text{BB}')$ 2.7 Hz.

These spin-spin coupling constants are close to those observed for bis(trimethylgermyl)- and bis(trimethylstannyl)-cyclopentadienes¹. If they are compared with the constants known for cyclopentadiene and its monometallated *h*¹-derivatives⁷, it will be seen that $J(\text{AB})$ is 0.6 Hz lower and $J(\text{AB}')$ 0.5 Hz higher in value. This may be explained by assuming that in these compounds the π -electrons are more extensively delocalised in the ring, owing to hyperconjugation involving two C-Si bonds, thus leading to a decrease in the C₁C₂ bond order and an increase in the C₂C₃ bond order. A similar effect holds for cyclopentadienyliides⁸, for example.

The lower field signal in the olefin region of the spectrum (AA' part) belongs to the 2,3 protons, that at higher field (BB' part) to the 1,4 protons; in other words, the

* This agrees with the gas-phase electronography of (I) reported by Veniaminov *et al.*⁵.

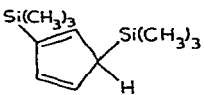
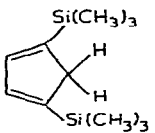
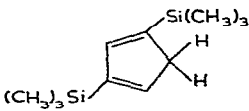
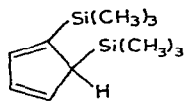
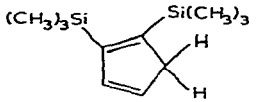
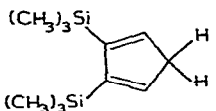
chemical shifts obey the same sequence as that observed for cyclopentadiene and the Group IVB cyclopentadienyls^{7,9}. This assignment follows from the results obtained from a study of the metallotropic rearrangement in (Ia), to be discussed below.

Detailed scanning of the spectra of solutions in $C_6D_5CD_3$ reveals a number of weaker signals belonging to other isomers of (I). Table 1 summarises the spectrum types and the chemical shift ranges expected for ring protons and $(CH_3)_3Si$ groups for each of the isomers (Ib) to (Ig).

The chemical shifts have been estimated on the basis of the data known for silylated cyclopentadienes⁷, assuming that the trimethylsilyl group affects the shielding of the neighbouring protons in essentially the same fashion. This also enables

TABLE 1

PMR SPECTRUM TYPES AND CHEMICAL SHIFT RANGES EXPECTED FOR RING PROTONS AND TRIMETHYLSILYL GROUPS OF THE ISOMERS (Ib)–(Ig)

Structure of isomers	Spectrum types for ring protons	Expected chemical shifts ranges (δ -scale (ppm)) for			
		Olefin protons	CH groups	CH ₂ groups	(CH ₃) ₃ Si groups
	(Ib) ABMX or AKMX	6.3–6.8	3.40–3.50		2 Signals at 5-position –0.1–0; at 2-position 0.15–0.3
	(Ic) A ₂ X ₂ AMX ₂	6.6–6.9 6.7–7.2		2.9–3.2 2.9–3.2	1 Signal 0.15 to 0.2 2 Signals 0.15 to 0.2
	(Id)				
	(Ie) ABMX or AKMX	6.3–6.8	3.40–3.50		2 Signals at 5-position –0.1–0; at 1-position 0.15–0.25
	(If) ABX ₂ or AMX ₂	6.3–6.8		2.9–3.2	2 Signals 0.15–0.2
	(Ig) A ₂ X ₂	6.6–6.9		2.9–3.2	1 Signal 0.15–0.2

the prediction that the relative magnitudes of the CH_2 chemical shifts would follow the sequence: $\{Ic\} > \{Id\}$, $\{Ig\} > \{If\}$, provided all the isomers are present in the mixture.

Figure 1, b and d-f, shows the detailed scanning of the methyl region (-0.15 to $+0.3$ ppm, of the CH and CH_2 signal (2.9 to 3.5 ppm), and of the olefin region. Apart from the signals of (Ia), five more singlets are present in the methyl region. Two of them (at -0.107 and 0.267 ppm) are of equal intensity, and are significantly broadened at $+30^\circ$. The first signal is related to the $(\text{CH}_3)_3\text{Si}$ group in the 5 position, while the second is related to the $(\text{CH}_3)_3\text{Si}$ group in the vinyl position. An INDOR experiment involving the signal at -0.107 ppm (Fig. 1c) showed that the intensity of this signal falls off when the singlet at $+0.267$ ppm is irradiated (saturation transfer effect). Consequently, the sample contains either isomer (Ib) or (Ie) associated with the two $(\text{CH}_3)_3\text{Si}$ signals discussed above, the isomer taking part in a dynamic process identify the signals corresponding to the ring protons. No methyne signal is observed by the temperature behaviour of the spectrum which will be discussed below.

To distinguish between the possible isomers (Ib) or (Ie) it is necessary to identify the signals corresponding to the ring protons. No methyne signal is observed at 3.40 to 3.50 ppm at $+30^\circ$, owing to its considerable broadening due to a dynamic process. At -30° , however, the signal can be observed as the multiplet at 3.403 ppm in Fig. 1e. Unfortunately, the low intensity of the signal makes it impossible to apply INDOR or tickling experiments to establish the olefin signals of the isomer, the signals being buried beneath the AA'BB' spectrum of isomer (Ia). Irradiation of the 6.3 to 6.8 ppm region of the spectrum at -30° with a second RF field of sufficient power for spin decoupling led to the signal at 3.403 ppm narrowing by a factor of 1.2 to 1.5 times, thus proving the presence of olefin signals in this particular region. However, no

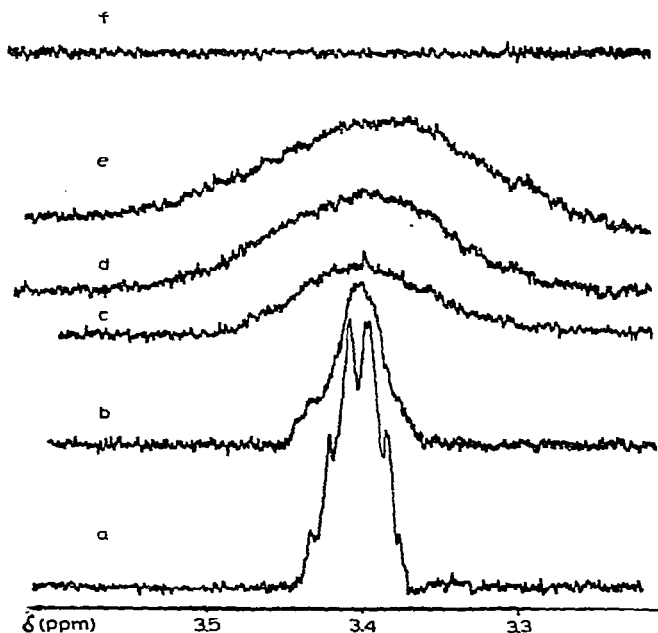


Fig. 2. Methyne proton signal for isomer (Ib) at various temperatures: a, -30° ; b, -20° ; c, $+1^\circ$; d, $+5^\circ$; e, $+10^\circ$; f, $+10^\circ$ the olefin region being irradiated with the second RF field (100 MHz, solution in toluene- d_8).

selective decoupling, and hence no exact chemical shifts, could be achieved. The same experiment carried out at -10° (the half-width $\Delta\nu_{1/2}$ of the line at 3.403 ppm is 17 Hz at this temperature) makes the line disappear, owing to the saturation transfer effect, Fig. 2.

Apart from the signals discussed, two triplets of equal intensity (A_2X_2 spectrum), separated by 1.7 Hz, are also observed; one of these triplets (at 3.091 ppm) is associated with the CH_2 group, the other (at 6.843 ppm) with the olefin protons (Fig. 1d, f). The first triplet, after irradiation of the second with a second RF field, transforms to a singlet (Fig. 3a, b). The INDOR spectrum while monitoring the terminal lines of the signal at 3.091 ppm, gives a response just at the lines of the second triplet. These signals indicate the presence of either isomer (Ic) or (If), the methyl signal of the isomer present being at 0.197 ppm (Fig. 1b); this follows from the 1/1/9 intensity ratio which corresponds to that expected, and also from the identical fashion in which the signals change as the temperature is varied, as discussed below.

Finally one more signal, the quadruplet at 2.945 ppm, occurs in the 2.9–3.5 ppm region of the spectrum. This signal contains splittings equal to 1.4 and 1.65 Hz and is the X_2 part of the AMX_2 spectrum associated with either (Id) or (Ig) in Fig. 1d. The olefin signals of the isomer cannot be observed directly owing to the low concentration of the isomer, to the considerable multiplicity of the signal and to the interference of other signals. These signals have been isolated by means of the spin decoupling technique. When a second RF field is applied at a frequency corresponding to δ 6.813 ppm the 1.4 Hz splitting disappears, while the 1.64 Hz splitting disappears when the spectrum is irradiated at δ 6.993 ppm (Fig. 3c, d), thus indicating that the two olefin

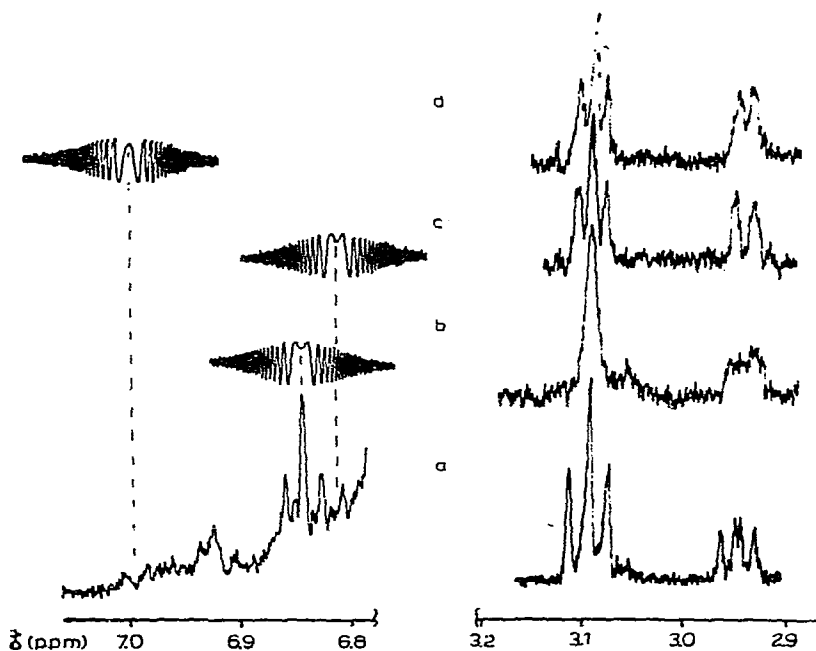


Fig. 3. Double-resonance spectra for the ring protons of (Ic) and (Id) (100 MHz, in toluene- d_8): a, mono-resonance spectrum; b to d, double-resonance spectra with second RF field frequency corresponding to: b, 6.843 ppm; c, 6.813 ppm; d, 6.993 ppm.

protons have chemical shifts of 6.813 and 6.993 ppm. The methyl signals of the isomer lie at 0.137 and 0.223 ppm (Fig. 1d).

From these results it may be concluded that bis(trimethylsilyl)cyclopentadiene is a mixture of isomers. In addition to (Ia), isomers (Ib) or (Ie), (Ic) or (If), (Id) or (Ig) are also present. For this reason metallotropic rearrangement must proceed by one of two possible routes (1,2 or 1,3 shift, see Scheme 1). The resulting isomer, (Ib) or (Ie), can rearrange prototropically. The PMR data however do not allow the complete verification of the structures of the isomers formed, since a complete analysis of the spectra was not possible due to the low concentration of all the isomers [except for (Ia)] in the mixture and by the superposition of the signals in the olefin region of the spectrum. Integration of the methyl region of the spectrum gives (Ia)/(Ib or Ie)/(Ic or If)/(Id or Ig) equal to ca. 132/3.6/2.2/1 at -30° , in other words the total content of all isomers other than (Ia) is 6% or less. The spin-spin coupling constant found for the A_2X_2 spectrum, 1.7 Hz, is more nearly that expected for (Ic) rather than (If), *cf.* the values of $^4J(25)$ 1.7 and $^3J(15)$ 1.4 Hz for silylated cyclopentadienes⁷. This, however, does not provide conclusive proof, and for this reason Diels-Alder or metallation reactions of the compound have been studied and the resulting products analysed in order to find the structures of the isomers of (I).

2. Reactions of bis(trimethylsilyl)cyclopentadiene with dienophiles or a metallating agent (aminostannane)

For (trimethylsilyl)cyclopentadiene, the 5 isomer was shown^{10,11} to be less reactive than the 2 isomer and somewhat more reactive than the 1 isomer as far as Diels-Alder transformations were concerned. For this reason Diels-Alder reactions can hardly be expected to give a reliable composition for the mixture, but despite this

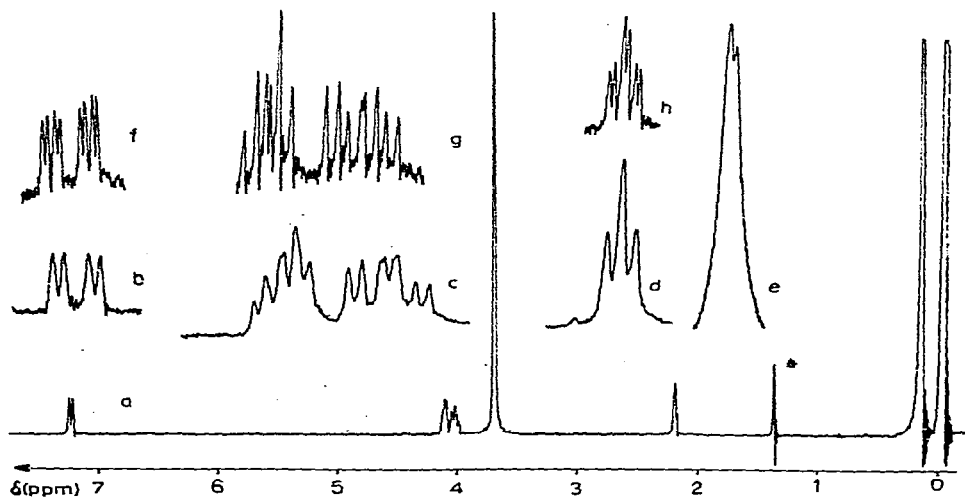
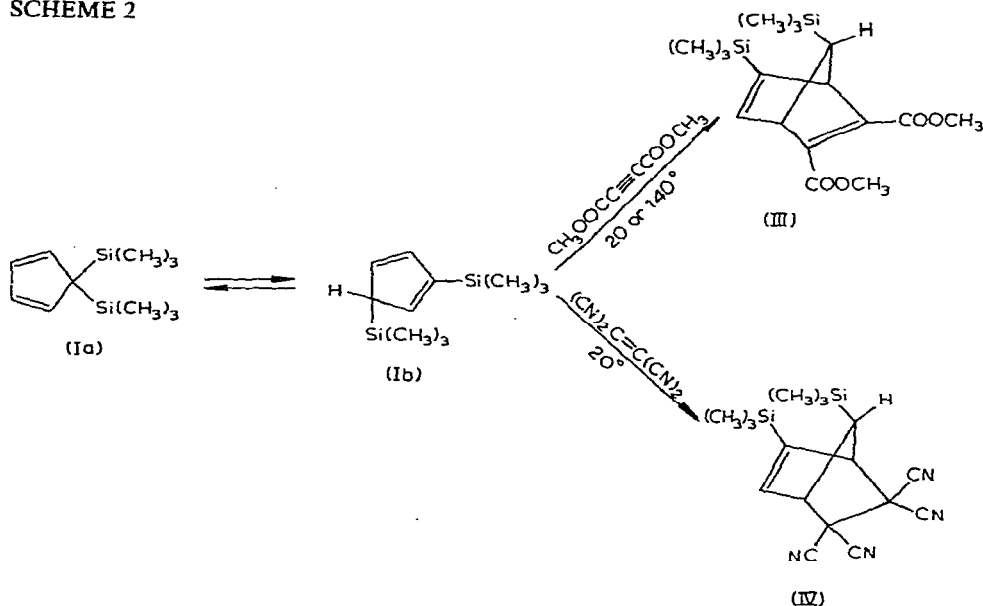


Fig. 4. PMR spectra of Diels-Alder adducts (III) and (IV) (100 MHz, cyclohexane internal reference). a, Overall spectrum of the adduct (III) in CCl_4 , the asterisk indicates the signal of internal C_6H_{12} ; b to e, signals of the protons H_6 (b), H_1 and H_4 (c), H_7 (d), and carbomethoxyl protons (e) in the spectrum of (III) scanned at lower sweep rate and sweep-width (the 2- and 3-carbomethoxyl proton peak separation is equal to 0.3 Hz); f to h, the respective signals in the spectrum of the $CDCl_3$ solution of (IV).

qualification they are quite applicable to the examination of the structures of those isomers whose concentration may be low but whose reactivity towards the dienophile is high. For bis(trimethylsilyl)cyclopentadiene (I), the reactivity of the major 5,5 isomer (Ia) is also rather low. We have studied the reactions of (I) with tetracyanoethylene at 20° or with dimethyl acetylenedicarboxylate at 20° and 140°. In every case the adducts (III) and (IV), which correspond to the 2,5 isomer (Ib), have been isolated. No other compounds could be isolated or identified spectrally. The concentrations of these are probably at or below 1%.

SCHEME 2



The structures of (III) and (IV) follow from the spectra shown in Fig. 4. Integration reveals just one olefin proton and two bridgehead protons for both the compounds. The orientation of the $(\text{CH}_3)_3\text{Si}$ group in the 7-position in adduct (IV) follows from the long-range spin-spin coupling constant, ${}^4J(67)$ 0.4 Hz.

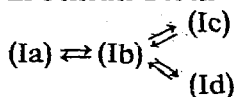
TABLE 2

PMR SPECTRAL DATA FOR THE ADDUCTS (III) AND (IV)^a

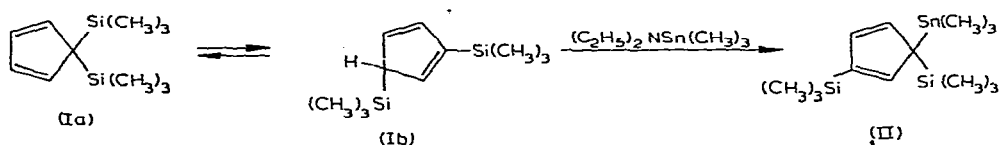
Compound ^b	Chemical shifts							Coupling constants					
	H_1	H_4	H_6	H_7	^c	^d	^e	J_{14}	J_{16}	J_{17}	J_{46}	J_{47}	J_{67}
(III)	4.04	4.14	7.16	2.23	3.68	0.11	-0.08	2.4	2.8	1.1	0.8	1.1	0
(IV)	3.99	4.06	6.82	1.81		0.28	0.05	3.0	1.7	1.0	1.0	1.0	0.4

^a Chemical shifts are in ppm (δ -scale), coupling constants in Hz (absolute value); the shifts are accurate to ± 0.01 ppm; the constants to ± 0.1 Hz. ^b Solutions in CCl_4 (III) and in CDCl_3 (IV). ^c Esteral methyl groups in (III); their peak separation is equal to 0.3 Hz at 100 MHz. ^d 5-Positioned trimethylsilyl group. ^e 7-Positioned trimethylsilyl group.

Diels–Alder reactions allow the structures (Ib) and (Ie) of the isomer equilibrated with (Ia) to be established unequivocally and indicate that (Ib), and not (Ie), exists in this system. From this it follows that only one of the rearrangement routes shown in Scheme 1 is involved in this reaction.



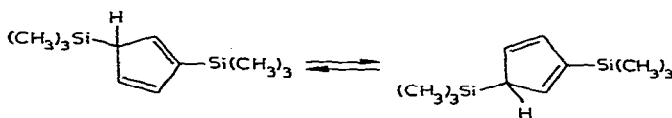
The structure of isomer (Ib) may also be established by the metallation reaction with an aminostannane, this being specific to compounds containing an acidic hydrogen atom. This reaction was used in our previous work¹ to demonstrate the existence and structure of the short-lived 2,5-bis(trimethylstannyl)cyclopentadiene isomer. In the reaction between (I) and excess (diethylamino)trimethylstannane, bis(trimethylsilyl)(trimethylstannyl)cyclopentadiene (II) is obtained in 64% yield³.



Details of the verification of structure (II), of dienic reactions and other properties of polymetallated cyclopentadienes will be published more fully elsewhere.

3. Degenerate metallotropic rearrangement through 1,2 shift in 2,5-bis(trimethylsilyl)cyclopentadiene (Ib)

At -30° bis(trimethylsilyl)cyclopentadiene is a mixture of four isomers: (Ia), (Ib), (Ic), and (Id). Integration in the methyl region of the spectrum gives an isomer ratio of ca. 132/3.6/2.2/1 at this temperature. On gradually raising the temperature from -30° up to $+10^\circ$, an increase in the intensities of the signals of all the isomers, (Ib) to (Id), occurs but the shapes of the signals all remain unaffected except for the CH proton signal of (Ib) at 3.403 ppm (Fig. 2, Table 1). The latter signal gradually broadens and finally disappears at $+30^\circ$. Note that the methyl signals retain their half-width at $+20^\circ$. This temperature dependence indicates that a dynamic process occurs involving (Ib), the process being degenerate and not affecting the chemical environment of the trimethylsilyl group, but, on the other hand, making the H_5 methyne proton and one of the olefin protons interchange their positions (see above regarding saturation transfer experiments at $+10^\circ$). The only possible process of this type is a degenerate metallotropic rearrangement proceeding via a 1,2 shift of $Si(CH_3)_3$.

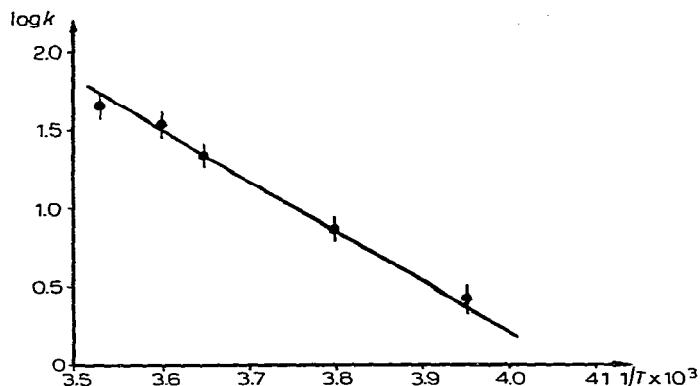


The slow exchange approximation approach, as applied to the H_5 signal width (see Table 3), gives the energy and entropy of activation as $E_a 14.5 \pm 1.8$ kcal/

TABLE 3

HALF-WIDTH OF THE METHYNE SIGNAL OF (Ib) AT VARIOUS TEMPERATURES

		$t(^{\circ}\text{C})$ -30	-20	-10	+1	+5	+10
$\Delta\nu_{\frac{1}{2}}$	(Hz)	2.4	3.4	4.8	9.6	13.6	17.0
$\Delta\nu_{\frac{1}{2}}^*$	(Hz ^a)	0	1 \pm 0.2	2.4	7.2	11.2	14.6

^a $\Delta\nu_{\frac{1}{2}}^* = \Delta\nu_{\frac{1}{2}} - 2.4$.Fig. 5. Log k vs. $(1/T)$ for the degenerate metallotropic rearrangement in (Ib).

mole and $\Delta S^{\ddagger} - 1.5 \pm 4$ e.u. respectively. The linear nature of the $\log k = \log (\pi \cdot \Delta\nu_{\frac{1}{2}})$ vs. $1/T$ plot is shown in Fig. 5.

Despite their approximate nature (owing to the significant multiplicity of the H_5 signals and to the relative inaccuracy of the linearisation technique), the thermodynamic quantities have values close to those found for the metallotropic rearrangement in 5-(trimethylsilyl)cyclopentadiene. Thus, the introduction of a second $(\text{CH}_3)_3\text{Si}$ group in a somewhat remote position in the ring has little effect on the degenerate process, indicated by the very slight increase in ΔG_{300} [16.6 kcal/mole for (Ib) relative to 15.2 kcal/mole for $\text{C}_5\text{H}_5\text{Si}(\text{CH}_3)_3$, ref. 7].

4. The metallotropic tautomeric equilibrium (Ia) \rightleftharpoons (Ib)

The $(\text{CH}_3)_3\text{Si}$ signals of all the isomers retain their shapes as the temperature is raised from -30° to $+20^{\circ}$. However, the intensity of the signal corresponding to the 2,5 isomer increases while that for the 5,5 isomer decreases, indicating that the equilibrium (Ia) \rightleftharpoons (Ib) is being shifted to the right. The (Ib) to (Ia) ratio is 1/23.9 at

TABLE 4

THE $(\text{CH}_3)_3\text{Si}$ LINE HALF-WIDTH FOR THE 2,5 ISOMER AT VARIOUS TEMPERATURES

		$t(^{\circ}\text{C})$ 15	20	25	30	35	40	45	50	55
$\Delta\nu_{\frac{1}{2}}$	(Hz)	0.7	1.4	1.55	1.7	2.8	4.15	5.5	8.2	9.4
$\Delta\nu_{\frac{1}{2}}^*$	(Hz ^a)	0.3	1.0	1.15	1.3	2.4	3.75	5.1	7.8	9.0

^a $\Delta\nu_{\frac{1}{2}}^* = \Delta\nu_{\frac{1}{2}} - 0.4$.

-20° , $1/17.5$ at -5° and $1/11.8$ at $+10^\circ$. Above $+10^\circ$ the $(\text{CH}_3)_3\text{Si}$ signals associated with (Ib) and (Ia) gradually broaden, Fig. 6. This is best observed for the (Ib) signals lying at -0.107 and 0.267 ppm which broaden in an identical fashion. The INDOR

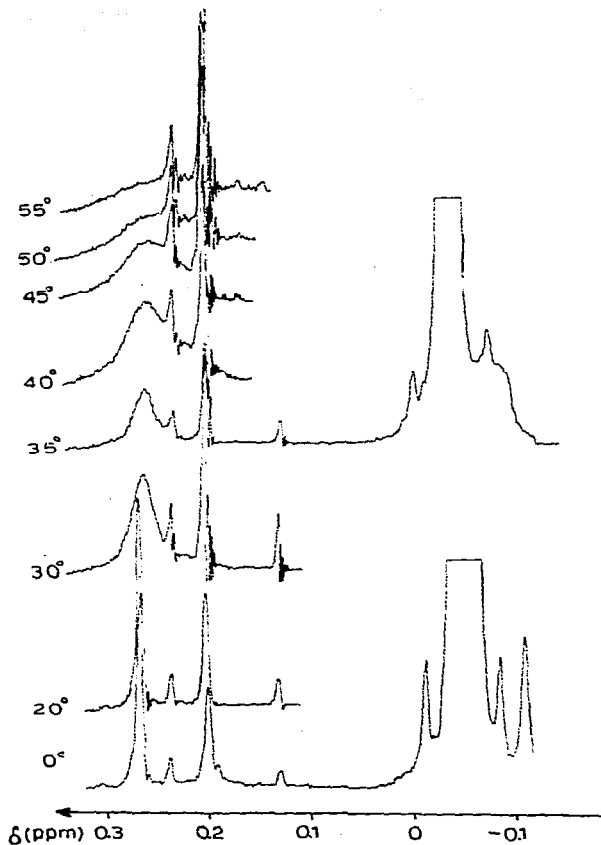


Fig. 6. $(\text{CH}_3)_3\text{Si}$ signals (100 MHz, toluene- d_8 solution) at various temperatures.

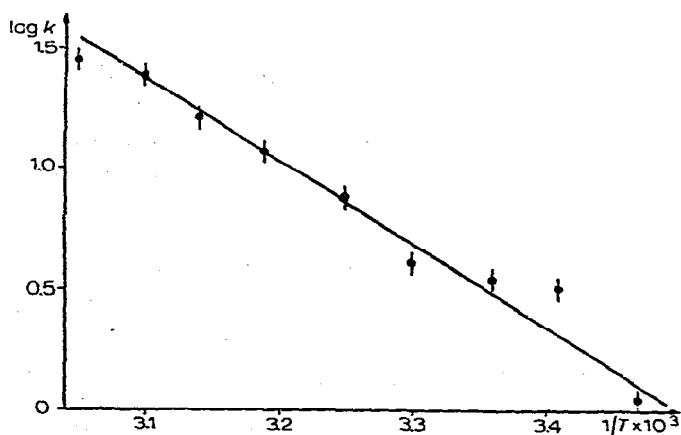


Fig. 7. $\log k$ vs. $(1/T)$ for the (Ib) \rightarrow (Ia) rearrangement.

saturation transfer for the signals has been described above (see Fig. 1c). Table 4 shows the half-width for the signal at 0.267 ppm associated with the $2(\text{CH}_3)_3\text{Si}$ group of (Ib) at various temperatures. Slow exchange analysis of the temperature dependence (the line-width has been assumed to be 0.4 Hz at zero exchange) gives E_a 15.8 ± 1.0 kcal/mole and ΔS^\ddagger -4.7 ± 4 e.u. for the rearrangement of (Ib) to (Ia), Fig. 7. On increasing the temperature further, the $(\text{CH}_3)_3\text{Si}$ signals of (Ia) coalesce with those of (Ib). The averaged signal becomes narrower and narrower and is shifted upfield. To eliminate the effect of self-association and solvation upon the chemical shifts, we studied the spectra of (I) dissolved in decalin (concentration, 2%) (Fig. 8). The averaged $(\text{CH}_3)_3\text{Si}$ chemical shifts found at various temperatures are listed in Table 5.

The data have been processed with a MINIMAX 1 program (as in the case of

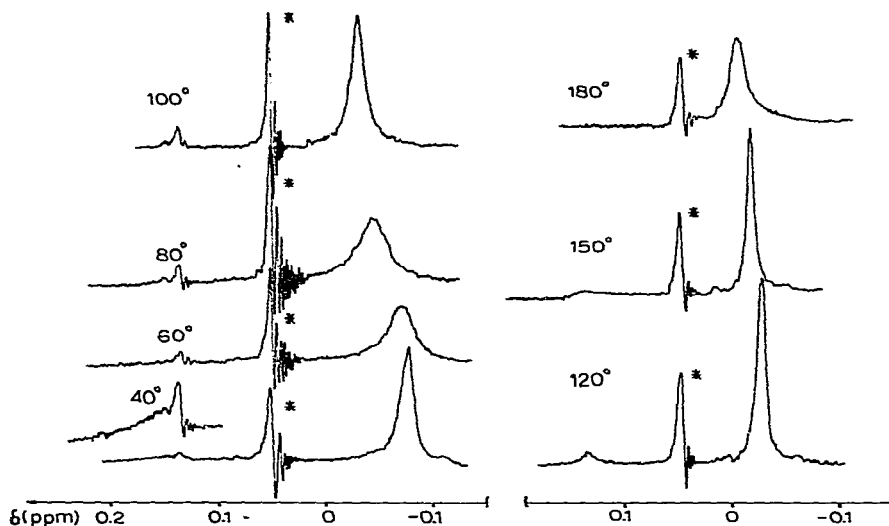


Fig. 8. The $(\text{CH}_3)_3\text{Si}$ signals of (I) (100 MHz, 2% solution in decalin) at various temperatures. Asterisk indicates the signals of a hexamethyldisiloxane internal reference.

TABLE 5

AVERAGED $(\text{CH}_3)_3\text{Si}$ CHEMICAL SHIFTS AND LINE HALF-WIDTHS FOR (Ia) AND (Ib) AT VARIOUS TEMPERATURES^a

	$t(^{\circ}\text{C})$	70	75	80	85	90	95	100
δ		-0.058	-0.048	-0.044	-0.039	-0.038	-0.035	-0.034
$\Delta\nu_{\frac{1}{2}}$	(Hz)	4.0	3.6	3.2	3.9	2.8	1.8	1.5
$\Delta\nu_{\frac{1}{2}}^*$	(Hz) ^b	3.6	3.2	2.8	2.5	2.4	1.4	1.1
	$t(^{\circ}\text{C})$	105	110	115	120	125	130	
δ		-0.032	-0.030	-0.028	-0.027	-0.025	-0.023	
$\Delta\nu_{\frac{1}{2}}$	(Hz)	1.4	1.1	1.0	1.0	0.9	0.9	
$\Delta\nu_{\frac{1}{2}}^*$	(Hz) ^b	1.0	0.7	0.6	0.6	0.5	0.5	

^a Chemical shifts are in ppm (δ -scale). ^b $\Delta\nu_{\frac{1}{2}}^* = \Delta\nu_{\frac{1}{2}} - 0.4$.

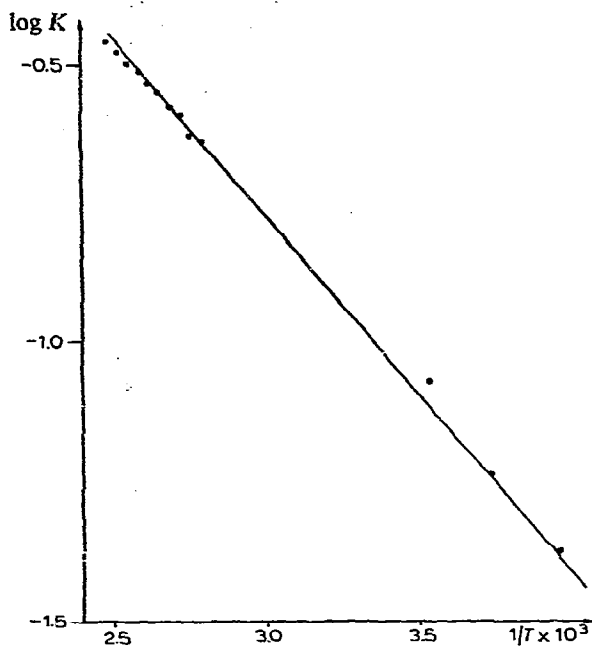


Fig. 9. Log K vs. $(1/T)$ for the (Ia) \rightleftharpoons (Ib) metallotropic equilibrium.

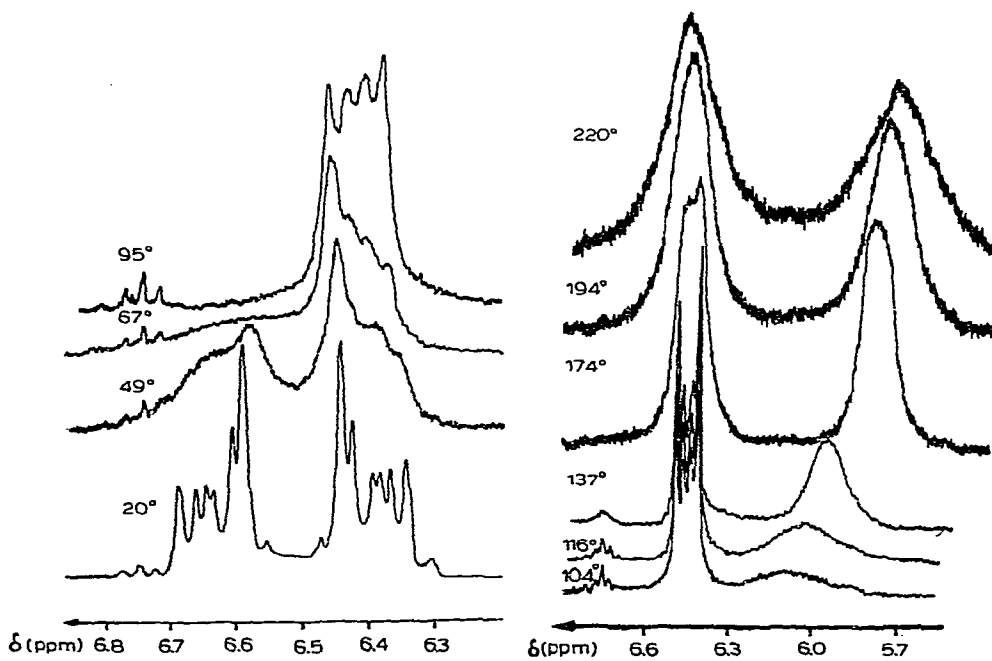


Fig. 10. The spectra of the olefin protons of bis(trimethylsilyl)cyclopentadiene at various temperatures (60 MHz, neat).

bis(trimethylgermyl)cyclopentadiene¹), to give ΔH 2.73 kcal/mole and ΔS 4.99 e.u. for the (Ib) \rightleftharpoons (Ia) equilibrium. The equilibrium constants found from the isomer ratio at lower temperatures (-10° , -5° and $+5^\circ$) agree well with the $\log K$ vs. $(1/T) \times 10^3$ curve shown in Fig. 9. The equilibrium constants and the rate constants for the rearrangement show that for the reverse process, (Ia) \rightarrow (Ib), E_a 18.6 ± 1 kcal/mole and ΔS^\ddagger 0.3 ± 4 e.u.

On increasing the temperature, the signals of the olefin protons behave in a similar manner to those of bis(trimethylgermyl)cyclopentadiene studied earlier¹. Figure 10 shows all the successive steps occurring in the system, the 2,3-proton signal of (Ia) being broadened and then gradually shifted upfield. The chemical shifts for the averaged signals of the ring protons of (Ia) and (Ib) for various temperatures are listed in Table 6. Up to 120° , the shapes of the signals associated with (Ic) and (Id) remain unchanged. Below this temperature, hydrogen migration is slow relative to the NMR time scale.

The data above demonstrate that the rearrangement of the 5,5 isomer (Ia) to the 2,5 isomer (Ib) is accompanied by a loss of enthalpy and a gain of entropy. This may be due to the significant spatial hindrance which occurs in (Ia) due to interaction of two large $(\text{CH}_3)_3\text{Si}$ groups in the 5-position. In bis(trimethylgermyl)cyclopentadiene, although the 5,5 isomer is energetically more favourable, a similar increase in the entropy is observed¹.

There is no significant difference between the activation energies associated with the degenerate rearrangement (1,2 shift) in the 2,5 isomer (Ib) and the nondegenerate rearrangement (1,3 shift) of (Ib) to (Ia). The problem as to whether the transformation of (Ia) to (Ib) is a true 1,3 shift or whether it consists of a succession of rapid 1,2 shifts involving the structure (Ie) remains unresolved. To date, there is no evidence in favour of the intermediate formation of this isomer. Thus no resonance signals were observed at lower temperatures although under these conditions the isomer should have been capable of detection even at concentration levels as low as 1%. The concentration cannot be greater than 1% at higher temperatures either, otherwise the fast exchange would have shifted the signals of the 1,4-protons of the ring upfield in contrast to the downfield shift observed experimentally, Table 6.

TABLE 6

AVERAGE OLEFIN PROTON CHEMICAL SHIFTS FOR (Ia) AND (Ib) AT VARIOUS TEMPERATURES (60 MHz, NEAT). THE SHIFTS FOUND ARE BASED ON THE CENTRE OF GRAVITY OF THE MULTIPLET^a

	$t(^{\circ}\text{C})$	-15	-4	+4	+20	+31	+39	+45	+62	+67	+74	+83	+100	+104
δ 2,3		6.68	6.69	6.68	6.68	6.68	6.68	6.68	6.63	6.60	6.51	6.45	6.31	6.14
δ 1,4		6.44	6.45	6.44	6.44	6.44	6.44	6.44	6.45	6.43	6.45	6.45	6.48	6.48
	$t(^{\circ}\text{C})$	+116	+124	+129	+134	+137	+142	+143	+149	+156	+157	+162	+174	+194
δ 2,3		6.12	6.01	5.99	5.97	5.95	5.94	5.92	5.90	5.87	5.87	5.87	5.80	5.80
δ 1,4		6.48	6.48	6.47	6.47	6.47	6.47	6.47	6.47	6.47	6.45	6.45	6.46	6.47

^a Chemical shifts are in ppm (δ -scale).

5. Hydrogen migration ($Ic \rightleftharpoons Ib$) and ($Id \rightleftharpoons Ib$).

At temperatures up to $+120^\circ$, the signals of (Ic) and (Id) are unaffected as far as their positions and shapes are concerned. At higher temperatures, however, (Figs. 8, 10 and 11), the signals of (Ic) and (Id) broaden significantly while the signals

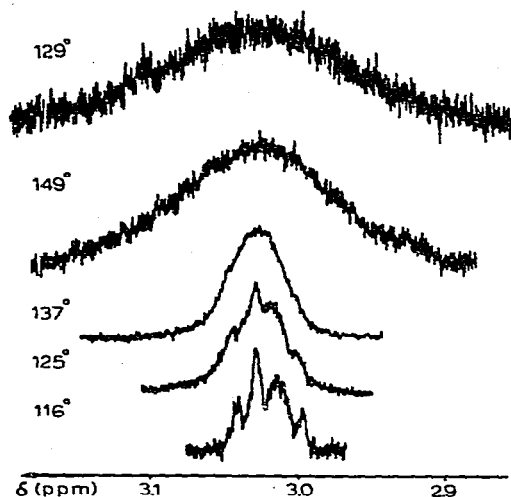


Fig. 11. PMR signal of the methylene protons in (Ic) and (Id) as a function of temperature (60 MHz, neat).

of (Ia) and (Ib), being subject to a fast exchange, also start to broaden once more. Above $+162^\circ$ the ring signals coalesce, as do the methyl signals. At intermediate rates of exchange ($+143^\circ$), irradiation of any of the ring signals with a second RF field causes all the other signals to disappear owing to the saturation transfer effect. The effects observed at $+120^\circ$ to $+220^\circ$ indicate that the hydrogen migrations ($Ib \rightleftharpoons Ic$) and ($Id \rightleftharpoons Ib$) are fast relative to the NMR time scale under these conditions. In the system under discussion no dimerisations can occur at these temperatures which may obscure the hydrogen migration in monosilylated cyclopentadienes. The line-width has been analysed for the $(CH_3)_3Si$ singlet of (Ic) at 124° to 160° giving an estimate of ca. 21 kcal/mole for the activation energy of the rearrangement of (Ic) to (Ib), this value being close to that found for other substituted cyclopentadienes and for cyclopentadiene itself¹²⁻¹⁴.

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REFERENCES

- 1 Yu. A. Ustynyuk, A. V. Kisin, and A. A. Zenkin, *J. Organometal. Chem.*, 37 (1972) 101.
- 2 Yu. A. Ustynyuk, N. M. Sergeev, A. V. Kisin, Yu. K. Grishin, N. N. Veniaminov, and G. A. Shchembelov, *Vth International Conference on Organometallic Chemistry*, Moscow, 1971, Abstr. No. 328.
- 3 I. M. Pribytkova, A. V. Kisin, Yu. N. Luzikov, N. P. Makoveyeva, V. N. Torocheshnikov, and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 30 (1971) C57.

- 4 E. W. Abel and S. Moorhouse, *J. Organometal. Chem.*, 29 (1971) 227.
 - 5 N. N. Veniaminov, Yu. A. Ustynyuk, N. V. Alekseev, I. A. Ronova, and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 13 (1972) 136.
 - 6 A. A. Fomichev, *Zh. Strukt. Khim.*, 9 (1968) 700.
 - 7 N. M. Sergeev, G. I. Avramenko, A. V. Kisin, V. A. Korenevsky, and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 32 (1971) 55.
 - 8 W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, 89 (1967) 1438.
 - 9 A. V. Kisin, V. A. Korenevsky, N. M. Sergeev, and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 34 (1972) 93.
 - 10 C. S. Kraihanzel and M. L. Losee, *J. Amer. Chem. Soc.*, 90 (1968) 4701.
 - 11 A. J. Ashe, III, *J. Amer. Chem. Soc.*, 92 (1970) 1233.
 - 12 G. I. Avramenko, N. M. Sergeev, and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 37 (1972) 89.
 - 13 W. Roth, *Tetrahedron Lett.*, (1964) 1009.
 - 14 S. McLean and P. Haynes, *Tetrahedron Lett.*, (1964) 2385.
- J. Organometal. Chem.*, 42 (1972)