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NMR SPECTROSCOPY OF METAL CYCLOPENTADIENYLS IX*. NON-DEGENERATE METALLOTROPIC REARRANGEMENT IN BIS(TRIMETHYLGERMYL)- AND BIS(TRIMETHYLSTANNYL)-CYCLOPENTADIENES

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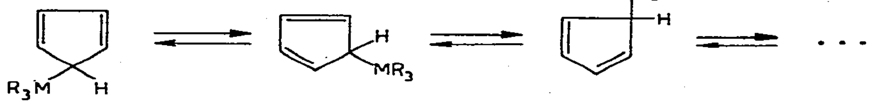
SUMMARY

The PMR spectra of $C_5H_4[Ge(CH_3)_3]_2$ and $C_5H_4[Sn(CH_3)_3]_2$ have been studied at temperatures over the range −130 to +190°. A non-degenerate metallotropic rearrangement has been found to occur in both compounds. The 5,5 isomers are transformed to the 2,5 isomers via a 1,3 metallic shift. The 5,5 isomers are the most stable in both cases. Chemical shifts of the ring and methyl protons have been studied for the germanium derivative as a function of temperature. The results have been processed by means of a MINIMAX 1 program (an improved version of the relaxation method) on a BESM-6 large computer. The $C_5H_4[Ge(CH_3)_3]_2$ metallotropic rearrangement has the thermodynamic constants $\Delta H = 4.8 \pm 0.3$ kcal/mole, $\Delta S = 11.5 \pm 1$ e.u. The metallotropic equilibrium lies well towards the 5,5 isomer for the tin compound, irrespective of the temperature. The metallotropism in this case has been demonstrated by the use of an aminostannane.

σ-Cyclopentadienyl derivatives of transition and non-transition metals have recently attracted the attention of many investigators, since these compounds are fluxional molecules capable of degenerate intramolecular rearrangements. Many papers have appeared relating to the σ-cyclopentadienyl derivatives of the Group IVB elements[1–6]. The results of these papers, as well as those obtained by us[7–20], may be summarised as follows.

(*i*) Compounds of formula $C_5H_5MR_3$ have non-planar cyclopentadienyl rings (C_s symmetry). The C_5 atom lies outside the plane of the ring while the metal atom is associated with the olefin atoms of the ring**.

(*ii*) These compounds are subject to an intramolecular metallotropic rearrangement which occurs through a 1,2 shift of the metal according to the scheme:



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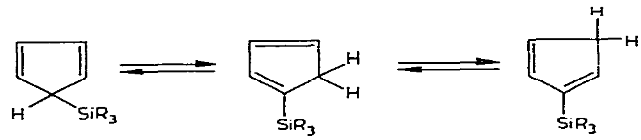
[*] For Part VIII see ref. 14.

[**] *Note added in proof*: Bentham and Rankin[30] have recently shown that in $C_5H_5SiH_3$, the cyclopentadienyl ring is planar.

The rate of rearrangement increases, while the activation energy decreases, as the atomic number of the element increases in the series Si, Ge, Sn. For the series $C_5H_5Si(CH_3)_nCl_{3-n}$ (where n is 0, 1, 2, 3) the rate decreases with an increase in the number of electron-accepting substituents (chlorines).

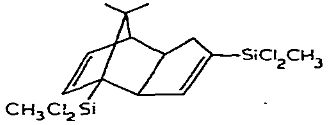
(*iii*). The silicon compounds $C_5H_5Si(CH_3)_nCl_{3-n}$ undergo a further rearrangement, a prototropic rearrangement which is also characteristic of cyclopentadiene itself and of its alkylated derivatives. The rearrangement again occurs as a series of 1,2 shifts and is six to seven orders of magnitude slower than the metal migration. As a result all three isomers [(Ia), (Ib) and (Ic)] are present in the reaction mixture. An increase in the number of halogen atoms present leads to an increase in the content of vinylic isomers. Of these, isomer (Ib) is present in the highest concentration.



(Ia) (Ib) (Ic)

The equilibrium is completely shifted towards (Ia) for the Ge and Sn derivatives.

(*iv*). Isomers (Ib) and (Ic) can dimerise via a Diels–Alder reaction which is very selective and, in the case of (Ib), leads to dimer (II).



(II)

(*v*). All these data agree well with a model which assumes that the transition state involves a build up of multicentre bonds through the interaction of vacant metal *d* orbitals with ring π orbitals.

Introduction of a substituent into the cyclopentadienyl ring causes the rearrangement to become non-degenerate, *i.e.* a tautomeric metallotropic equilibrium. To date only the compounds $CH_3C_5H_4M(CH_3)_3$ (M is Si, Ge, Sn) have been studied by PMR spectroscopic methods[4,5], and even with these compounds the data are not extensive. This may be attributed to the fact that it is extremely difficult to analyse the exchange processes occurring in such complicated seven-spin systems, owing to the superimposition of the spectra due to the different isomers. On the other hand, metal cyclopentadienyls with substituents in the ring appear to be promising candidates for the study of rearrangement mechanisms, especially with regard to the question as to whether a metallic 1,2 shift occurs in these compounds. For this reason we have synthesised a number of polymetallated cyclopentadienes containing two, three, or four identical or different groups $M(CH_3)_3$ (M is Si, Ge, Sn) in the cyclopentadienyl ring[21] and have studied these by means of PMR, ^{13}C–$\{^1H\}$ NMR, ^1H–$\{^{119}Sn\}$ NMR and mass spectrometry. The present work is concerned with the PMR spectra of bis(trimethylgermyl)cyclopentadiene (III) and bis(trimethylstannyl)-cyclopentadiene (IV).

EXPERIMENTAL

The synthesis of compounds (III) and (IV) has been previously described[21]. PMR spectra were measured on a HA-100D (Varian, 100 Mc) spectrometer, the resolution was not worse than 0.2 Hz. The second RF field (INDOR-experiments) was set with a D-890B audio frequency oscillator accurate to ±0.1 Hz. Field sweep was used when studying the temperature dependences. At −90 to +20°, 10% (v/v) solutions of (III) and (IV) in cyclopentane were used; at higher temperatures the samples were neat liquids containing a C_5H_{10} additive. Cyclopentane was used as an internal reference. Chemical shifts are in δ-scale values $[\delta(C_5H_{10})\,1.500\ \text{ppm}]$. Before undertaking any measurements, the compounds were twice distilled in an argon atmosphere, degassed at 10^{-4} mm, and sealed.

Bis(trimethylgermyl)cyclopentadiene (III)

The PMR spectrum at −10° indicates the presence of a well-resolved AA'BB' system at lower fields, assigned to the cyclopentadienyl protons (Fig. 1b), and a singlet at 0.09 ppm belonging to six equivalent methyls, the intensity ratio being 1/1/9. The spectrum provides an unambiguous verification of the structure of the

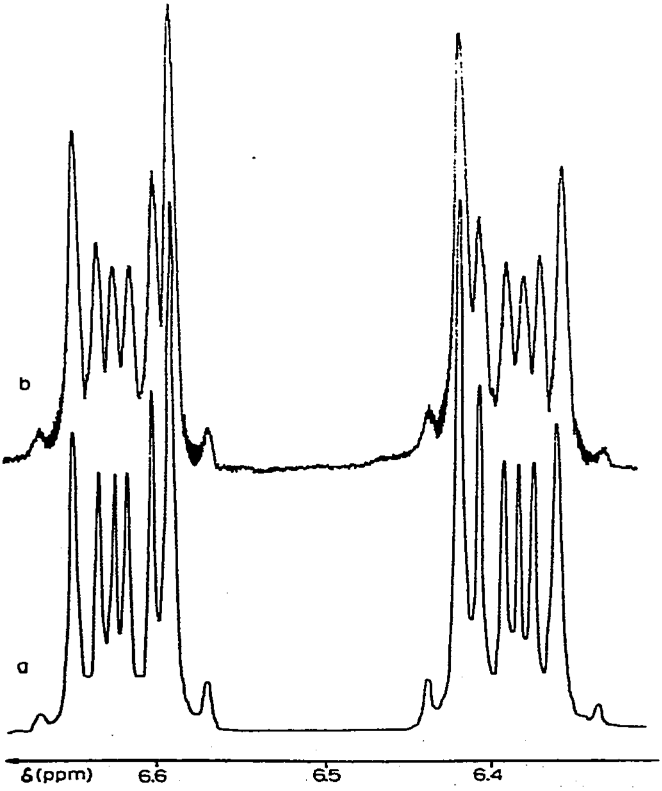


Fig. 1. PMR spectrum of olefin protons for bis(trimethylgermyl)cyclopentadiene at −10°: a, calculated using the YaMR-1 program; b, experimental.

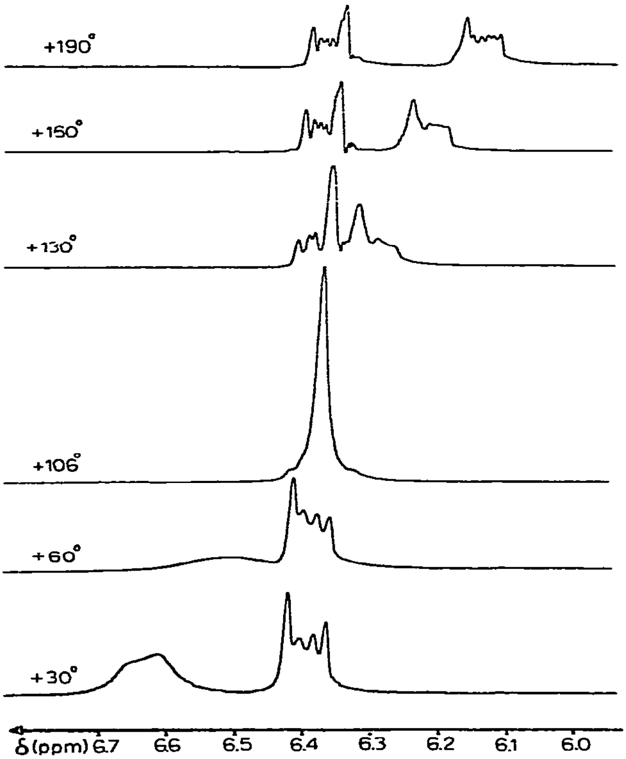


Fig. 2. PMR spectra of olefin protons for bis(trimethylgermyl)cyclopentadiene at various temperatures.

5,5 isomer (IIIa). Analysis of the AA'BB' spectrum gives: $\delta(AA')=6.62$, $\delta(BB')=6.39$ ppm; $J(AA')=J(BB')=2.30$, $J(AB)=J(A'B')=4.5$, $J(AB')=J(A'B)=1.3$ Hz. All the constants possess the same sign (positive). The spectrum calculated with these parameters using a YaMR-1 program[22] is shown in Fig. 1a.

In the study of metallotropic tautomeric mechanisms in metal cyclopentadienyls a crucial point is the assignment of the olefinic protons. The sign criterion suggested by us earlier[9,11] is irrelevant in this case. However, by using the PMR evidence (to be published later) accumulated for the compounds and the dynamic processes occurring therein, we may conclude that the higher-field signal is that of protons $H_{1,4}$ (BB' part) while $H_{2,3}$ lies at lower fields (AA' part). In other words, the chemical shigts are arranged in the same manner as they are in cyclopentadiene and in the $C_5H_5MR_3$ compounds (M = Si, Ge)[11,12,23].

One striking feature is the formation of the *gem*-disubstituted compound (IIIa) from the organometallic compound (V) and trimethylbromogermane. Other similar reactions are also unusual[21]. Electrophilic attack on substituted cyclopentadienyl anions is known to result in the 1,5 and 2,5 rather than 5,5 isomers[24], irrespective of the substituent present in the ring. For this reason compounds (IIIb) and (IIIc)* might have been expected as the predominant products although, in

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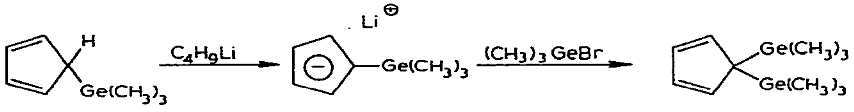
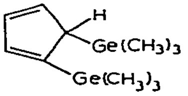
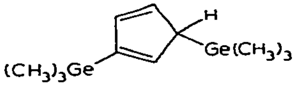
* The existence of (IIIc) has been proved by Pribytkova[31] using a Diels–Alder reaction of (III) with dimethyl acetylenedicarboxylate or tetracyanoethylene.



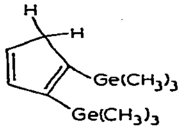
(V) (IIIa)



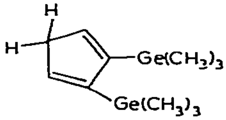
(III b)



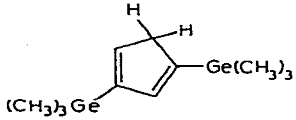
(III c)



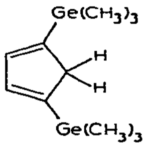
(III d)



(IIIe)



(III f)



(IIIg)

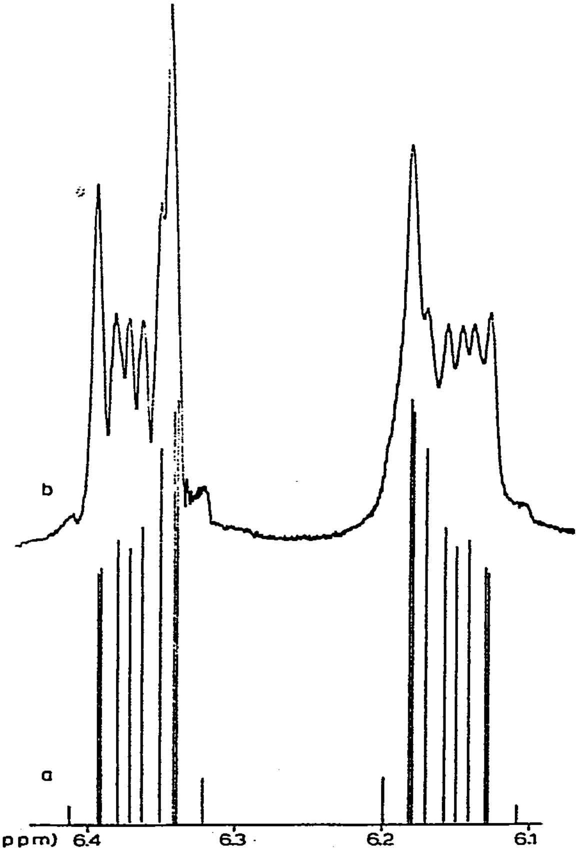


Fig. 3. PMR spectrum of olefin protons for bis(trimethylgermyl)cyclopentadiene at +180°: a, calculated; b, experimental.

principle, compounds (IIId-g) are also probable as they might be formed through a prototropic rearrangement. The spectrum, however, exhibits no other signals. It is possible that the initial product formed is (IIIc) which rapidly rearranges to the thermodynamically more stable isomer (IIIa) via a 1,3 metallotropic shift. This suggestion agrees very well with the rates of the tautomeric transformation (IIIa)→(IIIc) discussed below.

The PMR spectra of (III) are temperature dependent, thus revealing the presence of a metallotropic rearrangement in the system, (Fig. 2). The spectrum is not affected by cooling the sample down to −30°, but on heating the $H_{2,3}$ signal (AA′ part) is broadened (at +20°), and then gradually shifted upfield. The $H_{1,4}$ chemical shift remains practically constant and undergoes a much weaker broadening effect. Both the chemical shifts coincide at 106°. At even higher temperatures, the $H_{2,3}$ signal moves further upfield to give a new AA′BB′ system in which $H_{1,4}$ is located at lower fields and is well resolved while $H_{2,3}$ is located at higher fields and is significantly broadened. At 180°, the parameters are: $\delta(AA') = 6.36$, $\delta(BB') = 6.13$ ppm; $J(AA') = J(BB') = 2.05$, $J(AB) = J(A'B') = 4.00$, $J(AB') = J(A'B) = 1.10$ Hz. The calculated spectrum is shown in Fig. 3 together with the experimental one. It is evident that all the four spin–spin coupling constants are lower for the high-temperature spectrum.

Over the temperature range −10 to +190°, the CH_3 signal moves gradually downfield. All the chemical shifts are listed in Table 1 for the various temperatures. All the temperature dependences of the spectrum were reversible and reproducible.

The temperature behaviour of the spectrum may be explained as follows. 5,5-Bis(trimethylgermyl)cyclopentadiene (IIIa) rearranges metallotropically via a reversible 1,3 shift involving one of the $(CH_3)_3Ge$ groups and gives the isomer (IIIc).

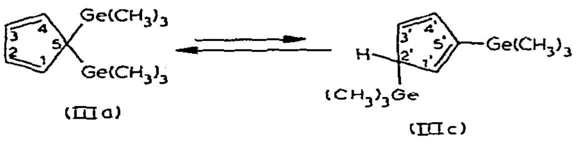
TABLE 1

PROTON CHEMICAL SHIFTS AND EQUILIBRIUM CONSTANTS OF METALLOTROPIC REARRANGEMENT IN BIS(TRIMETHYLGERMYL)CYCLOPENTADIENE (III) AT VARIOUS TEMPERATURES[a]

t (°C)	T (°K)	$\delta^{obs}_{2,3}$	$\delta^{obs}_{1,4}$	δ^{obs}_{Me}	K_1	K_2
−10[b]	263	6.616	6.394	0.089		
−0	273	6.613	6.391	0.089		
+10	283	6.610	6.390	0.090		0.016
+20	293	6.606	6.387	0.092		0.051
+20[c]	293	6.636	6.387			
+40	313	6.617	6.389	0.106		0.089
+50	323	6.572	6.387	0.107		0.114
+60	333	6.511	6.385	0.108	0.211	0.139
+80	353			0.109		0.167
+106	379	6.37		0.115	0.554	0.361
+130	403	6.292	6.373	0.122	0.843	0.690
+140	413	6.275	6.368	0.123	1.021	0.750
+150	423	6.230	6.366	0.124	1.162	0.815
+160	433	6.203	6.365	0.126	1.338	0.960
+170	443	6.178	6.363	0.127	1.529	1.042
+180	453	6.157	6.363	0.129	1.716	1.227
+190	463	6.133	6.361	0.130	1.966	1.333

[a] Chemical shifts are in δ scale throughout. [b] For the 10% solution in C_5H_{10} at −10 to +20°. [c] Neat liquids at +20 to +190°.

At room temperature, the equilibrium is shifted towards (IIIa) almost completely, this isomer being more stable thermodynamically. An increase in the temperature leads to an increase in the (IIIc) content in the system. Under fast exchange limiting conditions (in our case, above 50°), the spectrum exhibits averaged signals belonging to $H_{2,3}$ in (IIIa) and $H_{2',3'}$ in (IIIc), $H_{1,4}$ in (IIIa), and $H_{1',4'}$ in (IIIc), as well as the averaged signals of the CH_3 groups. The $H_{2'}$ signal in (IIIc) should be shifted by 2 to 2.5 ppm upfield from $H_{2,3}$ in (IIIa), as observed in $C_5H_5Ge(CH_3)_3$[12]. The chemical shifts of $H_{1,4}$ in (IIIa) and $H_{1',4'}$ in (IIIc) should differ only slightly, and the same is true for the signals corresponding to the $(CH_3)_3Ge$ groups in the allylic positions. In contrast, the signal corresponding to the $(CH_3)_3Ge$ groups in vinylic positions in (IIIc) should be shifted by 0.1 to 0.2 ppm downfield. Consequently, the averaged signal of $H_{2,3}$ and $H_{2',3'}$ should shift upfield with an increase in the temperature since an increase in the (IIIc) content has occurred; at the same time, the averaged $H_{1,4}$ and $H_{1',4'}$ signal should be affected slightly while the $(CH_3)_3Ge$ signal should shift downfield. The chemical shifts and the spin–spin coupling constants in the fast exchange conditions are governed by the relationships



$$\delta^{obs}_{2,3} = n \cdot \delta_{2,3} + (1-n) \cdot \frac{\delta_{2'} + \delta_{3'}}{2} \tag{1}$$

$$\delta^{obs}_{1,4} = n \cdot \delta_{1,4} + (1-n) \cdot \frac{\delta_{1'} + \delta_{4'}}{2} \tag{2}$$

$$\delta^{obs}_{Me} = n \cdot \delta^{IIIa}_{Me} + (1-n) \cdot \frac{\delta^{IIIc}_{Me(2')} + \delta^{IIIc}_{Me(5')}}{2} \tag{3}$$

$$J^{obs}_{AB} = n \cdot J_{12} + (1-n) \cdot \frac{J_{1'2'} + J_{3'4'}}{2} \tag{4}$$

$$J^{obs}_{AB'} = n \cdot J_{13} + (1-n) \cdot \frac{J_{1'3'} + J_{2'4'}}{2} \tag{5}$$

$$J^{obs}_{AA'} = n \cdot J_{14} + (1-n) \cdot J_{1'4'} \tag{6}$$

$$J^{obs}_{BB'} = n \cdot J_{23} + (1-n) \cdot J_{2'3'} \tag{7}$$

where n is the fraction of (IIIa) in the mixture, $\delta^{obs}_{2,3}$, $\delta^{obs}_{1,4}$ and δ^{obs}_{Me} are experimental chemical shifts, $\delta_{2,3}$, $\delta_{1,4}$ and δ^{IIIa}_{Me} are the chemical shifts of the respective protons for (IIIa) at −10°, $\delta_{1'}$, $\delta_{2'}$, $\delta_{3'}$, $\delta_{4'}$, $\delta^{IIIc}_{Me(2')}$ and $\delta^{IIIc}_{Me(5')}$ are the chemical shifts of the respective protons for (IIIc) (unknown quantities). The spin–spin coupling constants are denoted similarly.

Based on the spin–spin coupling constants of $C_5H_5MR_3$ ($M{=}Si$, Ge)[11,12], it is reasonable to assume that $J_{12} \approx J_{3'4'} > J_{1'2'}$, $J_{13} \approx J_{1'3'} > J_{2'4'}$, $J_{23} \geqslant J_{2'3'}$, and $J_{14} \geqslant J_{1'4'}$. It is obvious from relationships (4) to (7) that the existence of the equilibrium (IIIa)$\rightleftarrows$(IIIc) should decrease the values of all the constants.

The rearrangement is highly selective. Isomer (IIIb) does not participate in the equilibrium since the $H_{1,4}$ signal does not shift upfield. This isomer may be just a short-lived species, somewhat similar to short-lived isoindene species trapped through a Diels–Alder reaction in the metallotropic rearrangement of (trimethylsilyl)indene[25,26].

The expressions (1) to (7) enable the constants and the thermodynamic characteristics of the (IIIa)$\rightleftarrows$(IIIc) equilibrium to be determined provided that all the chemical shifts and spin–spin coupling constants are known for isomer (IIIc). The latter quantities, however, are difficult to measure because the (IIIc) content is extremely low at the low temperatures where the rearrangement is sufficiently slow. The problem has been approached iteratively. The $H_{2,3}$ and CH_3 chemical shifts are most sensitive to the variation in temperature and the equilibrium constant K and the values ΔH and ΔS are related to $\delta_{2,3}^{\text{obs}}$ and $\delta_{\text{Me}}^{\text{obs}}$ as follows:

$$K_1 = \frac{\delta_{2,3} - \delta_{2,3}^{\text{obs}}}{\delta_{2,3}^{\text{obs}} - \delta_x} \quad \text{where} \quad \delta_x = \frac{\delta_{2'} + \delta_{3'}}{2} \tag{8}$$

$$K_2 = \frac{\delta_{\text{Me}}^{\text{IIIa}} - \delta_{\text{Me}}^{\text{obs}}}{\delta_{\text{Me}}^{\text{obs}} - \delta_x^{\text{Me}}} \quad \text{where} \quad \delta_x^{\text{Me}} = \frac{\delta_{\text{Me}(2')}^{\text{IIIc}} + \delta_{\text{Me}(5')}^{\text{IIIc}}}{2} \tag{9}$$

$$R \cdot \ln K_1 - \Delta S + \frac{\Delta H}{T} = 0 \tag{10}$$

$$R \cdot \ln K_2 - \Delta S + \frac{\Delta H}{T} = 0 \tag{11}$$

A MINIMAX 1 program* has been used to find the parameters δ_x, ΔS, and ΔH which satisfy eqns. (10) and (11), the experimental temperatures together with $\delta_{2,3}^{\text{obs}}$, and $\delta_{\text{Me}}^{\text{obs}}$ being summarised in Table 1. The program determines optimal values of functions of the type $F(\vec{p}, \vec{q})$ where $\vec{p} = (p_1, p_2, \dots p_k)$ are the parameters to be optimised, $\vec{q} = (q_1, q_2, \dots q_r)$ is a vector whose coordinates describe the physical and chemical characteristics of the objects studied. In our case, $\vec{p} = (\delta_x, \Delta S, \Delta H)$ while $\vec{q} = (T, \delta^{\text{obs}})$ and F is given by

$$F(\vec{p}) = \sum_{i=1}^{n} f(\vec{p}, \vec{q}_i), \tag{12}$$

where n is the number of experimental points, $f(\vec{p}, \vec{q}_i)$ being the left side of equations (10) or (11) for the i-th experimental point. By solving (13),

$$F^*(\vec{p}^*) = \min_{\vec{p}} F(\vec{p}) \tag{13}$$

we obtain the vector $\vec{p}^*$, which provides optimal values for the approximately linear log K *vs.* $1/T$ relationship in terms of the criterion selected.

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* The MINIMAX 1 program was written for a large BESM-6 computer in ALGOL. It employs an improved version of the relaxation method.

Eqn. (13) was solved for two independent arrays of experimental $\delta^{\rm obs}_{2,3}$ and $\delta^{\rm obs}_{\rm Me}$ values, *i.e.* for the two vectors, $q_1 = (T, \delta^{\rm obs}_{2,3})$ and $q_2 = (T, \delta^{\rm obs}_{\rm Me})$. The variations in $\delta^{\rm obs}_{2,3}$ and $\delta^{\rm obs}_{\rm Me}$ are characteristic of the same process (the variation in the constant K is identical in both cases), and thus the calculations should provide two equal values of ΔH and ΔS. The results are shown in Table 2. The values of ΔH and ΔS obtained via the independent routes are identical within the experimental accuracy of the data. Fig. 4 shows the log K *vs.* $1/T$ plots for the δ_x, $\delta_x^{\rm Me}$, ΔH and ΔS calculated in this manner.

TABLE 2

THERMODYNAMIC CHARACTERISTICS OF THE (IIIa)⇌(IIIc) METALLOTROPIC REARRANGEMENT IN BIS(TRIMETHYLGERMYL)CYCLOPENTADIENE (III)

Calculated using a MINIMAX 1 program, together with the experimental $\delta^{\rm obs}_{2,3}$ and $\delta^{\rm obs}_{\rm Me}$ values.

Experimental parameter	δ_x (ppm)	$\delta_x^{\rm Me}$ (ppm)	ΔH (kcal/mole)	ΔS (e.u.)
$\delta^{\rm obs}_{2,3}$	5.872		4.837	11.721
$\delta^{\rm obs}_{\rm Me}$		0.151	4.862	11.258

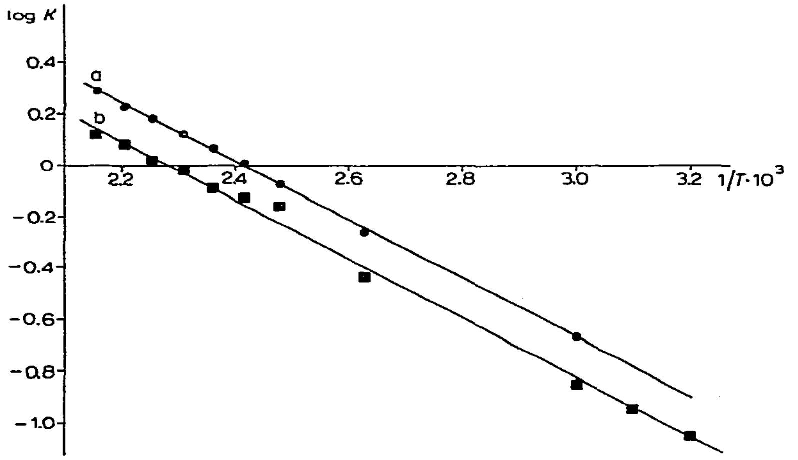

Fig. 4. log K_1 (a) and log K_2 (b) *vs.* $1/T$ for metallotropic rearrangement in bis(trimethylgermyl)cyclopentadiene.

Bis(trimethylstannyl)cyclopentadiene (IV)

This compound has been synthesised from cyclopentadiene and excess $(C_2H_5)_2NSn(CH_3)_3$[21]*.

The PMR spectrum consists of a methyl singlet at 0.04 ppm [$J(^{117,119}\text{Sn}-^1\text{H})$ 52.4, 54.8 Hz] and an AA'BB' multiplet at lower fields (Fig. 5b), the intensity ratio being 9/1/1 corresponding to structure (IVa). This structure was recently verified electronographically[28]. The parameters of the AA'BB' system are δ(AA')=6.57,

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* The compound was apparently first obtained by Jones and Lappert[27] who were attempting the synthesis of $C_5H_5Sn(CH_3)_3$.

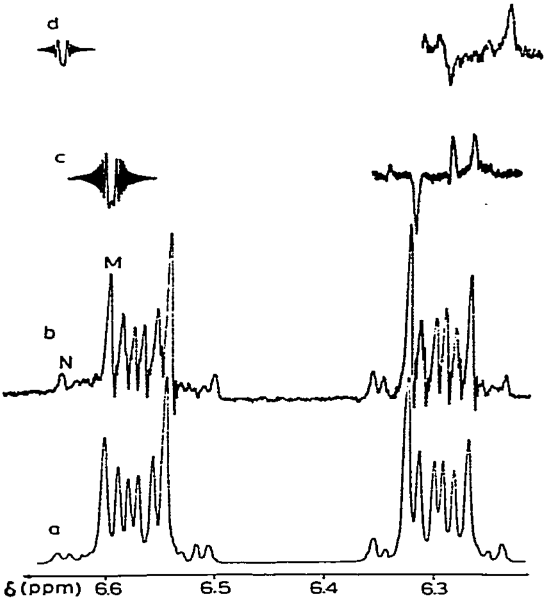

Fig. 5. PMR spectrum of olefin protons for bis(trimethylstannyl)cyclopentadiene: a, calculated; b, experimental; c, INDOR spectrum, while monitoring the M line; d, INDOR spectrum, while monitoring the N line.

$\delta(BB') = 6.30$ ppm; $J(AA') = J(BB') = 2.7$, $J(AB) = J(A'B') = 4.4$, $J(AB') = J(A'B) = 1.2$ Hz. With both pairs of olefin protons, the satellites caused by spin–spin interaction with the magnetic isotopes of tin were observed: $|J(^{117,119}Sn-^{1}H_A)|$ 8.4, $|J(^{117,119}Sn-^{1}H_B)|$ 6.4 Hz. To find the relative signs of these constants, an INDOR experiment has been carried out (Fig. 5 c-d). Monitoring the lines belonging to the high-field satellite in the BB′ part of the spectrum gives the INDOR signal at the low-field satellite in the AA′ part. Hence, the constants ^3J(Sn–H) and ^4J(Sn–H) are of opposite signs. The calculated spectrum for the olefin protons obtained through the use of the YaMR-1 program is shown in Fig. 5a. The condition $|^4J(Sn-H)| > |^3J(Sn-H)|$ is satisfied for tetraallyltin[29], and on the basis of this analogy the low-field signal (AA′ part) may be assigned to the $H_{2,3}$ protons and the high-field signal (BB′ part) to the $H_{1,4}$ protons. In other words, the chemical shifts are arranged in the same manner as they are in cyclopentadiene and the metallated derivatives[11,12,23]. In subsequent papers it will be shown that this assignment also applies to all the 5,5-dimetallated cyclopentadienes.

The PMR spectrum of (IV) is not affected by temperature over the range -130 to $+200°$*. Despite this fact it should be noted that the tautomeric equilibrium (IVa)$\rightleftarrows$(IVc) also applies for compound (IV). The concentration of (IVc) is however extremely small and independent of the temperature so that the spectrum remains unaffected. To verify the existence of the metallotropic equilibrium (IVa)$\rightleftarrows$(IVc), we have studied the metallation process with an aminostannane. The reaction is in fact specific to compounds containing an acid proton[27] and in the case in question it

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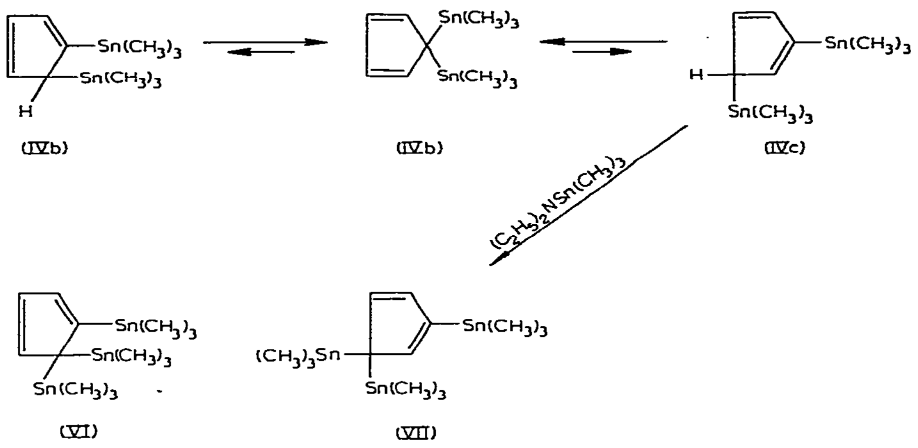
* A solution of (IV) in Freon (CF_2Cl_2) was used over the range -130 to $-90°$.



only occurs if isomers (IVb) or (IVc) are present; (IVb) should give the product (VI) whereas (IVc) gives (VII). Eliminating these isomers from the mixture should shift the equilibria (IVa)$\rightleftarrows$(IVb) and/or (IVa)$\rightleftarrows$(IVc), so that when an excess of the reactant is present the 5,5 isomer should be completely converted. It was in fact found that (IV) reacts with the aminostannane at 100° over a period of three hours to produce (VII) in an 86% yield[21]* and no evidence was obtained of the existence of (VI). The reaction is relatively fast, and this fact, together with the extremely low concentration of isomer (IVc) in the system, provides strong evidence in favour of a high rate for the metallotropic tautomerisation (IVa)$\rightleftarrows$(IVc). From this the following conclusions may be made.

(*i*) There is evidence in favour of the existence of the equilibrium (IVa)$\rightleftarrows$(IVc). It is so strongly shifted towards the 5,5 isomer, however, that PMR spectroscopy is unable to detect it. The thermodynamic parameters for this equilibrium are also difficult to obtain, unlike the situation which exists with compound (III).

(*ii*). The concentration of (IVb), if it exists at all, is negligible in comparison with that of (IVc).

At the moment, however, the (IIIa)$\rightleftarrows$(IIIc) and (IVa)$\rightleftarrows$(IVc) rearrangements described in this paper cannot be definitely attributed to 1,3 metallic shifts. It is possible that they may occur by an alternative mechanism consisting of two successive 1,2 shifts involving the short-lived species (IIIb) and (IVb).

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* The structure of (VII) will be discussed in a forthcoming paper.

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