

Synthesis, structure and fluxional behaviour of isomeric bis(trimethylstannyl)dihydropentalenes

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(Received March 23rd, 1987)

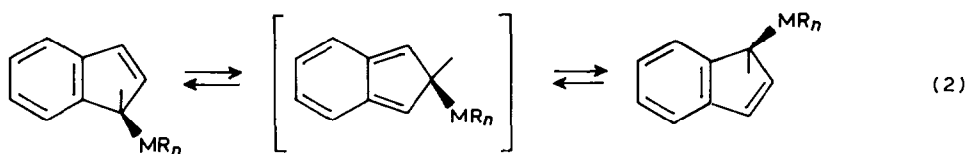
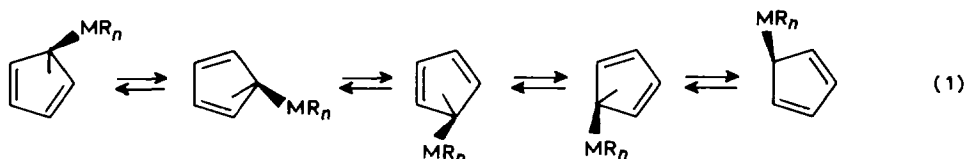
Abstract

Interaction of dihydropentalene (IV) with trimethylstannyl-diethylamide in molar ratios of 1:1 or 1:2 leads to mono- or bis-organotin derivatives of IV, respectively. X-ray analysis of *trans*(*E*)-bis(trimethylstannyl)dihydropentalene (Va) has been carried out, $R = 3.4\%$. Molecules of Va are centrosymmetric. The parameters of monoclinic cell: a 8.680(1), b 7.322(1), c 13.073(2) Å, β 97.74(1)°, space group $P2_1/c$, $Z = 2$. Geometrical parameters of Va have been determined and their values are discussed in comparison with the same parameters for η^1 -cyclopentadienyl compounds of elements. Chemical shifts ^{13}C , ^1H and ^{119}Sn and coupling constants ^{13}C – ^{119}Sn and ^{117}Sn – ^{119}Sn of bis- and tris-organotin derivatives of IV have been determined. Rapid intramolecular suprafacial metallotropic rearrangement, proceeding as a [1,5]-sigmatropic shift of SnMe_3 group, has been found in Va and *cis*-(*Z*)-bis(trimethylstannyl)dihydropentalene (Vb). Activation parameters have been evaluated by the analysis of temperature dependence of ^{13}C NMR spectra within the framework of degenerate two-site exchange in the isomers Va and Vb, E_A : 42.2 ± 0.9 and 31.2 ± 0.6 kJ · mole $^{-1}$; ΔH_{298}^* : 39.8 ± 0.9 and 27.7 ± 0.6 kJ · mole $^{-1}$; ΔS_{298}^* : -6.2 ± 4.0 and -87.0 ± 3.1 J · mole $^{-1}$ · K $^{-1}$ and ΔG_{298}^* : 41.6 ± 1.5 and 54.6 ± 1.1 kJ · mole $^{-1}$, respectively.

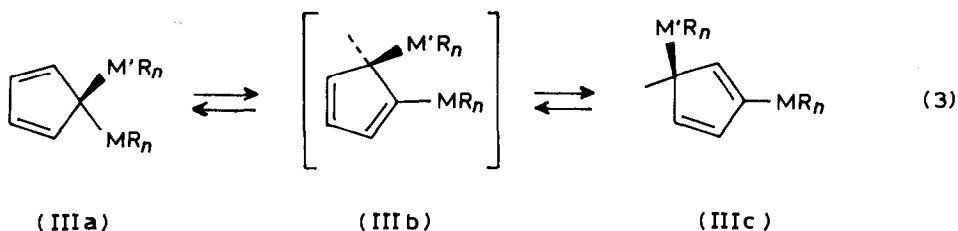
Introduction

η^1 -Cyclopentadienyl (I) and η^1 -indenyl (II) compounds of transition and non-transition elements represent two classes of fluxional molecules, in which a rapid intramolecular metallotropic rearrangement is found, proceeding as a [1,5]-sigmatropic shift of organoelement group from one carbon atom of the five-membered

ring to the next. The mechanism and the activation parameters of such processes have been determined for a wide range of silicon, germanium, tin, boron, iron, ruthenium, titanium compounds and for compounds of other elements (see [1] and ref. given in this paper).



Non-degenerate rearrangements were also studied in disubstituted and poly-metallated cyclopentadienes and indenenes [2]. For example, dimetallated cyclopentadienes (III) are equilibrium mixtures of the IIIa and IIIc tautomers, the rearrangement of which is via the intermediate IIIb [3].



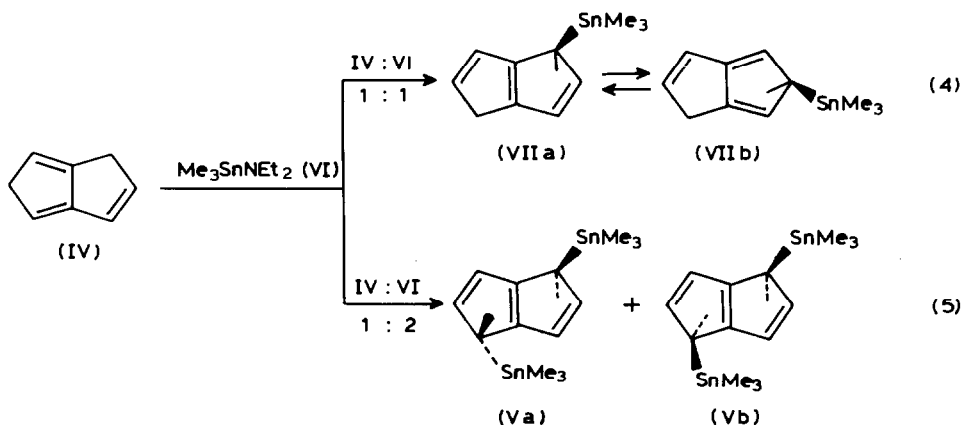
Rapid rearrangements (1)–(3) are revealed in the dynamic NMR spectra as characteristic signals, the position and shape of which are temperature-dependent.

The search for and the study of other polycyclic systems in which metallotropic rearrangements of this type are possible are of definite interest. The dihydropentalene (IV) system is the best example in this respect. Dihydropentalene exists as the most stable 1,5-isomer – bicyclo[3.3.0]octatriene-2,5,7 (IVa). Quite recently we described a suitable preparative method of synthesis [4] for this compound and the analysis of its ^1H - and ^{13}C - $\{^1\text{H}\}$ NMR spectra [5]. η^1 -Organometallic derivatives of this hydrocarbon have not been described so far. In this work we have carried out the synthesis and X-ray analysis of bis(trimethylstannyl)-dihydropentalene (V) and have studied ^1H , ^{13}C and ^{119}Sn NMR spectra of this compound.

Synthesis and crystal structure of bis(trimethylstannyl)-dihydropentalene (V)

The interaction of trimethylstannyl-diethylamide (VI) with IV in a molar ratio of 1:1 in boiling hexane, leads to the introduction of one SnMe_3 group and to the formation of a tautomeric mixture of VIIa and VIIb, which convert rapidly into each other because of the migration of the SnMe_3 group inside one five-membered

ring [6]. Increasing the ratio of VI/IV to 2:1, a mixture of *E*- and *Z*-isomers in the ratio of 6:1 of Va to Vb is mainly formed, as well as a small amount of VII and tris(trimethylstannyl)-dihydropentalene (VIII).



Va and Vb were initially separated from VII and VIII by in vacuo distillation and then low-temperature crystallization from pentane at -80°C led to the isolation of a pure *E*-isomer (Va). Va, in the form of light-yellow crystals, is stable in vacuum or under pure dry argon at room temperature for several weeks, with no isomerization of Va into Vb being observed. However, the stannyl-cyclopentadienes V and VII are similarly very sensitive to the moisture and oxygen in the air.

The structure of Va was determined by an X-ray diffraction study. Cell parameters and intensities of 1814 independent reflections with $I \geq 2\sigma$ were measured with an Enraf-Nonius CAD-4 four-circle diffractometer (λ Mo- K_α , graphite monochromator, $\theta \leq 23^\circ$) at -80°C .

The structure was solved by the heavy atom method, by use of the SHELX program, carried out on an ES-1060 computer, with fixed hydrogen atoms, and refined by least squares in a full matrix anisotropic (isotropic for hydrogen atoms) approximation to $R = 0.034$. Hydrogen atoms were located from the difference maps.

Parameters of the monoclinic cell: a 8.680(1), b 7.322(1), c 13.073(2) Å, β 97.74(1)°, space group $P2_1/c$, $Z = 2$.

Molecule Va contains two trimethylstannyl groups with C(2) and C(2') atoms and is centrosymmetric. The centre of inversion lies in the middle of the C(1)–C(1') bond (Fig. 1). Geometrical parameters of Va are presented in Tables 1, 2 and 3. Tin atoms in Va have a close to tetrahedral configuration. The Sn–CH₃ distances are similar within the range of error (2.144(8)–2.145(8) Å) and are somewhat less than the sum of the single-bond covalent radii of carbon and tin ($0.77 + 1.40 = 2.17$ Å [7]). The C(2,2')–Sn bonds are somewhat longer – 2.209(7) Å, indicative of their lower stability. The olefin carbon atoms C(3), C(4), C(3'), C(4') lie in one plane (deviations are 0.003–0.005 Å) and the C(2) and C(2') atoms – the carriers of the Sn(CH₃)₃ group bend towards tin atoms by 0.068 Å (the five-membered ring has an “envelope” conformation), the dihedral angle between planar four- and three-membered fragments of the ring is 2.9°. The C(2,2')–Sn bond makes an angle of 68.4° with the plane formed by olefin carbons. So, tin atoms appear to be drawn nearer to

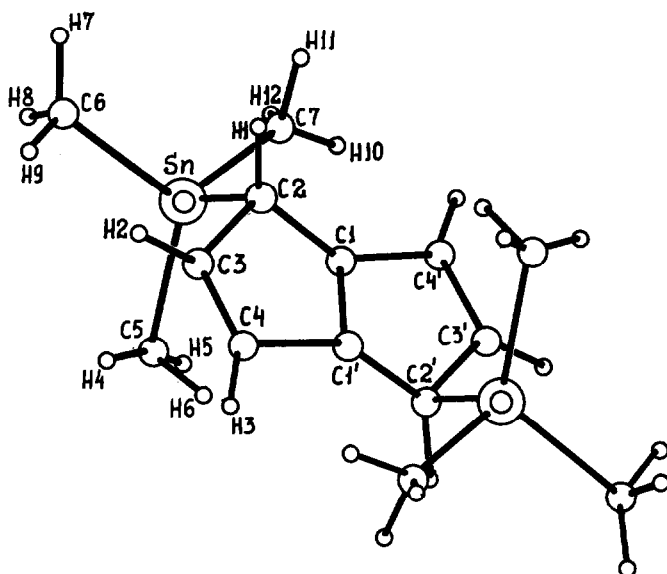


Fig. 1. Molecular geometry of *E*-bis(trimethylstannyl)dihydropentalene.

the olefin carbons C(3) and C(3'), to a distance of 2.968(7) Å, which is somewhat less than the sum of the Van der Waals radii of carbon and tin (3.87 Å [8]).

To understand the specificities of Va geometry, it is useful to compare these results with the data for metal η^1 -cyclopentadienyls. The most important structural char-

Table 1

Atomic coordinates ($\times 10^4$) for the molecule of *E*-bis(trimethylstannyl)dihydropentalene (Va) ^a

Atom	x	y	z
Sn	0.2267(1)	0.2238(1)	0.39310(9)
C(1)	0.4989(7)	0.4599(9)	0.4523(5)
C(2)	0.3461(8)	0.490(1)	0.3923(5)
C(3)	0.2658(8)	0.610(1)	0.4610(6)
C(4)	0.3565(8)	0.634(1)	0.5514(6)
C(5)	0.207(1)	0.159(1)	0.5509(6)
C(6)	-0.0002(8)	0.254(1)	0.3070(6)
C(7)	0.3673(9)	0.030(1)	0.3245(7)
H(1)	0.343	0.524	0.319
H(2)	0.164	0.661	0.436
H(3)	0.674	0.300	0.385
H(4)	0.132	0.224	0.575
H(5)	0.255	0.044	0.573
H(6)	0.303	0.211	0.591
H(7)	-0.005	0.275	0.236
H(8)	-0.066	0.138	0.318
H(9)	-0.054	0.355	0.343
H(10)	0.468	0.022	0.349
H(11)	0.389	0.049	0.253
H(12)	0.3585	-0.081	0.325

^a Numbering of atoms is given in Fig. 1.

Table 2

Anisotropic temperature factors ^a

Atoms	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Sn	0.0207	0.0252	0.0192	0.0003	0.0034	-0.0008
C(1)	0.0210	0.0221	0.0221	0.0012	0.0055	-0.0011
C(2)	0.0239	0.0254	0.0219	0.0023	0.0022	-0.0020
C(3)	0.0240	0.0226	0.0373	0.0027	0.0040	0.0040
C(4)	0.0237	0.0242	0.0316	-0.0006	0.0087	0.0009
C(5)	0.0494	0.0390	0.0263	0.0067	0.0085	0.0054
C(6)	0.0257	0.0453	0.0330	0.0016	-0.0016	-0.0036
C(7)	0.0348	0.0331	0.0451	-0.0105	0.0115	0.0039

^a $B_{H(iso)} = 0.05$. Numbering of atoms is given in Fig. 1.

acteristics of η^1 -cyclopentadienyl compounds of non-transition and transition elements is the geometry of the cycle and the angle between the carbon–element bond and the plane of the diene system. Some known structural data obtained by X-ray diffraction studies and by the electron diffraction method are given in Table 4.

At present, in all the investigated derivatives of transition metals η^1 -cyclopentadienyl fragment is planar and the bond length distributions are of typical butadiene type. The situation differs for the compounds of non-transition elements. There are reliable electron diffraction (ED) and X-ray (XR) data for (η^1 -C₅H₅)SiH₃ [9] and (η^1 -C₅H₅)GeH₃ [10]. They reveal the presence of planar cycles in the molecules. The atoms of the elements are drawn nearer to the diene systems due to increasing the angles between the C(5)–Si and C(5)–Ge bonds and the cycle to 8.5° and 9.5° respectively, against half of the tetrahedral angle. For the methyl derivatives η^1 -C₅H₅M(CH₃)₃ (M = Si [11], Ge [12] and Sn [13]) the ED data were interpreted within the framework of two models – with non-planar [11–13] and planar [14] cycles. Close values of *R* (see Table 4) were obtained for both models. A general and obvious conclusion from the data [11–13] is that the atoms of the elements are

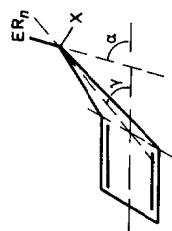
Table 3

Interatomic distances (*d*, Å) and valency angles (β , °) in the molecule of *E*-bis(trimethylstannyl)dihydropentalene (Va) ^a

Atoms	<i>d</i>	Angles	β
Sn–C(2)	2.209(7)	C(2)SnC(5)	107.2(3)
Sn–C(5)	2.145(8)	C(2)SnC(6)	107.7(3)
Sn–C(6)	2.144(7)	C(2)SnC(7)	106.7(3)
Sn–C(7)	2.144(8)	C(5)SnC(6)	110.0(3)
C(1)–C(1')	1.38(1)	C(5)SnC(7)	112.3(3)
C(1)–C(2)	1.463(9)	C(6)SnC(7)	112.5(3)
C(2)–C(3)	1.49(1)	C(2)C(1)C(1')	108.8(6)
C(3)–C(4)	1.34(1)	C(2)C(1)C(4')	141.8(6)
C(4)–C(1')	1.438(9)	C(1')C(1)C(4')	109.2(6)
Sn...C(3)	2.968(7)	C(1)C(2)C(3)	103.2(6)
Sn...C(4)	3.735(7)	C(2)C(3)C(4)	110.0(6)
Sn...C(1)	2.946(6)	C(3)C(4)C(1')	108.6(6)
Sn...C(1')	3.718(6)		

^a Numbering of atoms is given in Fig. 1.

Table 4

Geometrical parameters of η^1 -fragment in η^1 -cyclopentadienyl compounds of some elements

Compound	Bond lengths, Å				$\angle \gamma, ^\circ$	$\angle \alpha, ^\circ$	Method	R, %	Ref.
	C(2)-C(3)	C(3)-C(4)	C(1)-C(2)	C(1)-E					
C_5H_6	1.342(3)	1.469(2)	1.509(2)	-	0	63.5 ± 0.7	ED		[20]
$(\eta^1-C_5H_5)SiH_3$	1.389(13)	1.436	1.500(13)	1.881(10)	22 ± 4	78 ± 4	ED	13.5	[9]
$(\eta^1-C_5H_5)Si(CH_3)_3$	1.40(2)	1.40(2)	1.53(2)	1.90(1)	0	61.5	ED	7	[11]
$C_5H_4Si[(CH_3)_3]_2$	1.369	1.457	1.524	1.897	0	75 ± 4	ED	10.3	[4]
$(\eta^1-C_5H_5)GeH_3$	1.42(2)	1.42(2)	1.49(3)	1.89(1)	15 ± 4	66; 51	ED	11.2	[15]
$(\eta^1-C_5H_5)Ge(CH_3)_3$	1.42(2)	1.42(2)	1.49(3)	1.89(1)	0	64.5	ED	4.9	[14]
$(\eta^1-C_5H_5)Ge(CH_3)_3$	1.343(12)	1.443(12)	1.474(13)	1.965(9)	4.1(6)		XR		[10]
$(\eta^1-C_5H_5)Ge(CH_3)_3$	1.350(5)	1.468(23)	1.478(13)	1.969(5)	1.4(17)		ED		[10]
$(\eta^1-C_5H_5)Ge(CH_3)_3$	1.46(2)	1.46(4)	1.50(2)	1.97(1)	24 ± 4	76 ± 4	ED	16.5	[12]
$(\eta^1-C_5H_5)Sn(CH_3)_3$	1.40(2)	1.40(2)	1.49(3)	2.16(1)	19 ± 4	78 ± 4	ED	13.5	[13]
$C_5H_4Sn[(CH_3)_3]_2$	1.352	1.456	1.499	2.16	0	68.4	ED	12.7	[14]
$(\eta^1-C_5H_5)_4Sn$	1.38(2)	1.38(2)	1.47(3)	2.16(1)	13 ± 4	72 ± 4	ED	13.4	[16]
$(\eta^1-C_5H_5)_4Sn$	1.38(2)	1.38(2)	1.47(3)	2.16(1)	0	66; 51	ED	14.9	[14]
$(\eta^1-C_5H_5)_4Sn$	1.38(7)	1.48(6)	1.51(6)	2.18(4)	0	62.6; 53.1	ED	11.8	[17]
$(\eta^1-C_5H_5)_4Sn$	1.39(4)	1.39(4)	1.51(4)	2.27(3)	9.3	61.4	XR		[17]
$(\eta^1-C_5H_5)_4Sn$	1.44(5)	1.38(5)	1.52(5)	2.23(3)	6.6	64.3	XR		[18]
$(\eta^1-C_5H_5)_4Sn$	1.36(4)	1.51(5)	1.50(5)	2.29(3)	1.3	64.8	ED		
$(\eta^1-C_5H_5)_4Sn$	1.37(4)	1.41(5)	1.54(5)	2.29(3)	5.9	70.0	ED		
$(\eta^1-C_5H_5)_2Sn$	1.445	1.375	1.535	2.175	27	64	XR	11.3	[19]
$[Fe(CO)_2\eta^5-C_5H_5]_2$	1.343(9)	1.444(10)	1.470(8)	2.264(5)	3.9	62.3	XR	2.5	[21]
$(\eta^1-C_5H_5)_3Sb$	1.356(8)	1.431(8)	1.468(7)	2.238(5)	3.6	69.6			
$(\eta^1-C_5H_5)_3Sb$	1.349(8)	1.438(9)	1.466(8)	2.246(5)	4.7	76.5			

drawn nearer to the carbon atoms C(1) and C(4), to give distances of 3.41 Å (Si), 3.55 Å (Ge) and 3.60 Å (Sn), which are smaller than the corresponding sum of the Van der Waals radii. However, in the case of the model with the non-planar cycle, such closeness is achieved by increasing the angle γ , and in the case of the planar cycle – by increasing the angle between the M–C(5) bond and the plane of the cycle (angle α). Taking all the data given in Table 4 into consideration, a planar model seems to be more appropriate.

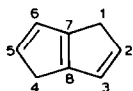
An analogous situation takes place for the bi-metallic derivatives $C_5H_4[M-(CH_3)_3]_2$ [14–16]. ED data for $C_5H_4[Sn(CH_3)_3]_2$, in the supposition of a planar cycle and X-ray analysis at low temperature [17], coincide well and indicate the difference in angles between the two C(5)–Sn bonds and the cycle plane.

X-ray data for the three η^1 -cyclopentadienyl compounds of tin show that substantial deviations from coplanarity by the cycle are possible. All four rings in the $(\eta^1-C_5H_5)_4Sn$ molecule are different, and dihedral angles lie in the range from 1.3 to 9.3°, and can be attributed to the effects of crystal packing [18]. However, the angle in $(\eta^1-C_5H_5)_2Sn[Fe(CO)_2\eta^5-C_5H_5]_2$ is about 27° and the bond length distribution in the ring is of antibutadiene type. Though the *R* factor (11.3%) in this study is rather high [19], there is no doubt about the substantial distortion of the cycle plane.

The reason for the peculiarity in the structure of $\eta^1-C_5H_5$ compounds of various elements, that of being in close proximity to the metal atom with diene system, is the hyperconjugation of the readily polarized C(5)–M bonds with π -electron system, which is specific to all the compounds of this type [22]. The lowering of the ionization potentials of coresponding MO [23] reveals itself in the characteristic tendency for the differences in length of the single and double C–C bonds of the cycle and vicinity of the metal atom to the diene system to decrease either by an increase in the angle between C–M bond and diene system plane or by cycle bend. Metallotropic rearrangements in η^1 -cyclopentadienyl compounds proceed readily and this is also a direct consequence of this electronic interaction. As is obvious from the structural data for Va (Table 3), both tin atoms and the C(3,3') atoms have been drawn closer together (2.968(7) Å). To compare the carbon–carbon bond length distribution in molecule Va with that in the appropriate, unstable, hydrocarbon 1,4-dihydropentalene (IVb) the geometry of IVb was calculated by the quantum-chemical method MINDO/3 [24] (which allows the geometry of hydro-

Table 5

Geometrical parameters of 1,4-dihydropentalene calculated by MINDO/3 with full optimization of geometrical parameters



C–C distances	(Å)	Angles	(°)
C(1)–C(2)	1.516	C(1)–C(2)–C(3)	110.5
C(2)–C(3)	1.362	C(2)–C(3)–C(8)	108.1
C(3)–C(8)	1.477	C(3)–C(8)–C(4)	142.2
C(8)–C(7)	1.409	C(8)–C(7)–C(1)	108.8
C(7)–C(1)	1.51	C(7)–C(1)–C(2)	103.1

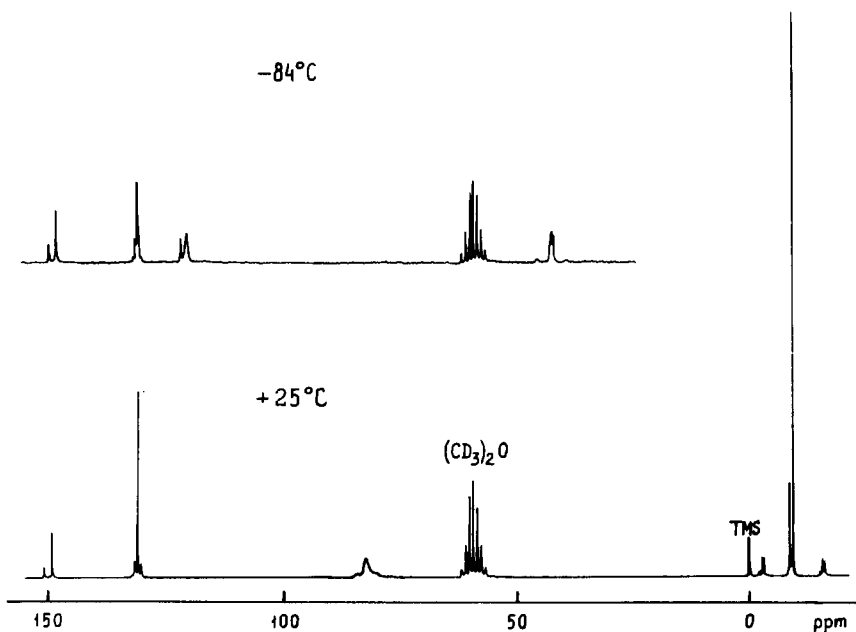


Fig. 2. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of bis(trimethylstannyl)dihydropentalene in $(\text{CD}_3)_2\text{O}$ at -84°C (top) and $+25^\circ\text{C}$ (bottom).

carbons to be calculated with a high degree of accuracy) with full optimization of geometrical parameters*. Comparing the calculated parameters for IVb (given in Table 5) with the experimental values for Va, one can see that the tendencies observed during the transition from cyclopentadiene to $(\eta^1\text{-C}_5\text{H}_5)\text{SnMe}_3$ are also observed for the pair IVb–Va: simple bonds are shortened and the length of the central double bond is increased. These changes in the geometry of the carbon skeleton are the consequence of hyperconjugation of the C–Sn bonds with the system of multiple bonds in the molecule.

$^{13}\text{C}\{-^1\text{H}\}$ NMR spectra and metallotropic rearrangements in molecules Va and Vb

The ^{13}C NMR spectrum (25 MHz) of the mixture of Va and Vb at -84°C in a solution of dimethylether- d_6 is given in Fig. 2. A set of 5 signals corresponds to each of the isomers (see Table 6). The ratio of signal intensities (Va):(Vb) is 6:1. The assignment of signals to C(1,4) and C(7,8) does not cause difficulties for either isomer; and assignment for C(2,5) and C(3,6) unambiguously follows from the character of temperature dependence, described below. It should be noted that the low-abundance isomer Vb has narrow lines ($\Delta\nu_{1/2} < 1$ Hz), while signals of Va are markedly broadened ($\Delta\nu_{1/2} \approx 4\text{--}5$ Hz), indicating a rather rapid dynamic process, proceeding in this isomer at -84°C .

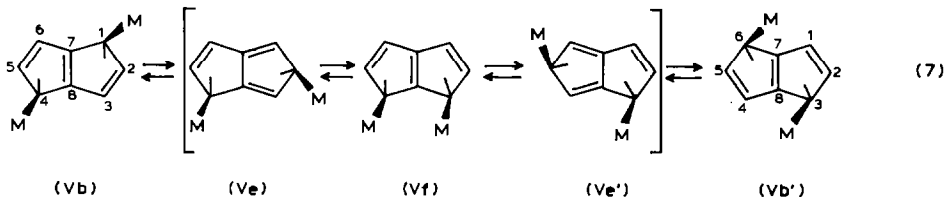
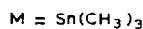
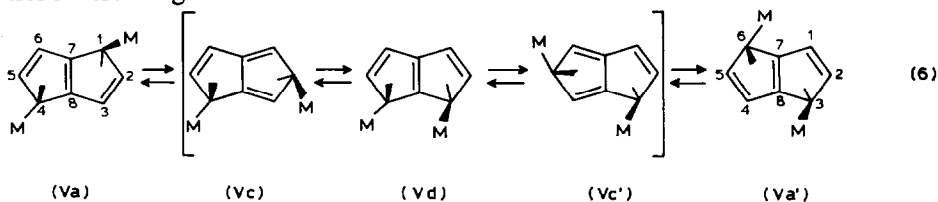
With a gradual increase of temperature from -84° to 25°C , a characteristic reversible temperature-dependence of shape and position of the C(1,4) and C(3,6)

* The authors express their gratitude to I.A. Yudelevitch for the calculations performed. Detailed data of the relative stability of dihydropentalene isomers, of the geometry and electronic structure will be published elsewhere.

signals is observed. The remaining signals in the spectra do not undergo substantial changes (Fig. 2). Primarily, a gradual broadening of the two signals indicated above is observed. At -25°C they disappear completely and a further increase of temperature leads to the appearance of an average signal C(1,3,4,6) which gradually narrows at 82.5 ppm, such that at $+25^{\circ}\text{C}$ $\Delta\nu_{1/2} = 26$ Hz, and $\Delta\nu_{1/2} = 13$ Hz at $+40^{\circ}\text{C}$. Corresponding changes in the spectrum of Va take place at higher temperatures, which indicates that the dynamic process is occurring in it at a lower rate.

In the range of rapid exchange all the signals have satellites, owing to spin-spin coupling of the ^{13}C nuclei with the magnetic isotopes ^{117}Sn and ^{119}Sn . This fact shows the intramolecular character of the process. The relative intensities of the signals of Va and Vb are not affected by change in temperature, this indicates that there is no rearrangement of these isomers into one another. Changes of chemical shifts of the nuclei C(2,5), C(7,8) and CH_3 in the temperature range -84°C to $+25^{\circ}\text{C}$ do not exceed 0.2 ppm, which is mainly consistent with the observed temperature-dependent changes in the ^{13}C NMR spectra of rigid molecules.

The type of temperature-dependence of the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of the Va and Vb mixture indicates degenerate two-position exchange (eqs. 6, 7), the intermediates Vc-Vf were not revealed in the spectra and their steady-state concentrations were insignificant.



So, we observe two subsequent [1,5]-sigmatropic rearrangements, similar to process (2) in η^1 -indenyl compounds. Migrations of SnMe_3 -groups proceed independently in each of the five-membered rings, the shift is suprafacial and the inter-ring migrations are absent.

To evaluate the activation parameters of the metallotropic rearrangements in Va and Vb, the temperature dependence of ^{13}C NMR spectra was investigated within the framework of the degenerate two-site exchange in the temperature range from -84°C to $+40^{\circ}\text{C}$ (15 points for Va and 8 for Vb). The migration rate constants (K) are determined according to the eqns. 8 and 9 [25].

$$K = \pi(\Delta\nu^* - \Delta\nu^0), \quad K \ll \Delta\nu \quad (8)$$

$$K = \pi(\delta\nu)^2/2(\Delta\nu^* - \Delta\nu^0), \quad \Delta\nu^*/(\delta\nu) \ll 1, \quad (9)$$

Table 6

Chemical shifts values of nuclei ^{13}C (δ_{C} , ppm from TMS) in *E*- (Va) and *Z*- (Vb) isomers of bis(trimethylstannyl)dihydropentalene at the temperatures $+25^{\circ}\text{C}$ and -84°C ^a

	δ_{C}			
	$+25^{\circ}\text{C}$		-84°C	
	Va	Vb	Va	Vb
C(1), C(4)	82.5 (≈ 90)	82.5	42.51 (≈ 150)	42.37(150.15)
C(2), C(5)	131.13(30.52)	131.13	131.44(31.3)	131.71
C(3), C(6)	82.5 (≈ 90)	82.5	121.00	122.11
C(7), C(8)	149.33(7.63)	151.01(8.24)	148.81	150.24
CH_3	-9.55(339.36)	-8.99(336.30)	-9.54(343.63)	-8.87(340.88)

^a Numbering of carbon atoms is given in eqs. 6 and 7. Coupling constants ^{13}C -Sn are in parentheses: values averaged over magnetic isotopes of Sn are given for all carbon atoms except for the CH_3 group, coupling constants ^{13}C - ^{119}Sn are given for the CH_3 group.

where

$\Delta\nu^*$ = the width at half maximum intensity of the exchanged broadened signal,

$\Delta\nu^0$ = the line width in the absence of exchange,

$\delta\nu$ = frequency difference between sites in exchange system.

Arrhenius plots were calculated according to the least squares technique. Correlation coefficients equal to 0.997 and 0.998 for Va and Vb, respectively, were obtained (see Fig. 3).

The parameters E_A , ΔS_{298}^\ddagger , ΔH_{298}^\ddagger and ΔG_{298}^\ddagger listed in Table 7 have been calculated according to standard equations and for comparison the corresponding parameters of the metallotropic rearrangements (eq. 1) and (2) in $(\eta^1\text{-C}_5\text{H}_5)\text{Sn}(\text{CH}_3)_3$ and $\text{C}_9\text{H}_7\text{Sn}(\text{CH}_3)_3$ [26] are also listed. It is obvious from the obtained results that a noticeably lower rate of rearrangement into Vb compared with Va is determined by a sudden lowering of the activation entropy. Activation parameters characterize the effective [1,3]-shift of SnMe_3 group into V and thus include the indirect

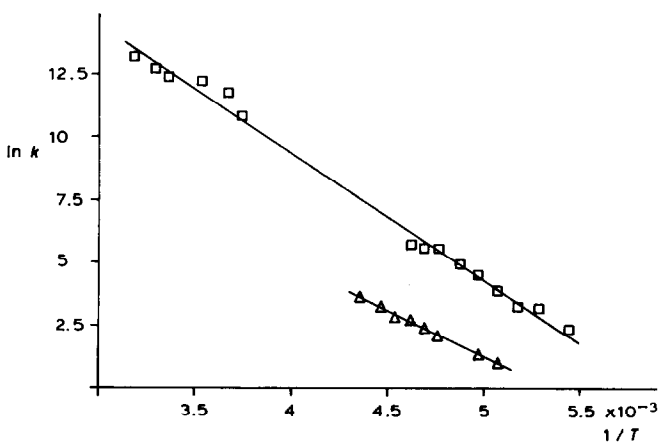


Fig. 3. Arrhenius plots of metallotropic rearrangements in *E*- (□) and *Z*- (Δ) isomers of bis(trimethylstannyl)dihydropentalene (see eqs. 6 and 7 respectively).

Table 7

The activation parameters of the metallotropic rearrangements in the trimethylstannyl derivatives of cyclopentadiene and indene and in *E*- and *Z*-isomers of bis(trimethylstannyl)dihydropentalene

Compound	E_A kJ·mole ⁻¹	ΔH^* kJ·mole ⁻¹	ΔS^* J·mole ⁻¹ ·K ⁻¹	ΔG^* kJ·mole ⁻¹
(η^1 -C ₅ H ₅)SnMe ₃ ^a	28.5 ± 2.9		12.6 ± 12.6	29.7 ± 2.9
(η^1 -C ₉ H ₇)SnMe ₃ ^a	50.6 ± 3.3		-55.6 ± 12.5	69.4 ± 3.3
<i>E</i> -isomer ^b	42.2 ± 0.9	39.8 ± 0.9	-6.2 ± 4.0	41.6 ± 1.5
<i>Z</i> -isomer ^b	31.2 ± 0.6	28.7 ± 0.6	-87.0 ± 3.1	54.6 ± 1.1

^a All parameters were calculated for 300 K [26]. ^b All parameters were calculated for 298 K.

contributions from intermediates Vc–Vf. The same was found for C₉H₇Sn(CH₃)₃ and other η^1 -indenyl compounds. An increase of the free energy of activation of rearrangement (2) to 35–36 kJ mol⁻¹ compared with (1) is connected with the production of energetically unfavourable isoindenyl intermediates. In the case of Vb, a larger negative entropy of activation seems to be due to the spatial strain caused by the interaction of the two neighbouring bulky SnMe₃-groups in intermediate Vf. The difference in activation energies for (η^1 -C₅H₅)Sn(CH₃)₃ and Va is 14.04 kJ·mole, and for (η^1 -C₅H₅)Sn(CH₃)₃ and Vb–27 kJ·mol⁻¹. It is likely that intermediates Vd and Vf are responsible for this increase in the free energy of activation.

¹H and ¹¹⁹Sn-{¹H} NMR spectra of Va and Vb

The ¹H NMR spectrum of Va and Vb mixture (100 MHz) at 25 °C corresponds to the rapid exchange limit and thus the resonance signals of H(1,4) and H(3,6) are observed as average. Assignments of the signals and chemical shift values are given in Table 8. The spectrum corresponds to the structure V and to the character of the proceeding dynamic process.

¹¹⁹Sn NMR spectrum (Fig. 4) gives an additional confirmation of the intramolecularity of the metallotropic rearrangements into Va and Vb as well as the absence of the inter-ring migrations and mutual transitions among isomers. Two main signals at 25.46 ppm and 19.66 ppm (See Table 9) with the ratio of intensities 6 : 1 are attributable to Va and Vb respectively. The spectrum of raw product contains signals due to admixtures VII, VIII and other possible products of the metallation

Table 8

Proton chemical shifts (δ_H , ppm) for *E*- (Va) and *Z*- (Vb) isomers of bis(trimethylstannyl)dihydropentalene at +25 °C and -100 °C, coupling constants ¹H–¹¹⁹Sn are in parentheses.

	+25 °C		-100 °C
	Va	Vb	Vb
H(1), H(4)	5.10 ^a	5.10	3.89(97)
H(3), H(6)	5.10 ^a	5.10	6.52 ^b
H(2), H(5)	6.31 ^a	6.31	6.35 ^b
CH ₃	-0.11 (54.32)	-0.03 (54.44)	

^a 0.5(J (H(1)–H(2)) + J (H(2)–H(3))) = 0.5(J (H(4)–H(5)) + J (H(5)–H(6))) = 2.93 Hz. ^b J (H(2)–H(3)) = J (H(5)–H(6)) = 4.4 Hz.

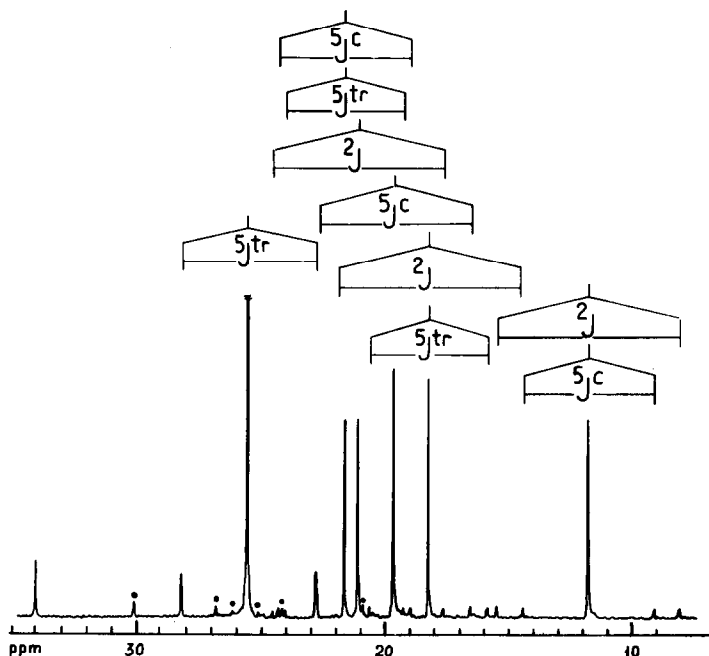


Fig. 4. The $^{119}\text{Sn}\{-^1\text{H}\}$ NMR spectrum of dihydropentalene trimethylstannyl derivatives in $(\text{CD}_3)_2\text{O}$. The scheme of $^{117}\text{Sn}\text{-}^{119}\text{Sn}$ satellite splittings is shown over the lines, ^{13}C -satellite signals are marked.

of IV. Each of the signals has satellites due to spin-spin interaction $^{119}\text{Sn}\text{-}^{13}\text{C}$, as well as $^{119}\text{Sn}\text{-}^{117}\text{Sn}$ between different tin isotopes of two chemical equivalent SnMe_3 groups. The distances between ^{13}C -satellites, caused by the interaction of CH_3 groups (relative intensity 1.5%), correspond to the values $^1J(\text{Sn}\text{-}\text{CH}_3)$. They can also be determined in $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra (see Table 6) with 339.4 and 336.3 Hz for Va and Vb respectively. Symmetrically positioned pairs of satellites for the signal of Va with the relative intensity of 1%, with splittings of 98, 61 and 8 Hz, correspond to the coupling constants of ^{119}Sn with the pairs of nuclei ^{13}C : C(1) and C(3), C(4) and C(6), C(7) and C(8) respectively, which are equivalent owing to the fast chemical exchanges of positions. A pair of signals with a 31 Hz splitting and relative intensity 0.5% is due to coupling with the nuclei C(2) and C(5). The long range coupling constant $^5J(\text{Sn}(1)\text{-C}(5))$ was not observed.

The coupling constants $^{119}\text{Sn}\text{-}^{117}\text{Sn}$ for Va and Vb are 199.5 Hz and 228.4 Hz, respectively, (Table 9). These are average values owing to the dynamic process, but the main contribution comes from the 1,4-isomers. Thus it may be stated, that the $^5J''(\text{Sn}\text{-}\text{Sn})$ value is smaller than the analogous $^5J^{cis}(\text{Sn}\text{-}\text{Sn})$ value. Data of the homoallylic coupling constants of such a type in rigid structures with fixed geometry are not numerous. The same relationship for the $^5J''(\text{H}\text{-}\text{H})$ and $^5J^{cis}(\text{H}\text{-}\text{H})$ values is found for cyclohexadien-1,4 [27] (8.04 and 9.63 Hz respectively).

Signals of the admixture compounds in the spectrum are attributable to VII, the content of which is 5%, and to the two other compounds. The signal at 21.08 ppm, having satellites with splitting 254.2 Hz and a relative intensity of 4%, evidently contains two equivalent $\text{Sn}(\text{CH}_3)_3$ groups. Judging from the value of the $^{119}\text{Sn}\text{-}^{117}\text{Sn}$

Table 9

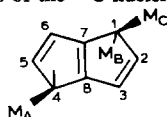
^{119}Sn NMR parameters for trimethylstannyldihydropentalene (VII), *E*- (Va), *Z*- (Vb) and *gem*- (Vg or Vh) isomers of bis(trimethylstannyl)dihydropentalene and tris(trimethylstannyl)dihydropentalene (VIII) at +25°C: chemical shifts ^{119}Sn (δ_{Sn}) ppm and coupling constants ^{119}Sn - ^{117}Sn (nJ , Hz).

Compound	δ_{Sn}^a	nJ
VII	33.95	
Va	25.46	$^5J^{tr} = 199.5$
Vb	19.66	$^5J^{cis} = 228.4$
Vg or Vh	21.08	$^2J = 254.2$
VIII	Sn(4)	$^2J = 274.2$
	Sn(1) ^{tr}	$^5J^{tr} = 176.4$
	Sn(1) ^{cis}	$^5J^{cis} = 195.9$

^a Values of δ_{Sn} are given in ppm from the external standard, $\text{Sn}(\text{CH}_3)_4$.

Table 10

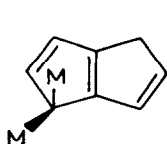
Chemical shifts values of the ^{13}C nuclei (δ_{C} , ppm from TMS) in tris(trimethylstannyl)dihydropentalene.



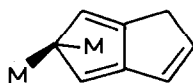
M = $\text{Sn}(\text{CH}_3)_3$

	δ_{C}		δ_{C}
$\text{CH}_3(\text{A})$	-8.43	C(2)	132.30
$\text{CH}_3(\text{B})$	-9.36	C(3)	122.38
$\text{CH}_3(\text{C})$	-8.88	C(5)	135.60
C(1)	41.34	C(6)	121.88
C(4)	45.64	C(7)	154.18
		C(8)	150.16

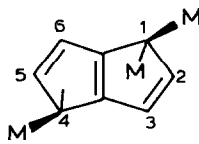
coupling, they are both joined to one carbon atom (typical values of the geminal Sn-Sn constants lie in the range of 202-677 Hz [28,29]). So the most likely structures for this isomer are Vg and Vh. Three remaining signals at 21.62 ppm, 18.25 ppm and 11.84 ppm, with a ratio of intensities of 1:1:1 contain satellites ^{117}Sn , which form a spin system AMX, the value of one coupling constant is close to that expected for $^2J(\text{Sn-Sn})$ and the other two couplings evidently correspond to $^5J^{tr}(\text{Sn-Sn})$ and $^5J^{cis}(\text{Sn-Sn})$ (see Table 9). The structure 1,1,4-tris-trimethylstannyl-1,4-dihydropentalene (VIII) is the most likely for this compound.



(Vg)



(Vh)



(VIII)

M = $\text{Sn}(\text{CH}_3)_3$

Experimental

The ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded on a JEOL "FX-100" spectrometer for ca. 40% and 10% v/v solutions of bis(trimethylstannyl)dihdropentalene in dimethyl ether- d_6 with TMS as internal standard. The accuracy of temperature measurements was $\pm 0.5^\circ\text{C}$.

The X-ray diffraction study of trans-1,4-trimethylstannyl-1,4-dihydro-pentalene (Va) was recorded on an Enraf-Nonius CAD-4 four-circle diffractometer at -80°C (λ Mo- K_α , graphite monochromator, $\theta/2\theta$ scan, $\theta \leq 23^\circ$).

The synthesis and purification of substances was carried out in an atmosphere of dry argon. Solvents used had been dried and degassed.

Trimethylstannyldihdropentalene (VII). A mixture of dihydropentalene (1.72 g, 16.5 mmol) and trimethylstannyldiethylamide (3.34 g, 14.2 mmol) was heated in 100 ml of hexane for 30 min. Volatile products were evaporated off at atmospheric pressure, and the residue was distilled in vacuo. Yield: 1.08 g (28.6%) trimethylstannyldihdropentalene, b.p. $74-82^\circ\text{C}/1$ mmHg. Found: C, 49.17; H, 6.14; Sn, 44.69. $\text{C}_{11}\text{H}_{16}\text{Sn}$ calc: C, 49.49; H, 6.04; Sn, 44.47%.

The second fraction (b.p. $84-120^\circ\text{C}/1$ mmHg) which from the NMR spectra was found to be a mixture of trimethylstannyl- and bis(trimethylstannyl)dihdropentalene.

Trimethylstannyldihdropentalene was obtained also by mixing dihydropentalene (2.4 g, 23 mmol) with trimethylstannyldiethylamide (2.78 g, 12.2 mmol) in 50 ml heptane and the mixture left at room temperature for 2 d. After removal of the solvents, 2.63 g (80.9%) of trimethylstannyldihdropentalene with b.p. $97-100^\circ\text{C}/3$ mmHg was obtained.

Bis(trimethylstannyl)dihdropentalene (V) A mixture of dihydropentalene (1.14 g, 10.9 mmol) and trimethylstannyldiethylamide (4.916 g, 20.8 mmol) was heated in 40 ml hexane for 30 min. After removal of the solvent 2.56 g (57.3%) of V, b.p. $135-140^\circ\text{C}/1$ mmHg was obtained.

Found: C, 39.57; H, 5.48; Sn, 54.86. $\text{C}_{14}\text{H}_{24}\text{Sn}_2$ calc: C, 39.13; H, 5.63; Sn, 55.24%.

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