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NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF METAL CYCLOPENTADIENYLS

V*. METALLOTROPIC REARRANGEMENT IN SILICON CYCLOPENTADIENYLS: 1,2 SHIFT AND SPECTRAL REGULARITIES IN σ-CYCLOPENTADIENYLS

N. M. SERGEYEV, G. I. AVRAMENKO, A. V. KISIN, V. A. KORENEVSKY AND
YU. A. USTYNYUK

N.M.R. Laboratory, Chemical Department, M.V. Lomonosov State University, Moscow (U.S.S.R.)

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SUMMARY

The saturation transfer technique, INDOR, and related computations have been used to provide a complete analysis of the PMR spectra of isomeric (trimethylsilyl)cyclopentadienes whilst the spectra of $C_5H_5Si(CH_3)_2Cl$ and $C_5H_5SiCl_3$ have been partially analysed. The main vinylic isomer in the series $C_5H_5Si(CH_3)_nCl_{3-n}$ (n is 0, 1, 2, 3) is the 1-substituted species while the 5-substituted isomers are subject to a metallotropic rearrangement. From the assumption that $^3J(HH) > 0$ and $^4J(HH) < 0$, it follows that the upfield olefinic signal of the 5-substituted isomers is related to the 1,4 protons. Unsymmetrical broadening shows that in all the compounds the migration proceeds predominantly through the 1,2 shift with a free energy of activation of 15 to 16 kcal/mole. As the electronegativity of the substituents attached to the silicon atom increases, the equilibrium associated with the prototropic rearrangement is shifted towards formation of the vinylic isomers while the corresponding metal migration rate decreases. A thorough analysis of the coupling constants, $J(HH)$, and chemical shifts, $\delta(H)$, associated with the protons of σ-cyclopentadienyl compounds shows that the constant $^3J_{15}$ is always positive and equal to 1.2 ± 0.2 Hz while $^4J_{25}$ is, as a rule, negative and variable within the range -1.6 to $+0.2$ Hz. In the absence of electron-withdrawing groups (*e.g.* as in carbonyls) at the metal, the condition $\delta_{14} < \delta_{23}$ invariably applies.

INTRODUCTION

Unambiguous proof of the σ-structures of, and metallotropic and prototropic rearrangements in, silicon cyclopentadienyls has now been obtained from studies mainly related to (trimethylsilyl)cyclopentadiene $C_5H_5Si(CH_3)_3$.

Electronography showed[1] that the C_5H_5-part of the molecule was envelope-

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* For Part IV see ref. 8.

structured, with the silicon atom being predominantly bonded to a carbon atom*, in agreement with earlier structural estimates based on PMR[3–5] spectroscopic studies (*cf.* also refs. 6,7). These results have recently been confirmed by ^{13}C spectroscopy[8]. The temperature dependence of the PMR spectra led to the conclusion[4–6] that the compound was subject to a metallotropic rearrangement.

Davison and Rakita[6] were the first to observe the unsymmetrical collapse of the olefinic multiplet in the spectrum of $C_5H_5Si(CH_3)_3$; they concluded that the migration was not random (either 1,2 or 1,3 shift), although from additional evidence, they proposed that a 1,2 shift occurred in the system.

Unfortunately, these authors never achieved a resolution sufficient to allow a full analysis of the spectra, and for this reason were unable to make an unambiguous assignment of the olefinic signals or to establish with certainty whether silicon migration occurred via a 1,2 or 1,3 shift. The use of PMR spectroscopy established[5] the isomerism of $C_5H_5Si(CH_3)_3$ which was thought to provide evidence in favour of the prototropic rearrangement. This isomerism was studied more extensively by Ashe who assigned the structures of the main isomers and determine the thermodynamic characteristics of the hydrogen migration[9]**.

Using a double resonance technique, we have established the structures of all the isomers of silicon cyclopentadienyl $C_5H_5SiCH_3Cl_2$ and have assigned the signals in the olefinic domain of the PMR spectrum of the fluxional isomer[11,12]. In this compound, silicon migration has been shown*** to proceed predominantly via a 1,2 shift.

Metallotropic rearrangements have also been observed in silicon indenyls such as 1-(trimethylsilyl)indene[7,14–16] and 1,2-bis(trimethylsilyl)indene[17]. The results obtained for these compounds demonstrate that the metal migrates apparently through 1,3 jumps via two concerted 1,2 shifts. The isoindenyl derivative formed through one 1,2 shift is so short-lived that it cannot be observed in the spectra****.

A metallotropic rearrangement has also been observed in (methylcyclopentadienyl)trimethylsilane $CH_3C_5H_4Si(CH_3)_3$, although the interpretation of the results was far from quantitative[20].

In this present paper, the PMR spectra of a series of σ-cyclopentadienyls, $C_5H_5Si(CH_3)_nCl_{3-n}$, are described and analyzed, with a view to establishing how a substituent at the silicon atom affects the course of the migration.

It has been shown[11,12] that the correct structure may be established and the olefinic protons correctly assigned only after a complete analysis of the spectra with the relative signs of J(HH) included. The problems associated with such an assignment using the experimental evidence previously acquired need further consideration

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* h^1-C_5H_5 type structure on Cotton's notation (see ref. 2); σ-structures (usual notation).

** While this paper was in preparation Egger and James[10] published the results of a complete study of the equilibrium associated with the three isomers of $C_5H_5Si(CH_3)_3$.

*** A typographical error in analysing the AA'BB'X spectra (see ref. 12), led to the erroneous assignment of the AA' and BB' signals in the spectrum and hence the predominant migration mechanism was misinterpreted. The corrected assignment (*cf.* the Errata mentioned in ref. 12) unambiguously demonstrates the 1,2 shift, and the respective corrections should be made in the text of the paper quoted above. Quite recently, Cotton and Marks, during an analysis of our spin-tickling data, have arrived at the same correct assignment[13].

**** The migration in indenyl compounds has also been discussed[18,19].

and consequently, coupling constants and the chemical shifts of the protons of σ-cyclopentadienyls have been thoroughly analyzed in this instance.

EXPERIMENTAL

$C_5H_5Si(CH_3)_3$ was synthesised using a method previously described[21], whilst other compounds in the series were obtained according to methods discussed in ref. 22. In order to eliminate any dimerisation products, all the samples were distilled immediately before recording their spectra.

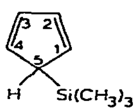
PMR spectra of $C_5H_5Si(CH_3)_nCl_{3-n}$ (n is 0 or 2) were measured on a C60HL (JEOL) spectrometer as described previously[11,12]. The spectra of $C_5H_5Si(CH_3)_3$ were measured on a HA-100D (Varian) spectrometer. The maximum resolution achieved was 0.1 Hz (0.2 to 0.3 Hz at lower temperatures). The temperature control was accurate to ±1°. Frequency sweep was used throughout. In the double resonance experiments, the frequency was adjusted by means of a D-890B Muirhead audio frequency oscillator accurate to ±0.1 Hz. The spectra of $C_5H_5Si(CH_3)_nCl_{3-n}$ (n is 0 or 2) were obtained either with the pure liquids or with solutions in CCl_4 using TMS as an internal reference. A benzene reference was used with solutions of C_5H_5-$Si(CH_3)_3$ in CS_2, since it was found that the methyl signals of this compound and the signal of TMS were superimposed*. All shifts recorded in the Tables are in δ-scale. The position of the benzene signal was taken to be equal to 7.26 ppm in order to convert the measured values into δ-scale.

RESULTS

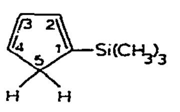
PMR spectrum of (trimethylsilyl)cyclopentadiene, the main vinylic isomer

The 100 MHz spectra of $C_5H_5Si(CH_3)_3$ obtained at −40 to +20° are shown in Fig. 1. Similar spectra have been previously reported[3-7] and were also probably observed in refs. 9 and 10. In most of these studies, however, the spectral analysis based on the results was not complete[3-6,9]. Since the spectra of $C_5H_5Si(CH_3)_3$ resemble those of $C_5H_5Si(CH_3)Cl_2$ (refs. 11, 12) rather closely, it is reasonable to assume that the former spectra may be analysed in the same way as that employed for the latter spectra**.

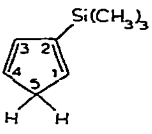
The spectra reveal the presence of three isomers of $C_5H_5Si(CH_3)_3$:



(I)



(II)



(III)

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* The solvent effect was not studied, although [judging from the behaviour of $C_5H_5Si(CH_3)_3$ in weak-solvating or non-anisotropic solvents such as CCl_4, cyclohexane, CS_2] it does not exceed ±0.02 ppm. Magnetically anisotropic solvents (benzene, toluene), however, shift the olefinic signals by 0.10 to 0.15 ppm upfield.

** The data reported in refs. 11 and 12 are used extensively in the discussion given below.

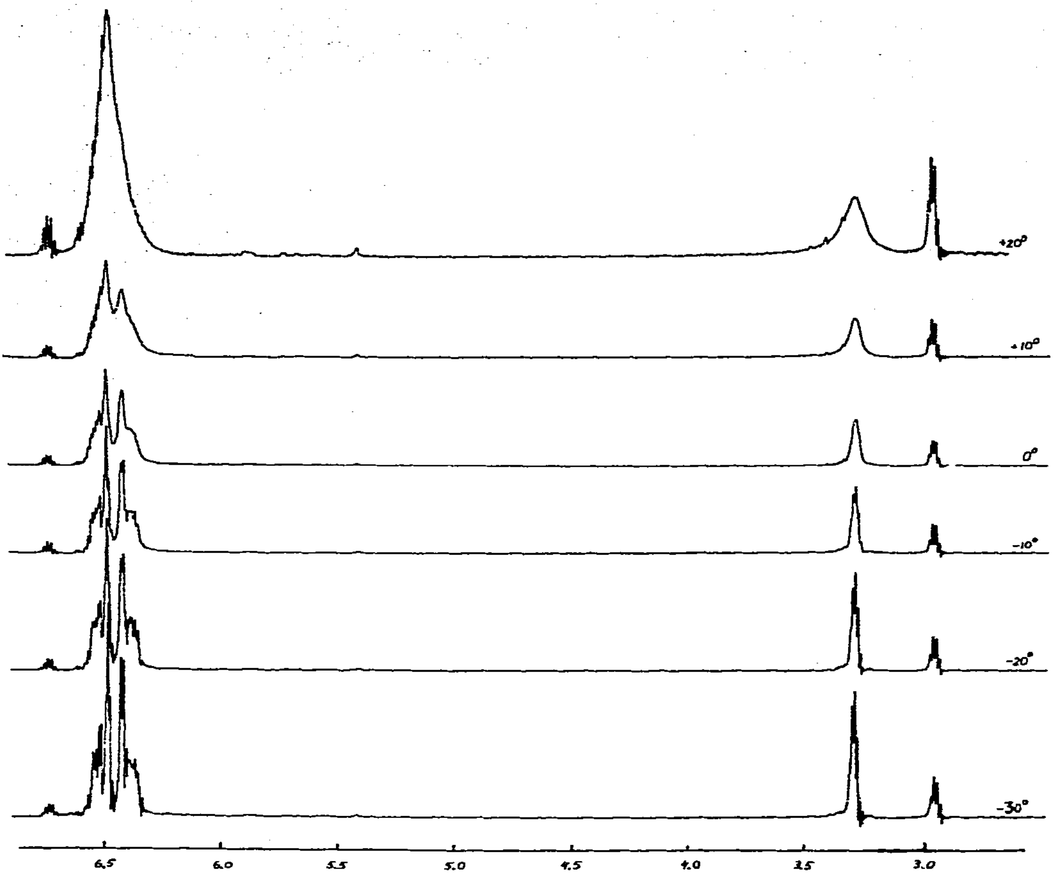

Fig. 1. Temperature-dependent PMR spectra (100 MHz) of $C_5H_5Si(CH_3)_3$. Temperatures are indicated in the spectra. The shifts are in δ-scale. The methyl region is not shown. The spectrum at 20° is shown at somewhat higher amplifications. For the assignment, see the text.

The furthest upfield signal (−0.02 ppm; not shown in Fig. 1) is that of the methyl groups of the predominating (ca. 90% of the mixture) isomer (I). The weaker signal at 0.22 ppm belongs to the methyls of the isomers (II) and (III)*. The other signals are assigned as follows: CH_2 protons of (II) at 2.9 ppm**; 2-proton of (II) at 6.85 ppm; olefinic protons of (I) and 3,4-protons of (II) at 6.4 to 6.6 ppm.

The saturation transfer effect[11] has been used*** in the study of the spectrum of the isomer (II). Figure 2b shows the spectrum obtained through irradiating the

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* In a weak solution of $C_5H_5Si(CH_3)$ in benzene, the signals of the methyls of (II) and (III) are resolved owing to the ASIS effect (*cf.* the spectrum of $C_5H_5Si(CH_3)Cl_2$ in ref. 11). In an earlier paper, Ashe observed three signals for the three isomers[9], with methyl shifts of −0.11, +0.14, +0.19 ppm for the (I), (II), (III) respectively. Similar values were reported in ref. 10.

** The signal coincides with the CH_2 signal of (III). As the concentration of the latter isomer, however, does not 2% its spectrum was not analysed. The analysis given below provides unambiguous proof of the structure of the main vinylic isomer.

*** *Cf.* recent applications of the effect to exchange processes in organometallics[7,23].

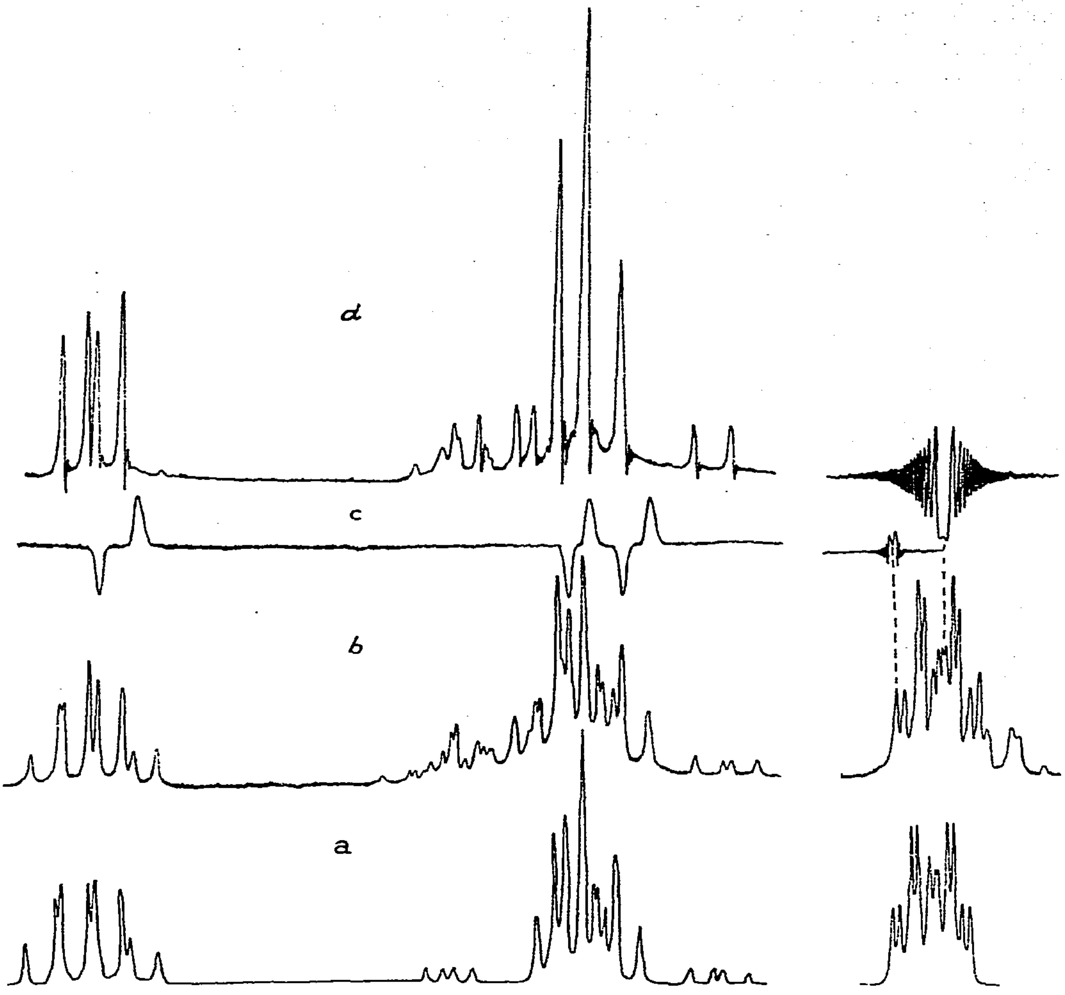

Fig. 2. (a). The theoretical spectrum of the main vinylic isomer of $C_5H_5Si(CH_3)_3$. The parameters are summarized in Table 6. (b). The experimental spectra of the vinylic isomers: at 6.80 to 6.50 ppm, the spectrum is recorded with the methyne proton of the isomer (I) being irradiated (the saturation transfer); at 2.95 to 3.00 ppm, the spectrum is recorded in the monoresonance conditions; at 6.65 ppm and at 2.95 ppm, additional signals are present which belong to isomer (III). (c). The INDOR spectrum, the extreme left line in the Y_2 proton spectrum being monitored. (d). Double resonance spectrum, the signal at 2.97 ppm (Y_2 part) being irradiated by a strong RF field; at 6.65 ppm, additional signals are present which belong to isomer (III). All the experimental spectra in Fig. 2 were recorded at room temperature.

methyne proton signal, and the respective spectrum of the vinylic isomers*. Increasing the irradiation power of the second RF field acting on the CH_2 protons causes the collapse of the spin multiplet and thus simplifies the spectrum of the vinylic isomer (II), the initial $AMXY_2$ spectrum of the latter transforming to a readily

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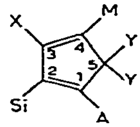
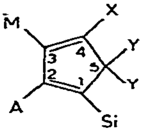
* The vinylic isomer spectrum is not distorted because $\gamma \cdot H_2/2\pi \sim 1/\sqrt{T_1 \cdot T_2}$.

analysable AMX spectrum. However, in contrast with the spectrum of the vinylic isomer of $C_5H_5Si(CH_3)Cl_2$ previously analysed[11], the spectra in Fig. 2b display perturbations due to a strong coupling between the M and X (3- and 4-, respectively) protons whose J/δ ratio is 1.2. The perturbations make the A proton signal (at the lowest field) unsymmetrical*, mix the transitions at the MX-part, and eliminate the degeneration at the Y_2-part. For example, the two transitions leading to the extreme left lines of the Y_2-protons spectrum, which are resolved in Fig. 2a, coalesce if the coupling is weak (see Fig. 2e in ref. 11).

The J(HH) coupling constants of the olefinic protons are positive for the AMX spectrum, as judged from the fact that their values are close to those given in ref. 11. To perform an analysis of the entire $AMXY_2$ spectrum, it is necessary to choose one of the eight (2^3) combinations of the relative signs of $J(AY_2)$, $J(MY_2)$, and $J(XY_2)$. It was shown[11] that the versions $(+++)$, $(-++)$, $(+--)$, $(---)$ are never implemented, since J(MY) and J(XY) must have different signs if $^3J(HH)>0$ and $^4J(HH)<0$ (see also Discussion). Further, the versions $(+-+)$ and $(-+-)$ are hardly probable because the condition[11,12,24] $J_{14} \approx J_{23} > J_{13} \cong J_{24}$ is, as a rule, satisfied. Thus, the final choice must be made between the two remaining versions (Table 1).

TABLE 1

POSSIBLE COMBINATIONS OF RELATIVE SIGNS OF J(HH)
THE ASSIGNMENT OF THE $AMXY_2$ SYSTEM FOR THE VINYLIC ISOMERS

Version	Coupling constant			Structure and assignment[a]
	AY	MY	XY	
I	+	+	−	
II	−	−	+	

[a] The assignment uses the criterion $^3J(HH) > 0$, $^4J(HH) < 0$.

From the results obtained from an analysis of the AMX sub-spectrum and from the J(HH) values given in ref. 11, and using a simulating YaMR-1 program, we have calculated a number of theoretical spectra for the $AMXY_2$ system. Figure 2a shows the theoretical spectrum which provides the best fit for all experimental spectra. The characteristic parameters (δ and J) are listed in Table 6. Although the M and X protons undergo strong coupling, the calculated spectra differ very little, irrespective of whether version I or II (Table 1) are used. Figure 2a shows the theoretical spectrum corresponding to version II. To verify the relative signs, it is necessary

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* As in ref. 11, the condition $|J(MX)| > |J(AM)| > |J(AX)|$ is assumed (*i.e.*, $\delta_A > \delta_X > \delta_M$).

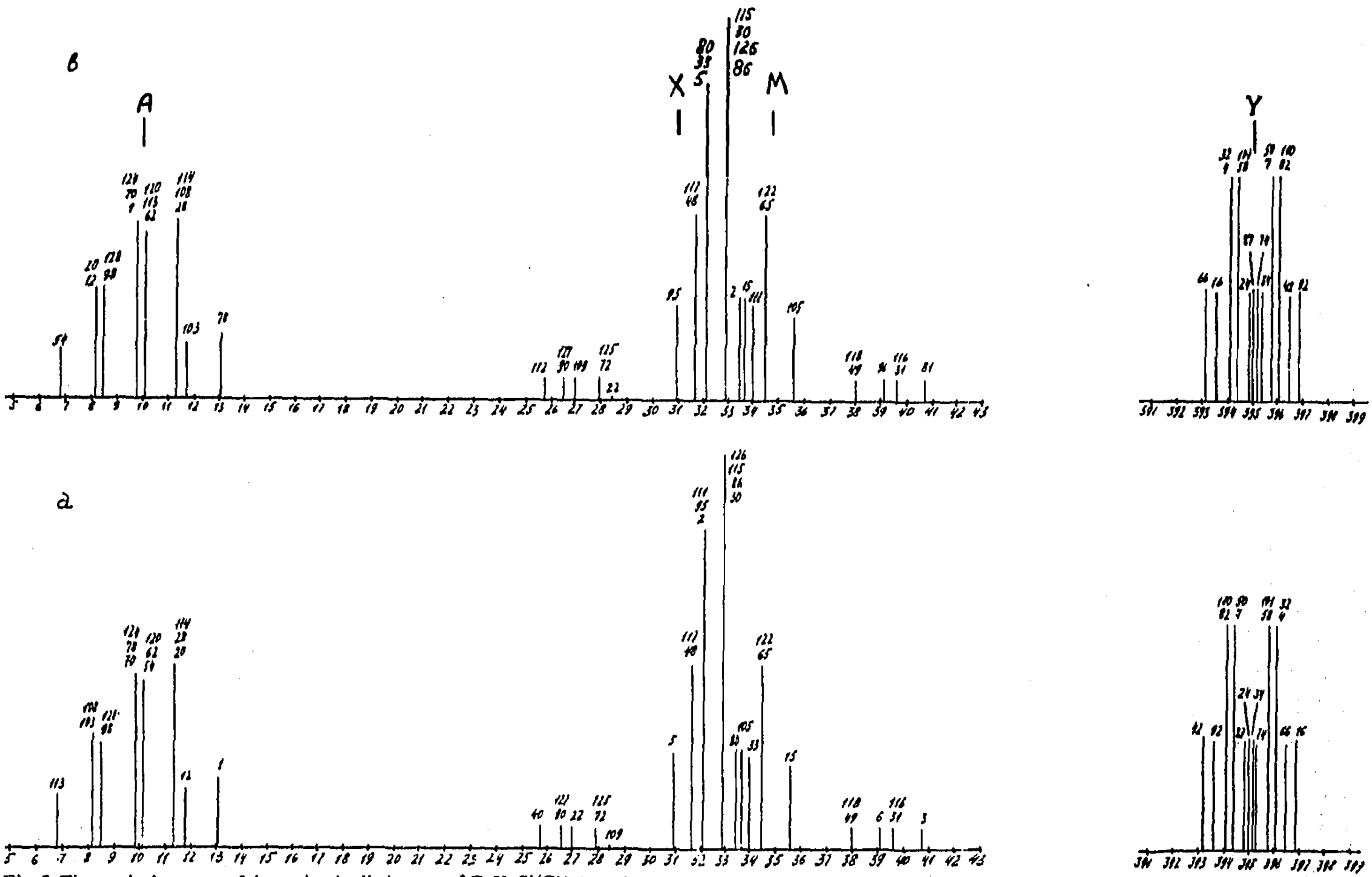

Fig. 3. Theoretical spectra of the main vinylic isomer of $C_5H_5Si(CH_3)_3$, calculated with the parameters listed in Table 6 and the signs listed in Table 1; a, version I; b, version II. The numbering of the transitions is also shown. Frequency measured in Hz relative to an arbitrary point on the left.

to apply a double resonance technique, *e.g.* tickling[11] or INDOR[25-27]. The latter technique appears to be more advantageous, since the use of tickling in a system containing an isomeric mixture could prove to be rather complicated. Figure 2c shows the experimental INDOR spectrum obtained while monitoring the extreme left hand line in the Y_2 proton spectrum. Figure 3 shows two spectra calculated for the $AMXY_2$ system, and the numbering of the transitions* (Figs. 3a and 3b correspond to the use of versions I and II, respectively). The effects expected in the INDOR spectra are summarised in Table 2.

TABLE 2

EXPECTED OVERHAUSER EFFECTS IN THE INDOR SPECTRA OF $AMXY_2$ SYSTEMS WHILE MONITORING THE EXTREME LEFT HAND LINES OF THE Y_2 PROTON SPECTRUM

Transition monitored in Y_2-part	Coupling type, Δ	Observed INDOR lines in parts		
		A	X	M
66	0	62	80	65
	2	103	30	105
16	0	12	30	15
	2	62	2	65
42	0	70	40	49
	2	20	90	6
92	0	108	90	100
	2	70	112	49

Table 2 and the spectra in Fig. 2c demonstrate that the use of INDOR shows that version II provides the correct combination of relative signs, and in Table 6 the signs of the coupling constants arising from the above experimental results are tabulated. From this it follows that the main vinylic isomer is isomer (II)**.

PMR spectra of 5-(trimethylsilyl)cyclopentadiene[isomer(I)]

Under non-fluxional conditions (at −30°, Fig. 1), isomer (I) should produce an AA'BB'X spectrum similar to that which was analysed for $C_5H_5Si(CH_3)Cl_2$ in ref. 12. Figure 4c shows the 100 MHz spectrum at about 3.3 ppm (the methyne proton, X-part of AA'BB'X system), and at about 6.5 ppm (the olefinic protons, AA'BB'-part of AA'BB'X system). The irradiation of the methyne proton leads to an AA'BB' spectrum, Fig. 4d, which may be analysed in a similar fashion to that employed in refs. 12 and 28. The entire AA'BB'X spectrum has been analysed with the aid of a YaMR-1 program. The constants $J(AX) = \pm 0.95$ Hz and $J(BX) = \pm 1.20$ Hz provide the best fit to the experimental spectrum. The calculated spectrum is shown in Fig. 4a.

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* The energy diagram for $AMXY_2$-system (AMX sub-system excluded) was given in ref. 11.

** Recently, Ashe has attempted to establish the structures of the isomers of $C_5H_5Si(CH_3)_3$ via the structures of the adducts formed in the reaction with acetylenedicarboxylic ester[9]. It should be noted, however, that such an analysis is based on the assumption that the prototropic rearrangement at 0° is slower than the Diels–Alder reaction. Though this assumption is *a priori* not necessarily true, it has been verified by the results reported in this paper.

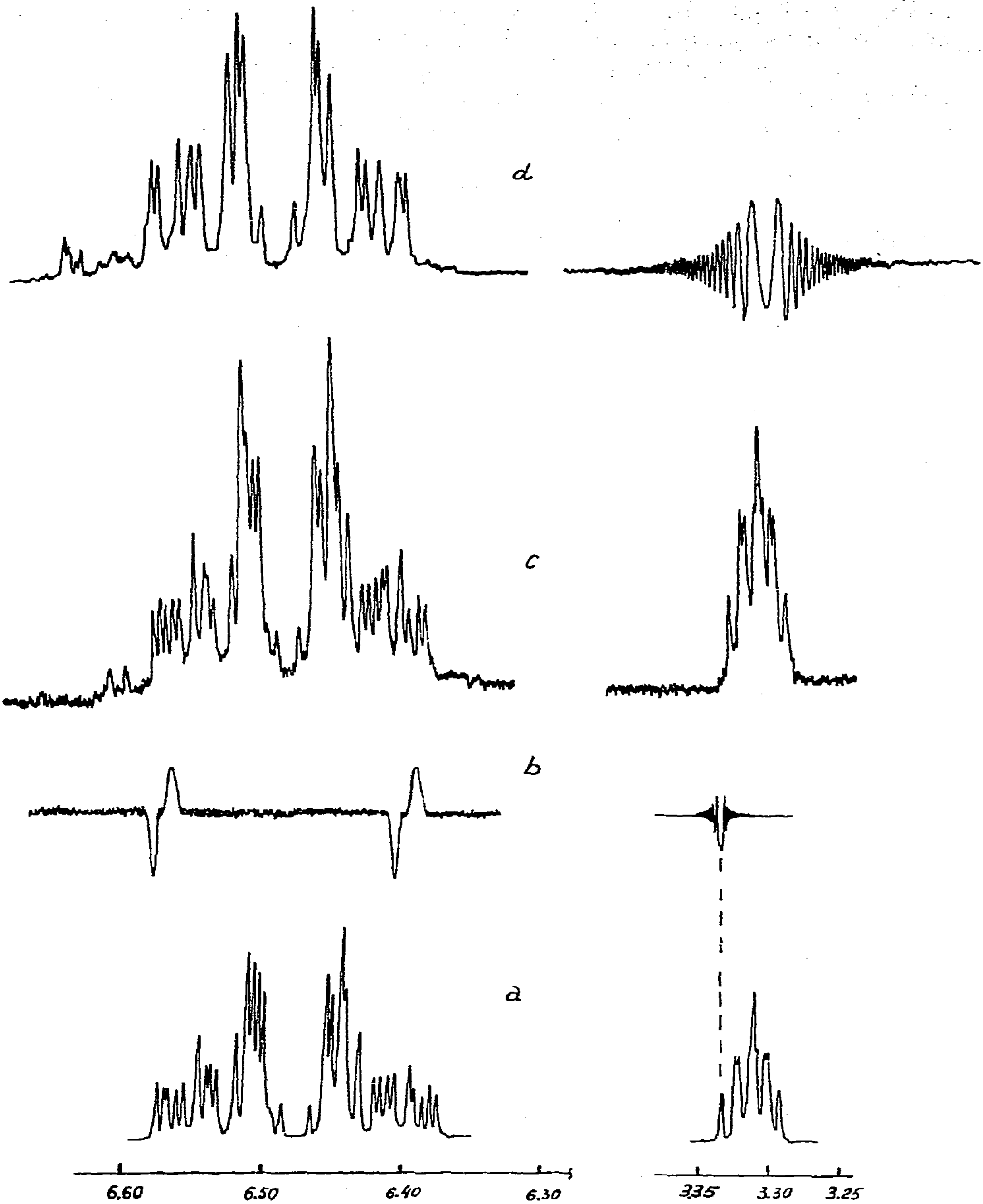


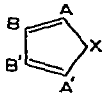
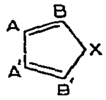
Fig. 4. (a). The theoretical spectrum of isomer (I) of $C_5H_5Si(CH_3)_3$ (AA'BB'X type), calculated with the parameters listed in Table 5. (b). The INDOR spectra obtained while monitoring the extreme left line in the X part. (c). The experimental spectrum at 6.30 to 6.60 ppm (AA'BB' part) and at 3.30 ppm (X part), recorded at −40°. (d). The double resonance spectrum, the signal at 3.31 ppm being irradiated by a strong RF field. The signals present at 6.65 ppm belong to the vinylic isomers.

If the condition (*cf.* Discussion) $J_{15}=J_{45}>0$, $J_{25}=J_{35}<0$, is assumed, then two versions of the assignment remain for selection (Table 3).

In Fig. 5 the transitions for both versions[*] are numbered. Figures 5a and 5b correspond to versions I and II, respectively. It should be noted that these versions lead to similar spectra, and for this reason a double resonance technique should be applied. The correct version has been found through an application of INDOR. If the extreme left line in the X-proton spectrum is monitored (58-transition in version II, 135-transition in version I), the Overhauser effect should be obtained either whilst observing the central 43, 132, 155, 205 (version I) or the extreme 16, 57, 118, 168 (version II) lines. The INDOR-spectrum (Fig. 4b) indicates that version II provides the correct combination.

TABLE 3

COMBINATIONS OF RELATIVE SIGNS IN, AND ASSIGNMENTS OF, THE AA'BB'X SYSTEM ($\delta_A > \delta_B$)

Version	Signs		Assignment
	$J(AX)=J(A'X)$	$J(BX)=J(B'X)$	
I	+	−	
II	−	+	

PMR spectra of (dimethylchlorosilyl)- and (trichlorosilyl)cyclopentadienes

The spectra of these compounds have been analysed as above (see also refs. 11, 12). The concentration of the vinylic isomer (III) is always at or below 10% that of the isomer (II), and for this reason an analysis of the spectrum of (III) is only possible in part. Although the analysis of (II) does not include the relative signs, since the absolute values of the J(HH) constants are closely related within the series of compounds reported in this study, the signs of the constants have been assumed on the basis of the data obtained for isomer (II) from the above analysis (*cf.* also ref. 11). The spectra of isomer (I) have been analysed at temperatures at which the rate of rearrangement is sufficiently small. The signals of the isomers (I), (II) and (III) are superimposed and the concentration of isomer (I) is low and for this reason the AA'BB'X spectrum of $C_5H_5SiCl_3$ could not be fully analysed. However, since the assignment of the olefinic signals is very important, tickling experiments were used as in the case of $C_5H_5SiCH_3Cl_2$, ref. 12. By this method, the upfield signal in the spectrum was shown to be related to the 1,4 protons of the cyclopentadienyl ring in both $C_5H_5SiCl_3$ and $C_5H_5SiCH_3Cl$.

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[*] The double resonance effects are more easily understood if use is made of the energy level pattern reported in ref. 12.

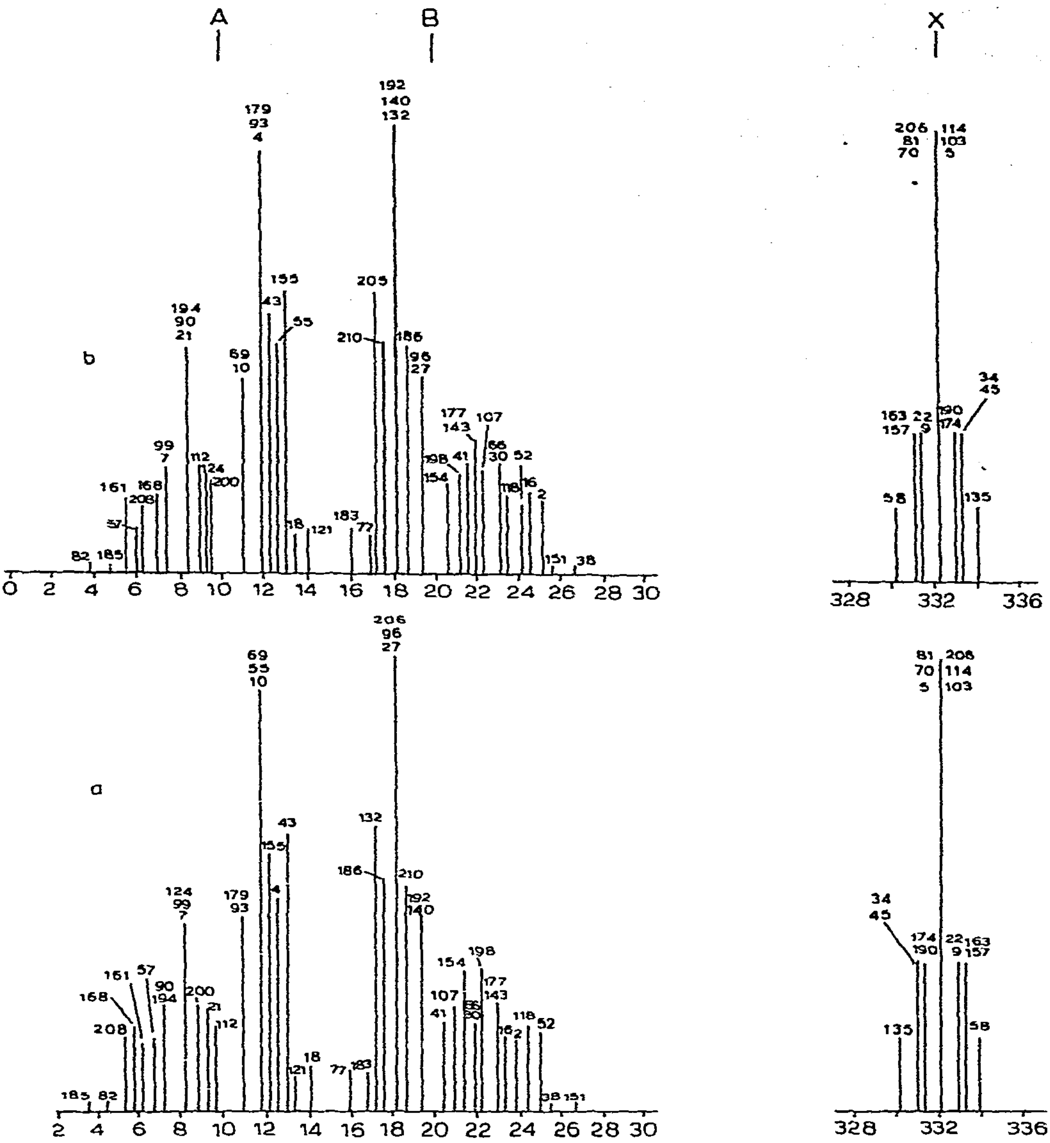

Fig. 5. Theoretical spectra (the transitions are numbered in the Fig.) of isomer (I) of $C_5H_5Si(CH_3)_3$, calculated with the parameters listed in Table 5 and the signs listed in Table 3. 5a, version I; 5b, version II.

Results of an analysis of PMR spectra

All the results obtained for the $C_5H_5Si(CH_3)_nCl_{3-n}$ series are summarised in Tables 4–7. The results in Table 4 clearly demonstrate that an increase in the number of chlorines attached to the silicon atom shifts the prototropic equilibrium towards the formation of vinylic isomers. On the other hand, the spectral data show that the values of δ and *J* vary insignificantly from one compound to another. Simple regularities occur in the behaviour of chemical shifts: thus, the signals associated

TABLE 4

ISOMER RATIOS FOR THE SERIES $C_5H_5Si(CH_3)_nCl_{3-n}$

n	Isomer content (%)			B.p.[a] [°C(mm)]
	(I)	(II)	(III)	
0	35	59	6	59(15)
1	50	45	5	58(15)
	75	22	3	62(15)
2	79	19	2	54(15)
3	90	9	1	54(15)

[a] The composition of the isomeric mixture depends somewhat on the conditions of distillation. The values in the table probably correspond to non-equilibrated conditions.

TABLE 5

PMR DATA FOR ISOMERS (I) (5-SUBSTITUTED ISOMERS) OF THE SERIES $C_5H_5Si(CH_3)_nCl_{3-n}$ (n IS 0, 1, 2, 3)[a]

n	Chemical shifts (ppm)						Coupling constants (Hz)					
	Position in the cycle					$\delta(CH_3)$	$J_{12}=J_{34}$	J_{23}	J_{14}	$J_{24}=J_{13}$	$J_{15}=J_{45}$	$J_{25}=J_{35}$
	1	2	3	4	5							
0	6.44	6.74	6.74	6.44	3.65		[b]	[b]	[b]	[b]	+0.9	−0.9
1^c	6.53	6.75	6.75	6.53	3.65	0.27	+5.2	+2.0	+2.0	+1.2	+1.1	−0.9
2	6.48	6.64	6.64	6.48	3.50	0.19	+5.4	+2.0	+2.0	+1.2	+1.0	−1.0
3^d	6.42	6.53	6.53	6.42	3.31	−0.02	+5.0	+2.2	+2.2	+1.4	+1.2	−0.95

[a] Chemical shifts are in ppm (δ-scale), coupling constants in cps; the shifts are accurate to ±0.01 ppm, the constants to ±0.1 Hz. [b] Analysis was not possible due to the superimposition of the signals. [c] Ref. 12. [d] The spectra were analysed in part in refs. 5, 6 and 9.

TABLE 6

PMR DATA FOR ISOMERS (II) (1-SUBSTITUTED ISOMERS) OF THE SERIES $C_5H_5Si(CH_3)_nCl_{3-n}$ (n IS 0, 1, 2, 3)[a]

n	Chemical shifts (ppm)					Coupling constants (Hz)					
	Position in the cycle				$\delta(CH_3)$	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}
	2	3	4	5							
0^b	7.27	6.54	6.78	3.13		+1.9	+1.3	−1.8	+5.2	−1.5	+1.3
1^c	7.09	6.54	6.73	3.13	0.82	+1.85	+1.20	−1.85	+5.10	−1.45	+1.25
2^b	6.95	6.52	6.65	3.05	0.56	+1.9	+1.3	−1.8	+5.2	−1.5	+1.2
3	6.82	6.58	6.61	2.97	0.22	+1.7	+1.2	−1.7	+5.1	−1.5	+1.2

[a] See footnote a to Table 5. [b] Signs of constants assumed to be the same as for n equal to 1 or 3; constants accurate to ±0.1 Hz. [c] Ref. 11.

with the methyl groups in all the isomers, the methyne proton in isomer (I), CH_2-groups in isomers (II) and (III), the proton (2-proton in isomer (II), 1-proton in isomer (III)) vinylic with respect to the substituent at a double bond, and the 4-proton in isomer (II) are shifted downfield when the number of chlorine atoms in the compounds increases. Table 5 demonstrates that the condition $\delta_{14} < \delta_{23}$ holds for isomer (I) of

TABLE 7

PMR DATA FOR ISOMERS (III) (2-SUBSTITUTED ISOMERS) OF THE SERIES $C_5H_5Si(CH_3)_nCl_{3-n}$ (*n* IS 0, 1, 2, 3)[a]

n	Chemical shifts (ppm)					Coupling constants[d] (Hz)					
	Position in the cycle				$\delta(CH_3)$	J_{13}	J_{14}	J_{15}	J_{34}	J_{35}	J_{45}
	1	3	4	5							
0	7.12	~6.5[b]	~6.5[b]	3.06		1.3	1.8	1.4	[c]	1.2	1.2
1	6.94	~6.5[b]	~6.5[b]	3.02	0.82	1.5	1.9	1.5	[c]	1.5	1.5
2	6.80	~6.5[b]	~6.5[b]	2.96	0.56	1.2	2.0	1.4	[c]	1.4	1.4
3[e]				2.94	0.22						

[a] See footnote *a* to Table 5. [b] Approximate values, from double resonance experiments. [c] Not observed, owing to the superimposition of the signals of 3- and 4-protons. [d] Except for *J*(35), all constants are, possibly, positive; accuracy ±0.2 Hz. [e] Other parameters could not be determined due to the very low concentration of the substrate.

all the compounds but that there is no clear dependence of the shifts δ_{23} and δ_{14} on the number of chlorine atoms attached to the silicon atom.

DISCUSSION

Proton coupling constants and chemical shifts in σ-cyclopentadienyl compounds

It has been shown that the assignment of structures (isomer (II) or isomer (III)) and of the olefinic signals (isomer (I)) is based on the relative signs of the constants *J*(HH). For this reason a systematic approach must be adopted in assigning the PMR parameters of σ-cyclopentadienyl compounds. The experimental data of which the authors are aware are summarised in Table 8 for values of *J*(HH), and Table 9 for values of the chemical shift.

The data in Table 8 enable the following observations to be made:

(a) All olefinic coupling constants are positive.

(b) The constants $J_{12} = J_{34}$ have the greatest magnitudes (+4.6 to 5.2 Hz).

(c) Among the olefinic constants, $J_{13} = J_{24}$ is the smallest (1.0 to 1.4 Hz).

(d) J_{23} is close to J_{14} (2.0 to 2.2 Hz)*.

(e) The constant $J_{25} = J_{35}$ varies over the widest range.

(f) The constant $^3J_{15} = {}^3J_{45}$ is always positive (1.1 to 1.3) while the constant $^4J_{25} = {}^4J_{35}$ is usually negative (−1.6 to +0.2).

These regularities apply to both the 5-substituted isomers (AA′BB′X systems) and to the vinylic isomers (1- or 2-substituted, $AMXY_2$ spectra). The regularities (a) to (f) are, in general, valid (see Table 8) for a number of related carbocycles containing a five-membered cycle with two conjugated double bonds (indenes, fulvenes, etc.), as well as for cyclopentene.

From (d) it follows that the olefinic protons cannot be assigned on the basis of

(continued on p. 70)

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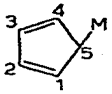
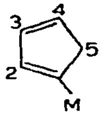
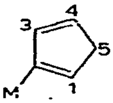
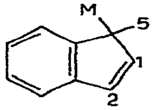
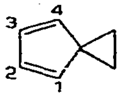
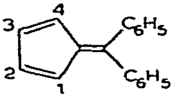
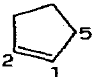
* It is noteworthy that the constants (Table 8) are always equal within the experimental error (as a rule they do not differ by more than 0.1 Hz). This can hardly be attributed to chance. The olefinic coupling constants (*cis*-butadienic conformations) are discussed in greater detail in refs. 24, 34 and 35.

TABLE 8

J(HH) COUPLING CONSTANTS IN SUBSTITUTED σ-CYCLOPENTADIENYL COMPOUNDS

No.	Compound	M	Coupling constants (Hz)						Foot-notes
			$J_{12(34)}$	$J_{13(24)}$	J_{23}	J_{14}	$J_{15(45)}$	$J_{25(35)}$	
5-Isomers									
(IV)		H	+5.05	+1.09	+1.93	+1.93	+1.33	−1.51	*a*
			+5.2	+1.0	+2.1	+2.1	+1.3	−1.6	*b*
			+2.29	−0.95	+0.86	+1.10	+1.76	−1.58	*c*
(I)		$Si(CH_3)_3$	+5.0	+1.4	+2.2	+2.2	+1.20	−0.95	*d*
(V)		$SiCH_3Cl_2$	+5.2	+1.2	+2.0	+2.0	+1.1	−0.9	*e*
(VI)		$Ge(CH_3)_3$	+5.0	+1.45	+2.2	+2.2	+1.1	−0.60	*f*
(VII)		$Sn(CH_3)_3$	+5.0	+1.2	+2.1	+2.1	+1.2	+0.25	*g*
(VIII)		$Fe(CO)_2$-π-C_5H_5	+4.66	+1.15	+2.02	+2.02	+1.17	±0.01	*h*
			+4.8	+1.3	+2.4	+2.0	±1.2	±0.4	*i*
(IX)		$Ru(CO)_2$-π-C_5H_5	+4.64	+1.17	+2.12	+2.06	+1.22	±0.1	*h*
			+4.8	+1.3	+2.4	+2.0	±1.2	±0.4	*i*
Vinylic isomers									
(II)		$Si(CH_3)_3$	+5.1	+1.20	+1.70		+1.20	−1.70(25) −1.50(35)	*d*
(X)		$SiCH_3Cl_2$	+5.2	+1.20	+1.85		+1.25	−1.85(25) −1.45(35)	*j*
(XI)		$SiCH_3Cl_2$		(+)1.5		(+)1.9	(+)1.5(15) (+)1.5(45)	(−)1.5	*j, k*
Related carbocycles									
(XII)		H	+5.58				+2.02	−1.98	*l*
(XIII)		$Sn(CH_3)_3$	+5.2				+1.5	(−)1.0	*m, n*
(XIV)		$Si(CH_3)_3$	(+)5.4				(+)1.5	(−)1.0	*m, o*
(XV)			+5.2	+1.5	+2.1	+2.0			*p*
(XVI)			+5.17	+1.38	+2.21	+1.94			*q*
(XVII)			+5.1				+2.1	−1.4	*r*

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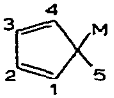
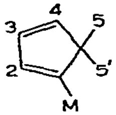
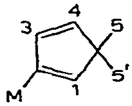
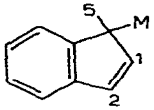
[a] Ref. 24. [b] Our analysis, neat liquid, using a C60HL spectrometer; a YaMR-1 simulating program was used. see the footnote on p. 71 in ref. 11. [c] Theoretical calculations[29]. [d] Our data. [e] Ref. 12. [f] Ref. 19; signs of $J_{10} \equiv J_{45}$ and $J_{25} \equiv J_{35}$ are assumed on the basis of the rules (*e*) and (*f*); see Discussion. [g] Ref. 30; the constants $J_{12} \equiv J_{34}$, $J_{13} \equiv J_{24}$, J_{23}, and J_{14} are assumed, the constant $J_{15} \equiv J_{45}$ and $J_{25} \equiv J_{35}$ are obtained from the averaged values, accuracy ±0.5 Hz. [h] From iterative analysis[31]; for signs of $J_{15} \equiv J_{45}$, see the rules (*e*) and (*f*) below. [i] Ref. 32. [j] Ref. 11. [k] The signs were not established. [l] Ref. 33. [m] Ref. 14. [n] Relative signs of J_{12} and J_{15} found from the averaged value. [o] Estimated. [p] Ref. 53. [q] Ref. 54. [r] Ref. 55.

TABLE 9

CHEMICAL SHIFTS OF PROTONS IN σ-CYCLOPENTADIENYL COMPOUNDS AND RELATED SYSTEMS[a]

No.	Compound	M	Chemical shifts			Conditions		Foot-notes
			1,4	2,3	5	Solvent	Temp. (°C)	
5-Isomers								
(IV)		H	6.27	6.42	2.80	Neat	20	*b*
			6.27	6.43	2.79	Neat	20	*c*
(I)		$Si(CH_3)_3$	6.44	6.55	3.31	$CS_2+C_6H_6$	−30	*d*
			6.48	6.48	3.21	Toluene	−40	*e*
			6.50	6.65	3.30	Neat	−30	*g, f*
			6.57	6.64	3.31	Neat	−40	*h, f*
			6.60	6.60	3.29	Neat	−10	*i, f*
(XVIII)		$Si(CH_3)_2Cl$	6.48	6.64	3.50	Neat	−3	*d*
(V)		$SiCH_3Cl_2$	6.53	6.75	3.65	Neat	+7	*d, j*
(XIX)		$SiCl_3$	6.44	6.74	3.65	Neat	+22	*d*
(VI)		$Ge(CH_3)_3$	6.33	6.44	3.45	Freon	−60	*k*
(VII)		$Sn(CH_3)_3$	6.51	6.51	4.25	Freon	−140	*k*
(VIII)		$Fe(CO)_2\text{-}\pi\text{-}C_5H_5$	6.33	6.00	3.50	CS_2	−80	*l, f*
			6.53	6.12	4.09	Acetone	−75	*m*
(IX)		$Ru(CO)_2\text{-}\pi\text{-}C_5H_5$	6.44	6.19	3.80	$CS_2+CD_3C_6D_5$	−82	*n, f*
			6.61	6.17	4.45	Acetone	−75	*m*
(XX)		HgC_5H_5	6.35	6.35	4.05	THF+DME	−100	*o, p*
(XXI)		HgCl	6.61	6.61	4.14	THF-d_8	−113	*o*
Vinylic isomers								
(II)		$Si(CH_3)_3$	6.61(4)	6.82(2) 6.58(3)	2.97	Neat	20	*d*
(X)		$SiCH_3Cl_2$	6.73(4)	7.09(2) 6.54(3)	3.13	Neat	20	*d, j*
(XI)		$SiCH_3Cl_2$	6.94(1) 6.5(4)	6.5(3)	3.02	Neat	20	*d, j*
Indenyl compounds								
(XII)		H	6.14	6.67	2.99	Neat	20	*q*
(XIII)		$Si(CH_3)_3$	6.54	6.88	3.43	Neat	25	*r*
(XXII)		$Ge(CH_3)_3$	6.50	6.80	3.50	Neat	29	*r*
(XXIII)		HgCl	6.74	6.88	4.44	THF	33	*s*
(XXIV)		$Sn(CH_3)_3$	6.64	6.85	3.85	CS_2	−60	*r*
(XXV)		Hg-indenyl	6.68	6.91	3.81	$CDCl_3$	−41	*t*
(XXVI)		$Fe(CO)_2\text{-}\pi\text{-}C_5H_5$	6.53	6.72	3.97	$CDCl_3$	25	*u*

[a] Shifts in ppm, δ-scale. [b] Our data, see footnote *b* in Table 8. [c] Ref. 24. [d] Our data. [e] Ref. 4. [f] Approximated through the spectrum. [g] Ref. 7. [h] Ref. 5. [i] Ref. 6. [j] *Cf.* also ref. 12. [k] Ref. 19. [l] Ref. 41. [m] Ref. 32. [n] Ref. 31. [o] Ref. 56. [p] The shift δ_5 was estimated from the shift averaged by fast migration. [q] Ref. 33. [r] Ref. 14. [s] Ref. 15. [t] Ref. 42. [u] Ref. 57.

the olefinic coupling constants alone*. Consequently, regularities (e) and (f) are especially important and merit discussion in greater detail.

The olefinic signals of the compounds $C_5H_5Si(CH_3)_nCl_{3-n}$, and of cyclopentadiene, have been assigned on the assumption that $^4J_{25} = {}^4J_{35} < 0$ and $^3J_{15} = {}^3J_{45} > 0$. In principle the double resonance experiments reported in this paper do not rule out the alternatives that $^4J > 0$ and $^3J < 0$ but merely demonstrate that the constants have different signs. For the Ge or Sn compounds the situation is even more complicated, since tickling or INDOR experiments are in this case rather cumbersome.

Nevertheless, it will be proved below that $^3J(HH) > 0$ and $^4J(HH) < 0$, although in some cases $^4J(HH)$ may be positive but not greater than 0.2 Hz.

(*i*). The assumption that $^4J_{25} = {}^4J_{35} < 0$ and that $^3J_{15} = {}^3J_{45} > 0$ is absolutely true in the case of cyclopentadiene. The olefinic signals in the PMR spectrum of this molecule show that $\delta_{14} < \delta_{23}$, as assigned on the basis of the elegant work by Roth[36]. The PMR spectra of cyclopentadiene have also been analysed by Cooper *et al.*[24] and by the present authors (Table 8, footnote[b]) and the results of all these studies agree and show that $J_{15} = J_{45} > 0$ and $J_{25} = J_{35} < 0$** and hence that conclusion (f) above is true.

(*ii*). For the analogous indenyl compounds, as well as for indene itself, the assignment of the H_1 and H_2 signals is unequivocal since the ring current of the aromatic nucleus shifts the H_2 signals downfield. Analysis of the indene spectra also shows that $^3J > 0$ and $^4J < 0$. The temperature-dependence of the spectra show that $^3J > 0$ applies for (trimethylstannyl)indene (Table 8, (XIII)). It should be noted that such relations also hold for the allyl part[37].

(*iii*). The data in Table 8 also demonstrate conclusion (e) above. All $^3J(HH)$ values differ by 0.3 Hz at the most while the values of $^4J(HH)$ range over an interval of 1.8 Hz. We have found a value of 0.25 Hz for $^4J(HH)$ during a study of the ^{13}C satellites in the PMR spectrum of $C_5H_5Sn(CH_3)_3$ under conditions of a fast metallotropic rearrangement[30]. The constants J_{15} and J_{45} were the average values obtained from ^{13}C satellite analyses. The olefinic constants were assumed as average values calculated for the series of isostructural compounds listed in Table 8. Despite the uncertainty (±0.1 Hz) in the component values, which gives a somewhat rough value for the estimated average (the accuracy is ca. ±0.5 Hz), it is clear that $J_{15} > 0$, while J_{25} is negative and close to zero.

(*iv*). Conclusion (f) is also verified by a VB analysis (π-approximation) of the structures of cyclopentadiene and indene[29].

(*v*). Finally, the vast literature on the $^3J(vic)$ values[35] indicates that this constant is unlikely to lie within the interval -1.0 to -1.5 Hz.

For these reasons the assignments given in Table 9 must be substantially correct.

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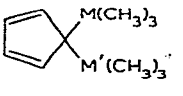
* In particular, such difficulties are inherent in the assignments for the PMR spectra of the compounds (M,M′ = Si, Ge, Sn)[50]:



** We assume that $\delta_{14} < \delta_{23}$, as proved by Roth[36].

It is now possible to discuss the other regularities which govern the behaviour of the J(HH) constants. The relation $|J_{25}=J_{35}|>|J_{15}=J_{45}|$ is satisfied for cyclopentadiene and its vinylic organosilicon derivatives (isomers (II) and (III)) but not for the 5-isomer (I). In contrast to our previous assumption[12], the geometrical structure apparently bears no direct relationship to the constants. Isomers(II) and (III) very probably possess planar rings (*cf.* the equivalence of the CH_2 signals in the spectrum) while isomer (I) is probably envelope-shaped, as proved electronographically[1]. The dihedral angle θ formed by the planes $C_5C_1H_1$ and $C_1C_5H_5$ decreases in going from the planar to the envelope structure ($\theta=59°$ for C_5H_6, $55°30'$ for 5-$(CH_3)_3Si$-C_5H_5, calculated through the data reported in refs. 38 and 1), and the Karplus equation requires that the constant $^3J(vic)$ increases, which, however, is not observed. It is possible that the system is too complicated to allow a simple angular parametrisation[39] of $^3J(vic)$ to be achieved. This possibility applies even more so for $^4J_{25}={}^4J_{35}$ which could plausibly be equated as $^4J(trans)$ (ref. 40). The inability of the constants to fit the relationships cited above may be due to the fact that the spin information is transferred along two different pathways within the C_5H_5 part of the molecule involving either an odd or an even number of bonds. The contributions of these pathways have opposite signs[29].

The constants ^3J(HH) and ^4J(HH) for cyclopentadienyl compounds correlate qualitatively with the constants for indenyl compounds, although the spectral parameters of the latter have not as yet been determined with sufficient accuracy. It is noteworthy that $^4J_{25}={}^4J_{35}$ correlates well with the rate of the metallotropic rearrangement which increases with the value of ^4J(HH). As yet the exact nature of this correlation is not clear but it is obviously not purely random. Possibly, the variations in $^4J_{25}={}^4J_{35}$ relate to the variations in the π-system which are caused by the p_π–p_π or p_π–d_π interaction with the metal. The intensity of this interaction may also govern the rearrangement rate.

Table 9 shows that the shifts δ_H correlate almost linearly in the cyclopentadienyl and indenyl series. This correlation demonstrates that although the variations in δ_H are much higher for the H, Si, Ge, Sn cyclopentadienyls as compared with the respective indenyls, the substituent effect is identical for both systems. This is also true for the J(HH) constants and the nature of the metallotropic rearrangement[19].

The shifts of the 1,4 and 2,3 protons are especially important. The values of these shifts are always very similar while $\delta(H_{1,2,3,4})$ do not correlate with any other parameters of the spectra. For the Group IVB elements (Si, Ge, Sn), the shifts δ_{14} and δ_{23} lie within the same interval, ca. 0.25 ppm; if other metals are included, then the range in the variation in δ_{23} is noticeably greater than that for δ_{14}. Thus, in contrast with the assumption by Whitesides and Fleming[43], the greatest variations are characteristic of the farthest (2,3) protons. As a rule (Table 9), the condition $\delta_{14}<\delta_{23}$ is satisfied. The 5-isomers containing carbonyl groups at the metal atom (Table 9, compounds VIII and IX) are, however, an exception. In this case $\delta_{14}>\delta_{23}$ and the 2,3 olefinic signals are shifted downfield significantly (to 6.00 and 6.19 ppm, respectively). This "anomalous" shift may be caused by magnetically anisotropic carbonyl groups. The condition $\delta_{14}<\delta_{23}$ is also not observed in the spectral behaviour of the 3,4 protons of the vinylic 1-isomers (Table 9, compounds VIII and IX), and for these reasons this condition cannot be regarded as characteristic of these compounds.

Metallotropic rearrangement in silicon cyclopentadienyls

The spectra of all the compounds $C_5H_5Si(CH_3)_nCl_{3-n}$ (n is 0, 1, 2, 3) depend on temperature (for $n=3$, see Fig. 1; for $n=1$, see Fig. 1 in ref. 12). This temperature dependence is due to the metallotropic rearrangement*. As the temperature increases the successive steps of the dynamic process (nonfluxional structure at −30°, broadening of the individual components of the multiplets at −10°, unsymmetrical broadening, and collapse, of the AA'BB' part at 0 to 10°, disappearance of the methyne signal at 60°, sharpening of the singlet which becomes a few cps wide at 120°) develop. In Fig. 1, the latter steps are not shown; (but see, *e.g.*, the spectra reported by Fritz and Kreiter[4]).

Unsymmetrical broadening, and collapse, of the AA'BB' (olefinic) signals proceed in such a manner that the upfield signal responsible for the 1,4 protons is broadened more rapidly. According to the approach of Whitesides and Fleming[43], the 1,2 shift is predominant during this process. It is, however, difficult to decide whether 1,3 migration is completely absent. Even in a nonfluxional molecule the signal is characterised by a certain unsymmetry due to some unsymmetry of the spectral parameters δ_i and J_{ij} (at −30°, Fig. 1; see also Fig. 4), as well as, possibly, by the presence of vinylic isomers, since the 3,4 olefinic signals of isomer (II) appear at approximately the same region where the more intense BB' signals of isomer (I) are located (at 6.50 ppm). However apparently insignificant, these corrections hinder the quantitative comparison of the 1,2 and 1,3 shifts**. It should be noted that the unsymmetrical collapse is a clear indication that the silicon migration is intramolecular. This intramolecularity is also confirmed by the insignificance of the solvent effect, as shown by the study of the methyne signal width at the line semi-height for $C_5H_5Si(CH_3)_3$ at 10 to 40° in various solvents [$CDCl_3$, CCl_4, CS_2, benzene, $CDCl_3/(CH_3)_3SiCl$, neat][52].

Other difficulties are inherent in estimating the thermodynamic characteristics of the rearrangement. Thus, despite the fact that the activation energies have been estimated several times[4,12,31], the calculation procedure was never discussed nor an analysis of the errors involved in the calculation given***.

Cotton and Marks[31] have published a bare set of activation energies (E_a) and entropies ($\Delta S^{\neq}$, log A) for the metallotropic rearrangement in σ-$C_5H_5Fe(CO)_2$-π-C_5H_5 and in the Ru-analogue, where the migration rate constant was given as:

$$k = A \cdot \exp(-E_a/R \cdot T) \qquad (1)$$
$$A = e \cdot \frac{k \cdot T}{h} \cdot \exp(\Delta S^{\neq}/R)$$

The accuragy claimed by these workers (0.1 kcal/mole and 0.4 e.u. for E_a and $\Delta S^{\neq}$, respectively) is, as shown below, too good to be true.

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* The scheme of the metallotronic rearrangement is given in ref. 12.

** Experiments have recently been performed in this laboratory which verify this unsymmetrical collapse as far as the ^1H spectra for the pure 5-isomer, the ^2D spectra for the equilibrated mixture of isomers $C_5D_5Si(CH_3)_3$ (content of ^2D, 90%), and the $^{13}C\text{-}\{^1H\}$ spectra for the equilibrated mixture of $C_5H_5Si(CH_3)_3$ isomers are concerned.

*** Recently, Campbell and Green[32] have published a procedure to calculate the activation parameters of the metallotropic rearrangement in the compounds studied by Cotton and Marks[31]. The equations of Campbell and Green differ somewhat from those used in this paper (see below), and if applied to our experiments would produce a slightly higher value of $\Delta S^{\neq}$.

The most important difficulty in estimating any thermodynamic data is the spin–spin interaction in a system of nuclei under the exchange conditions. The problem was first formally resolved by Alexander[44] for AB and ABX systems using density matrix methods. The approach by Binsch[45] seems to be more advantageous, however, for although this is also based on the density matrix method it uses the Louiville representation, thus allowing the more effective application of a large computer. The complete calculation of the AA′BB′X system involving the cyclic exchange is, however, still difficult and has not yet been performed. Spin–spin interaction in these systems somewhat restricts the application of the slow exchange approximation[46]. In this case, the line widths of the nuclei A, B and X (A are 1,4 protons) may be written as follows if the 1,2 mechanism is assumed:[43]

$$\begin{aligned} \pi\cdot\Delta\nu_{\frac{1}{2}(\mathrm{X})} &= \frac{1}{T^0_{2(\mathrm{X})}} + \frac{1}{\tau} \\ \pi\cdot\Delta\nu_{\frac{1}{2}(\mathrm{A})} &= \frac{1}{T^0_{2(\mathrm{A})}} + \frac{1}{\tau} \\ \pi\cdot\Delta\nu_{\frac{1}{2}(\mathrm{B})} &= \frac{1}{T^0_{2(\mathrm{B})}} + \frac{1}{2\tau} \end{aligned} \tag{2}$$

where $1/T^0_{2j}$ is the contribution of the initial spin–spin relaxation to the line width, and $1/\tau$, $1/\tau$, and $1/2\tau$ are diagonal elements of the kinetic transfer matrix[43,47]. Eqn. (2) demonstrates that the B signal will be less intensely broadened than the A signal. If the 1,3 mechanism applies then obviously an exactly opposite state of affairs will exist. Generally, the spin–spin interaction of the nuclei may be accounted for by selecting the appropriate $1/T_2$ values, *e.g.*, as in ref. 43. This contribution however should be essentially temperature-dependent, and particular, at $1/\tau \gg J$ the spin–spin interaction will be completely negligible. If, on the other hand, exchange occurs at a higher rate ($\tau \sim 1/\Delta\nu_{\overline{\mathrm{AB}},\mathrm{X}}$, where $\Delta\nu_{\overline{\mathrm{AB}},\mathrm{X}}$ is the mean difference between the shifts displayed by the AB and X parts of the spectrum; in the case described in this paper this is about 190 Hz, ($H_0 = 100$ MHz), then the line widths should be calculated at intermediate rates for the five-position exchange. This latter calculation may be somewhat simplified by assuming a three-position process[43]. After the lines have coalesced to give the singlet (at 100° in our case), the line width is given by*:

$$\pi\cdot\Delta\nu_{\frac{1}{2}} \simeq \frac{p_{\mathrm{AB}}}{T^0_{2\mathrm{AB}}} + \frac{p_{\mathrm{X}}}{T^0_{2\mathrm{X}}} + [p^2_{\mathrm{AB}}\cdot p^2_{\mathrm{X}}\cdot 4\pi^2\cdot\Delta\nu^2_{\overline{\mathrm{AB}},\mathrm{X}}\cdot(\tau_{\mathrm{AB}}+\tau_{\mathrm{X}})]$$

where the approximation $\Delta\nu_{\mathrm{AB}} = 0, p_{\mathrm{AB}} = 4/5, p_{\mathrm{X}} = 1/5, \tau_{\mathrm{AB}} = 4\tau_{\mathrm{X}} = 4\tau = 4/k$ is assumed; p_{AB} and p_{X} are probabilities of the states (A + B) and X, respectively. Thus, we obtain

$$k_{\mathrm{eff}} = \frac{1.61\cdot\Delta\nu^2_{\overline{\mathrm{AB}},\mathrm{X}}}{\Delta\nu_{\frac{1}{2}}-(\Delta\nu_{\frac{1}{2}})^*} \tag{3}$$

where $(\Delta\nu_{\frac{1}{2}})^*$ is the contribution of the relaxation mechanism to the line width.

We have calculated the migration rate constants from the values of $\Delta\nu_{\frac{1}{2}}$

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* The quantity $\Delta\nu_{\frac{1}{2}}$ was measured at 100 to 140° on a C60HL spectrometer at 60 MHz.

TABLE 10

LINE WIDTH, $\Delta\nu_{\frac{1}{2}}$, IN PMR SPECTRA OF $C_5H_5Si(CH_3)_3$. MIGRATION RATE CONSTANTS, k_{eff}, AT VARIOUS TEMPERATURES[a]

T (°K)	$\Delta\nu_{\frac{1}{2}}$[b] (Hz)	k_{eff}[c] (sec^{-1})	log k_{eff}
283	9	28	1.44
288	10	31	1.50
293	12.5	40	1.60
298	16	50	1.70
303	20	63	1.80
308	31	100	2.00
313	44	135	2.14
373	18.5	3.14×10^3	3.49
393	7.1	8.1×10^3	3.91
423	3	1.92×10^4	4.28

[a] A HA-100D spectrometer was used at 283 to 313° K, the C60HL one at 373 to 423° K. [b] For 283–313° K, $\Delta\nu_{\frac{1}{2}}$ is the methyne signal (at 3.30 ppm) width; for 373–423° K, $\Delta\nu_{\frac{1}{2}}$ is the width of the signal belonging to the five ring protons singlet. [c] k_{eff} is calculated by using eqns. (2) and (3) (see text) for the respective temperature regions.

measured at low (10 to 40°) and higher (100 to 150°) temperatures (Table 10). At low temperatures, the methyne signal (X) width is used, the rate constant being calculated through the use of eqn. (2) assuming that $1/T^0_{2(X)}=0$. At higher temperatures, the width used is that of the signal belonging to the five protons (at 4.15 ppm), the constants being calculated through the use of eqn. (3) assuming that $(\Delta\nu_{\frac{1}{2}})^*=0$. The plot of log k_{eff} *vs.* $(1/T)\cdot 10^3$ (Fig. 6), gives the following values for the parameters of eqn. (1):

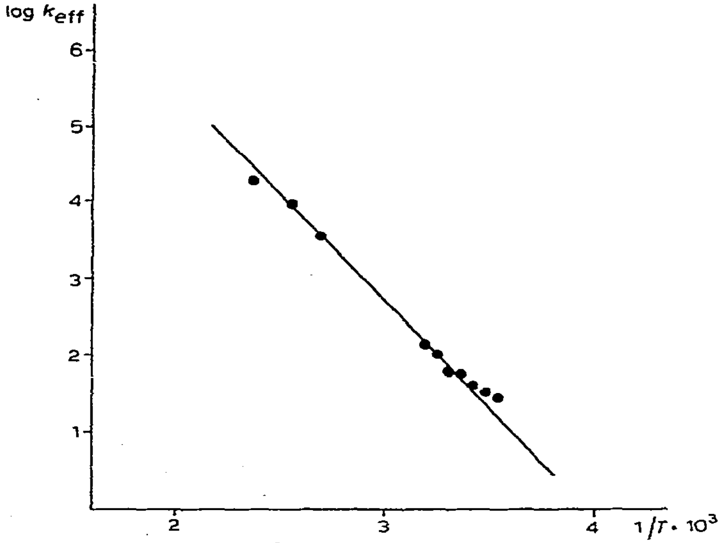

Fig. 6. log k_{eff} *vs.* $(1/T)\cdot 10^3$ for $C_5H_5Si(CH_3)_3 \cdot k_{eff}$ is the effective value of the rate constant for the metallotropic rearrangement.

$E_a = 13$ kcal/mole, $\log A = 11.3$, $S^{\neq} = -9.2$ e.u.

The plot in Fig. 6 is essentially non-linear at higher and lower temperatures. The values of $\Delta\nu_{\frac{1}{2}}$ obtained at lower temperatures are affected by the relaxation and the indirect spin–spin interaction, the latter increasing the value of k_{eff}. If the low-temperature region alone is used for the determination of the activation energy, significant errors are possible, for example, in our case the application of a linear approximation to the low-temperature region yields an activation energy equal to ca. 9 kcal/mole*.

Conversely, if at higher temperatures the relaxation is not taken into account, k_{eff} will fall. Consequently, in both the cases, the activation energy will be an underestimate if the temperature interval is not sufficiently wide and if the initial relaxation effect is not included in the calculation.

For cyclopentadienyl compounds, especially for the silicon derivatives, the singlet may be broadened owing to the prototropic rearrangement. Using the data recorded in ref. 36 it may be estimated that the hydrogen migration rate may be ca. 1 sec^{-1} at about 150°, and hence this could be quite significant vis-à-vis the NMR time scale. In summary, therefore, the activation energies are presumed to be accurate to at least ± 1 kcal/mole (this corresponds to ± 5 e.u. for the accuracy of $\Delta S^{\neq}$).

In the case of the $C_5H_5Si(CH_3)_nCl_{3-n}$ series, since the temperature range employed was rather narrow the activation energies are difficult to estimate**. Methyne signal broadening, however, is readily observable at moderate temperatures, 270 to 320°K, so that the rate (k_{300}, sec^{-1}) and the free energy of activation (ΔG_{300}*** accurate to ± 0.2 kcal/mole) may be estimated directly through the use of the equation,

$$k_{300} = \frac{k \cdot T}{h} \exp\left(-\Delta G_{300}/R \cdot T\right) \tag{4}$$

The temperatures for stereochemical rigidity, T_r, are listed below. These temperatures may be determined in various ways:

(a) by extrapolating the $\log k_{\text{eff}}$ *vs.* $(1/T) \cdot 10^3$ plot (Fig. 6) to k equal to 1 Hz ($\log k = 0$); this will be termed as $T_r(k=1)$; (b) by finding the temperature**** (T_r(exptl.)) at, and above, which the multiplet structure is broadened ($1/\tau = 1/T_2$, where T_2 is time of the spin–spin relaxation, the indirect spin–spin interactions being excluded). Both methods give the same value of T_r equal to $-20 \pm 3°$ for $C_5H_5Si(CH_3)_3$. The values of k_{300}, ΔG_{300}, $\log k_{300}$, and T_r(exptl.) are summarised in Table 11.

Table 11 demonstrates that an increase in the number of electron-withdrawing substituents attached to the metal atom leads to an increase in the free energy of activation, a decrease in the rearrangement rate, and to an increase in the temperature of stereochemical rigidity [T_r(exptl.)]. As the quantities E_a and $\Delta S^{\neq}$ quoted above are not particularly accurate, it is impossible to say whether the energy, or the entropy, of activation is responsible for this tendency.

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* Similar errors accompanied the studies of the migration in $C_5H_5SiCH_3Cl_2$ (ref. 12).

** At higher temperatures, the (chlorosilyl)cyclopentadienes dimerise very rapidly.

*** The quantity ΔG is usually much more accurate than E_a and $T \cdot \Delta S^{\neq}$ are, as found from NMR exchange experiments. See, *e.g.* ref 48.

**** Since the parameters E_a and $\Delta S^{\neq}$ can only be estimated with a low accuracy (see text), it is highly advisable to estimate the value of T_r(exptl.) in each case.

TABLE 11

CHARACTERISTICS OF THE METALLOTROPIC REARRANGEMENT IN THE $C_5H_5Si(CH_3)_{3-n}Cl_n$ SERIES

n	k_{300} (sec^{-1})	log k_{300}	ΔG_{300} (kcal/mole)	T_r(exptl.) (°K)
0	55	1.75	15.2	250
1	40	1.60	15.5	270
2	20	1.30	15.9	280
3	10	1.00	16.3	295

The low accuracy with which the characteristics of the metallotropic rearrangement in cyclopentadienyls can be measured makes it difficult to carry out any meaningful comparisons*. Other approaches, such as the programming of the multiposition exchange process and of density matrix methods sensitive to the spin–spin coupling of the nuclei, the use of ^{13}C spectroscopy (high-temperature sharpening), and of ^2D spectroscopy (slow-exchange limit), which enable the difficulties associated with the perturbations due to the spin–spin coupling** to be overcome, are more promising.

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* A general approach to the metallotropism of Si, Ge, Sn, Fe, Ru, and other metals is given in refs. 18, 19 and 49.

** Studies along these lines are at present in progress in this laboratory.

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