

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF METAL CYCLOPENTADIENYLS III.* ANALYSIS OF THE SPECTRUM OF 5-METHYLDICHLOROSILYL- CYCLOPENTADIENE (AA'BB'X SYSTEM)

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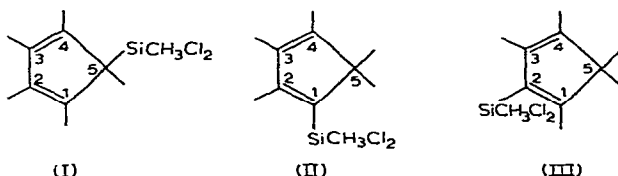
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SUMMARY

The PMR spectrum of 5-(methyldichlorosilyl)cyclopentadiene is analysed at various temperatures. At -10° , no dynamic process occurs and the spectrum is described as an AA'BB'X system. The parameters of the system have been analysed completely. The tickling experiments show that the downfield signal belongs to the 1,4-protons. The assignment, as well as the nature of the unsymmetric collapse, show that the metal migrates predominantly through a 1,3-shift. The methyne proton line width has been measured *vs.* temperature at $0-50^{\circ}$ and the activation energy of the metallotropic rearrangement is shown to be 9 ± 1 kcal·mole $^{-1}$. The prototropic rearrangement proceeds, *ceteris paribus*, by six to seven orders slower.

Earlier¹, we have shown that methyldichlorosilylcyclopentadiene is a mixture of the three possible isomers, (I), (II) and (III) and equilibrated through a prototropic rearrangement. Below 100° , the rearrangement is slow and thus the NMR time scale enables the system to be considered as quasi-stationary¹.



Isomer (I) is subject to a metallotropic rearrangement¹ fast enough at as low a temperature as 20° . This has been confirmed by the double resonance experiments which reveal the saturation transfer during the exchange.

In this paper, the spectrum of isomer (I) is analysed completely in the absence of dynamic processes and the most probable type of the metal migration is found. The temperature dependence of the spectrum allows the activation energy of the metallotropic rearrangement to be estimated.

* For Part II, see ref. 2.

EXPERIMENTAL

Methyldichlorosilylcyclopentadiene was obtained according to a published method³. To enrich the sample in isomer (I), the compound was distilled slowly at 45°/10 mm, when the concentration of 5-methyldichlorosilylcyclopentadiene became as high as 80%¹. The mono or double resonance spectra were measured on a C6OHL spectrometer (JEOL), resolution 0.2 cps (0.4 cps at low temperatures). The temperature was controlled by a JES-VT-3 bridge controller, accuracy $\pm 0.5^\circ$, and calibrated by measuring the position of the OH line in the spectrum of a 1,3-propanediol reference.

Analysis of the spectra of 5-methyldichlorosilylcyclopentadiene

Figure 1 shows the spectra obtained with the compound at various temperatures. The lines recorded at room temperature, (Fig. 1c) were assigned earlier¹. Isomer (I) has lines at about 6.5 ppm (δ -scale) and 3.5 ppm which belong to two pairs of olefinic protons and to one CH proton, respectively. At or below -10° , the lines of isomer (I) acquire their fine structure, (Fig. 1d) because the metallotropic rearrangement becomes slower. A decrease in the migration rate is also confirmed by the fact that the saturation transfer no longer takes place under these conditions (the double resonance experiments).

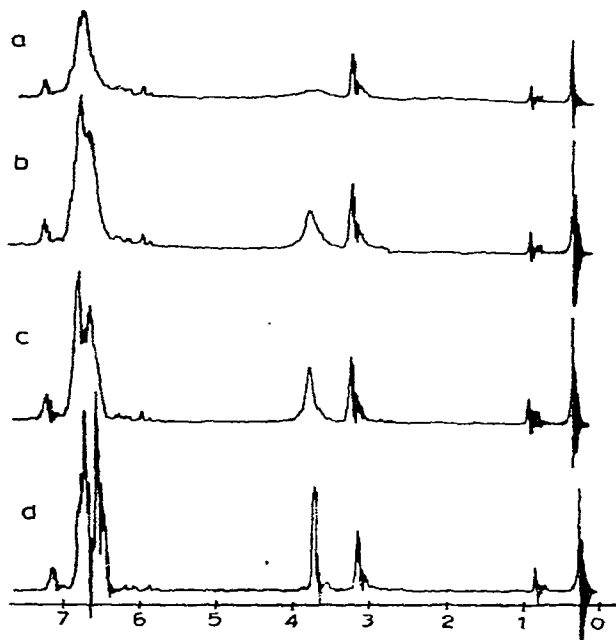


Fig. 1. PMR spectra of methyldichlorosilylcyclopentadiene at various temps.: (a) $+52^\circ$; (b) $+36^\circ$; (c) $+22^\circ$; (d) -10° .

A classification of the PMR spectra of cyclopentadienyl compounds already reported¹ ascribes the PMR spectrum of the stereochemically rigid isomer (I) to type AA'BB'X. Figure 2a shows part AA'BB' of the spectrum recorded at slow passage at

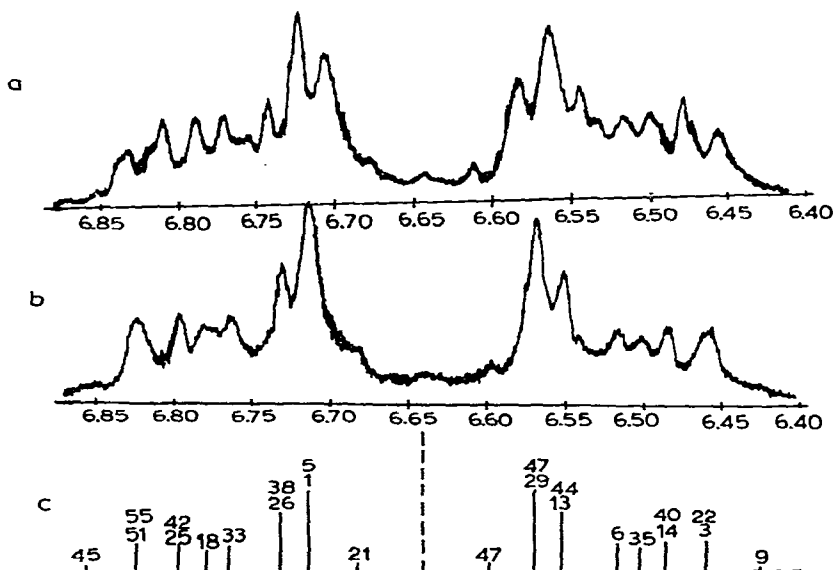


Fig. 2. The spectra of olefinic protons at -10° . (a) Monoresonance, AA'BB' part of AA'BB'X system; (b) double resonance, proton X irradiated; (c) system AA'BB', assignment of the lines.

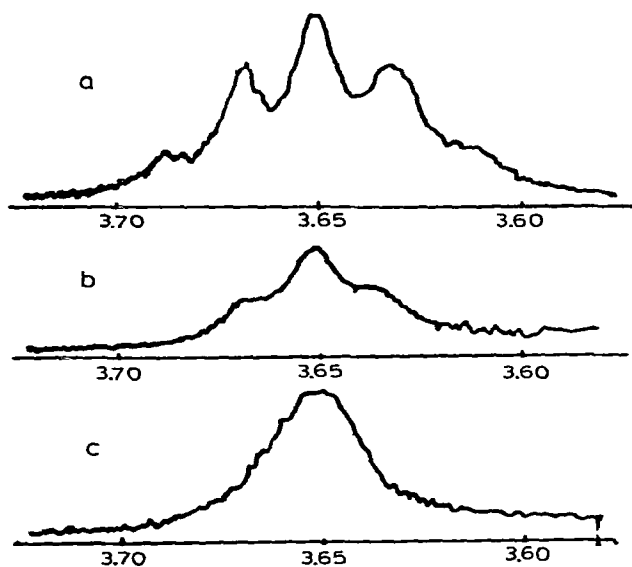


Fig. 3. Methyne proton spectra at -10° . (a) Monoresonance, X part of AA'BB'X spectrum; (b) double resonance, signal AA' irradiated; (c) double resonance, signal BB' irradiated.

-10° . Part X of the spectrum under the same conditions is shown in Fig. 3a. Irradiation of the methyne proton (part X) leads to the AA'BB' spectrum* of the olefinic protons (Fig. 2b). This spectrum has been analysed as for cyclopentadiene². The arrangement of the calculated spectrum is given in Fig. 2c (the energy diagram of the

* We assume that $\delta_A > \delta_B$.

AA'BB' system has been reported²). The calculations yield the values of δ_A , δ_B , and $J(AB')$, $J(A'B)$, $J(AA')$, $J(BB')$ constants (Table 1).

Irradiation of the olefinic signals does not produce a clear selective decoupling of the protons because the RF amplitude ($\gamma H_2/2\pi$) is comparable with the difference between the chemical shifts of nuclei A(A') and B(B'). However, the spectra shown in Figs. 3b and 3c verify that $|J(AX)| < |J(BX)| = 1.1$ cps.

TABLE 1

PMR SPECTRUM OF 5-(METHYLDICHLOROSILYL)CYCLOPENTADIENE AS ANALYSED IN THIS PAPER^a

CHEMICAL SHIFTS

Protons	AA'(1,4)	BB'(2,3)	X(5)	CH ₃
The shifts	6.75	6.53	3.65	0.27

SPIN-SPIN COUPLING CONSTANTS

12	13	14	15	23	24	25	34	35	45
+5.2	+1.2	+2.0	+0.9	+2.0	+1.2	-1.1	+5.2	-1.1	+0.9

^a The shifts are in ppm, δ -scale. Accuracy: the constants, ± 0.1 cps; the shifts, ± 0.01 ppm. Measurements were carried out at -10° .

The overall AA'BB'X spectrum was analysed similarly to the spectrum of cyclopentadiene (AA'BB'X₂ system²). A number of theoretical versions has been computed with a YaMR-1 (NMR-1) program and the following constants best fit the experiment: $J(AX)=J(A'X)=0.9$ cps, $J(BX)=J(BX')=1.1$ cps. For all practical purposes, the spectrum is not affected by the signs of constants $J(AX)$ or $J(BX)$.

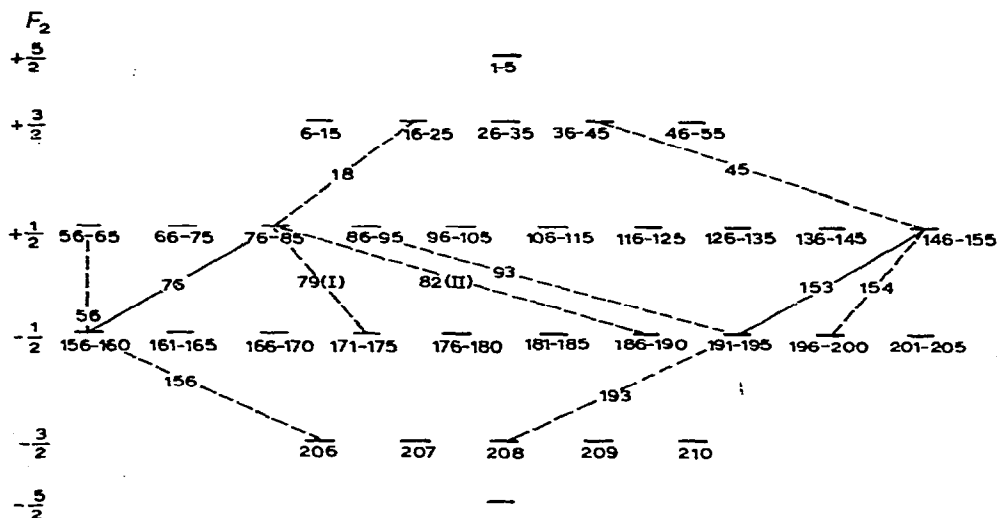


Fig. 4. Diagram of energy levels and transitions (shown by the number positioned under each level) in system AA'BB' (five-spin system). (—) irradiated signals; (----) observed signals. The lines marked by I are observed with the first array of the signs and not observed with the second.

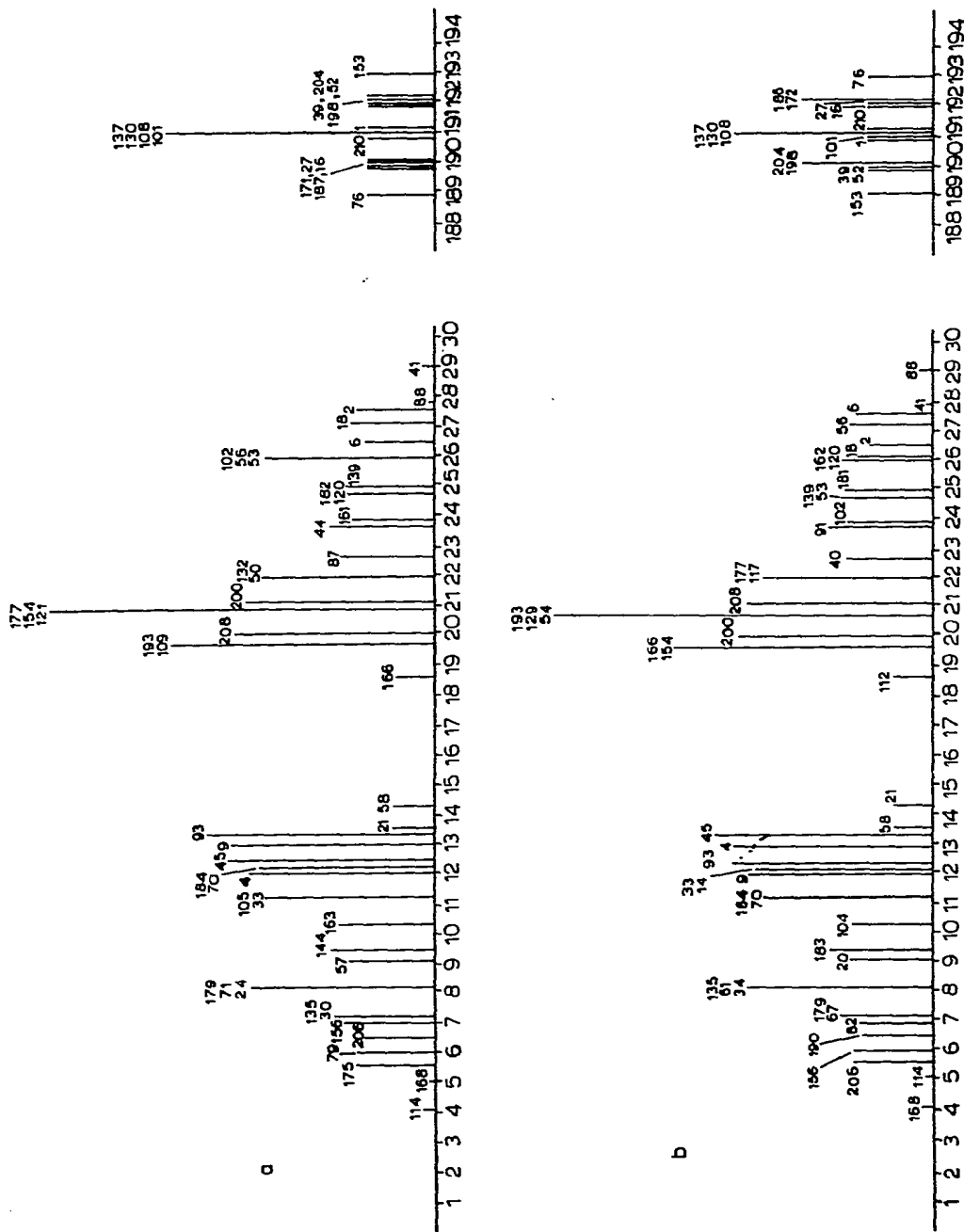


Fig. 5. AA'BB'X spectra calcd. for versions I(a) and II(b), arrangement of the transitions; X part is always positioned on the right.

When assigning the signals to the 1,4- or 2,3-protons of the cyclopentadienyl nucleus we have applied the criterion^{1,2} that is based on the determination of the relative signs of constants $J(\text{AX})$ and $J(\text{BX})$ by tickling. In our case, we have to resolve two versions only*.

- I. $J(\text{AX}) = J(\text{B'X}) = +0.9$ cps and $J(\text{BX}) = J(\text{B'X}) = -1.1$ cps
- II. $J(\text{AX}) = J(\text{A'X}) = -0.9$ cps and $J(\text{BX}) = J(\text{B'X}) = +1.1$ cps

Figure 4 shows the energy level diagram for the AA'BB'X system (considered as a five-spin system). On the basis of this diagram, the transitions are arranged in the theoretical versions I (Fig. 5a) and II (Fig. 5b). The simplest experiment that could resolve the two versions consists in irradiation of the farthest positioned lines in the X-part, X₁ and X₅. If version I is correct, irradiation of line X₁ (transition 76, Fig. 5a) should lead to splitting of transitions 79, 156 and 56, 18 which are components of lines A₁, A₂ (A-part) and B₃, B₄ (B-part) observed experimentally. Irradiation of line X₅ (153 in version I) should lead to splitting of transitions 49, 53, 154, 93 and hence should affect the central lines of the spectrum, A₃, A₄, B₁, B₂. On the other hand, version II should lead to the central lines affected by irradiation of line X₁, and lines A₁, A₂, B₃, B₄ affected by irradiation of line X₅. Thus, each experiment enables the correct version to be distinguished. The tickling will act only upon the separate components of composite lines, A₁-A₄ and B₁-B₄ (Fig. 6a), therefore the double resonance lines will have a complex nature and the multiplet structure will be distorted

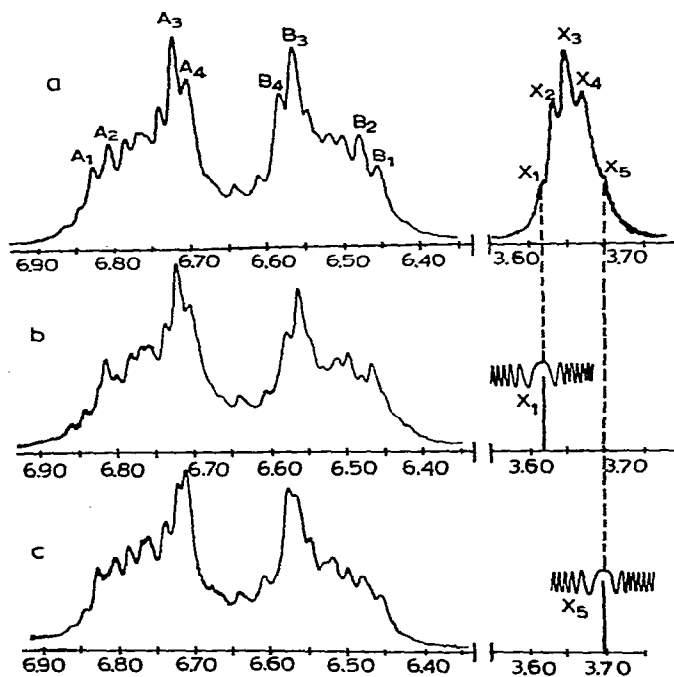


Fig. 6. The tickling expts. in the spectrum of 5-methyldichlorosilylcyclopentadiene, AA'BB' system, AA'BB' part: (a) Monoresonance; (b) line X₁ irradiated; (c) line X₅ irradiated.

* Except for $J(\text{AX})$ and $J(\text{BX}')$, all constants are assumed positive.

as a whole. Actually, when irradiating line X_1 (transition 76 in version I), a complicated picture is observed: a broadened signal which takes the place of lines A_1 and A_2 (Fig. 6). The experiments (Fig. 6) rule out version II. A complete analysis of the spectrum of 5-methyldichlorosilylcyclopentadiene is shown in Table 1.

DISCUSSION

After having analysed the variation of the spectrum of methyldichlorosilylcyclopentadiene with temperature, the saturation transfer during the double resonance experiments and the structures of the isomers containing silicon located at a vinylic position, we believe that the compound discussed in this paper undergoes a degenerated metallotropic rearrangement (metal migration) of isomer (I) (Fig. 7) and a prototropic rearrangement (hydrogen migration) leading to all three isomers (I, II, and III) of the compound (Fig. 8).

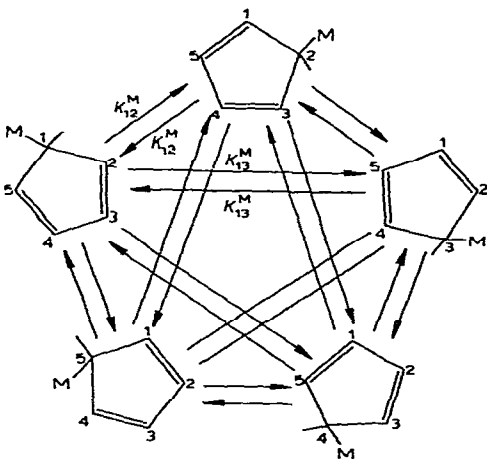


Fig. 7. A scheme showing a degenerated metallotropic rearrangement. k_{12}^M and k_{13}^M are rate constants of 1,2- and 1,3-shifts, respectively. All the structures are identical, they correspond to isomer (I).

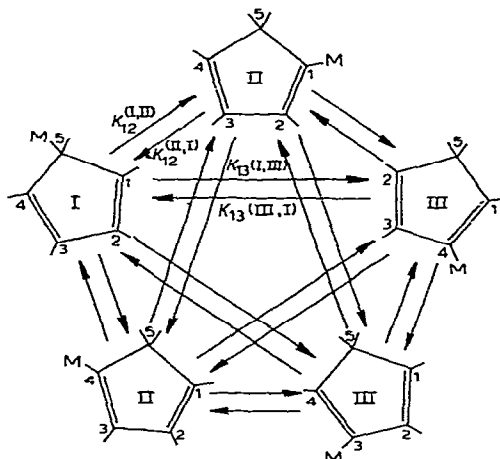


Fig. 8. A scheme showing a prototropic rearrangement. The notation of the hydrogen migration: *e.g.* $k_{13}^{(I, III)}$ means that hydrogen migrates through a 1,3-shift whereby isomer (I) transforms to isomer (III).

The metal can migrate through either a 1,2- or 1,3-shift, the rate constants being k_{12}^M or k_{13}^M , respectively. Theoretical considerations have shown^{4,5} that both processes are possible but their rates may differ significantly. In principle, the NMR technique may help in finding a favourable type of migration by analysing line shapes resulting from the exchange. Thus far, however, the difficulties inherent in such an analysis (the many-sites exchange problem, strong coupling in the spectra) limit us to a semi-quantitative discussion.

Whitesides and Fleming⁷ calculated line shapes in the spectrum of compound $C_5H_5CuP(C_2H_5)_3$ at various temperatures (a three-site exchange in terms of the Bloch equations as modified by McConnell, multiplicity of the spectrum being accounted for by introduction of effective spin-spin relaxation time) and showed that the exchange unsymmetric collapse proceeded in such a manner that olefinic protons that related to the methyne proton by the one-step migration of the metal underwent

greater broadening. Hence, if the 1,2-mechanism is correct, the broadening will be observed predominantly with 1,4-protons. Such an unsymmetry of broadening was actually observed with $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{-}\sigma\text{-C}_5\text{H}_5$ ⁶, $\text{C}_5\text{H}_5\text{CuP}(\text{C}_2\text{H}_5)_3$ ⁷, and $\text{C}_5\text{H}_5\text{Si}(\text{CH}_3)_3$ ^{8,9}. The spectra shown in Fig. 1 b and c demonstrate the greater broadening for olefinic protons of type BB' (protons 2,3 according to Table 1). Hence, the migration proceeds predominantly through a 1,3-shift. These data, however, do not rule out the 1,2-mechanism because to do this would need an accurate calculation of the line shapes, which is hindered by the difficulties mentioned above. We are trying to resolve the problem by using ¹³C spectroscopy¹⁰ or ²D spectroscopy*.

The activation energy of a dynamic process may be estimated most reliably with the slow exchange¹¹. With methyldichlorosilylcyclopentadiene, such estimations have been carried out by measuring the line width of the methyne proton located at 3.65 ppm (Fig. 1) at 0–50°. This temperature interval is the most convenient because at higher temperatures the signal becomes so strongly broadened as to be unmeasurable. On the other hand, below 0° the signal multiplicity must be taken into account.

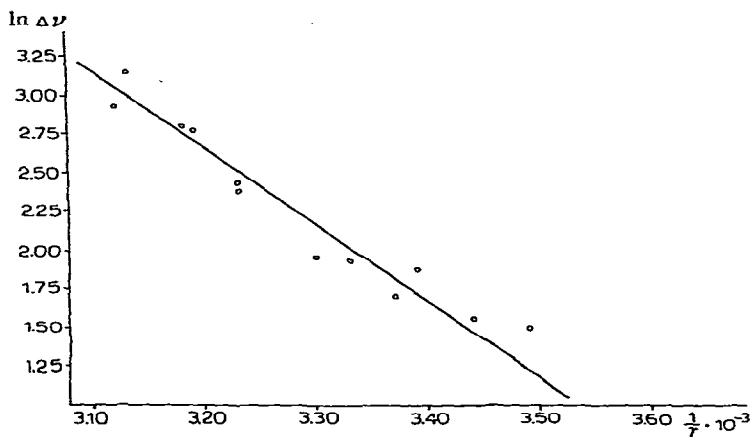


Fig. 9. Logarithmic line width ($\Delta\nu$) vs. inverse temperature ($1/T$), for methyne proton in the spectrum of 5-methyldichlorosilylcyclopentadiene.

Within the range of temperatures applied, the quantity $\ln \Delta\nu$ ($\Delta\nu$ is the width of the CH proton line at the semi-height) proved to vary as $1/T$ (Fig. 9), thus the activation energy of the metal migration may be estimated as $9 \pm 1 \text{ kcal}\cdot\text{mole}^{-1}$. Although the estimation is not very accurate, we can say that the value obtained by Fritz and Kreiter⁸ for $\text{C}_5\text{H}_5\text{Si}(\text{CH}_3)_3$ ($3 \text{ kcal}\cdot\text{mole}^{-1}$) is somewhat lower than would be expected**. Also, we have treated the data for $\text{C}_5\text{H}_5\text{CuP}(\text{C}_2\text{H}_5)_3$ obtained by Whitesides and Fleming and found that the activation energy is somewhat higher than $10 \text{ kcal}\cdot\text{mole}^{-1}$. Activation energies of $10\text{--}15 \text{ kcal}\cdot\text{mole}^{-1}$ are also characteristic of degenerated intramolecular rearrangements of other types.

It has been mentioned above that the assignment of olefinic signals lying in the

* Note added in proof. Recently Binsch has shown¹⁷, that these difficulties may be overcome by using the density-matrix formation based on the Ziouville representation. We hope to use this approach in future.

** The same conclusion is reached when one remembers that the NMR technique applied is not sensitive to processes whose activation energies are below $5 \text{ kcal}\cdot\text{mole}^{-1}$ ^{11,12}.

AA'BB' part of the spectrum is decisive in determining the preferable type of the metal migration. This was discussed by Cotton *et al.*⁶ for $\pi\text{-C}_5\text{H}_5\text{-Fe(CO)}_2\text{-}\sigma\text{-C}_5\text{H}_5$ or by Whitesides and Fleming⁷ for $\text{C}_5\text{H}_5\text{CuP(C}_2\text{H}_5)_3$. The assignment made by Cotton *et al.* assumed that constant J_{15} (or J_{45}) was about 2 cps while constant J_{25} (or J_{35}) was close to zero. This assumption is disproved by the data obtained from the accurate analysis of the spectra of cyclopentadienyl protons (refs. 1, 2, and Table 1 of this paper). Whitesides and Fleming⁷ assumed that the shifts (located at about 6.6 ppm) of the 2,3-protons of cyclopentadienyl compounds were characteristic. The data obtained with the shifts of the 1,4- and 2,3-protons indicate that this assumption may or may not be true. Consequently, the results reported^{6,7} concerning a preferable type of migration are ambiguous if they are used without applying the strict criterion already suggested by us².

Of course, it is clear that the rearrangement type will depend significantly on the metal or on substituents attached to the cyclopentadienyl system. Despite the lack of reliable data, one can also suppose that a migration type depends somehow on the geometry of the cyclopentadienyl fragment. A planar configuration (C_5H_6 , $\pi\text{-C}_5\text{H}_5\text{-Fe(CO)}_2\text{-}\sigma\text{-C}_5\text{H}_5$) would lead to migration proceeding through the 1,2-shift, as with the prototropic rearrangement in cyclopentadiene^{13,2}. With an envelope-shaped cyclopentadienyl ring, the 1,3-shift would be observed predominantly.

Our data on spin-spin coupling constants in cyclopentadiene or in isomers (I), (II) and (III)^{1,2} indicate that an increase in constants ${}^3J(\text{HH})$ (or J_{15} , J_{45}) suggests a distorted configuration. This constant is *ca.* 1.3 cps for a planar C_5H_6 molecule or for isomers (II) and (III)^{1,2}. Similarly to $\text{C}_5\text{H}_5\text{Si(CH}_3)_3$ ¹⁵, the cyclopentadienyl ring may be envelope-shaped in isomer (I). When atom C_5 declines from the molecular plane (atoms C_1 , C_2 , C_3 , C_4), the dihedral angle formed by planes $\text{H}_1\text{C}_1\text{C}_5$ and $\text{C}_1\text{C}_5\text{H}_5$ increases, thus the Karplus equation¹⁶ (${}^3J(\text{HH}) = A \cos^2 \varphi + B$) should result in a decreased value of ${}^3J(\text{HH})$. Actually, this constant is as low as 0.9 cps in isomer (I).

Below 100°, a prototropic rearrangement is slow in methylchlorosilyl-cyclopentadiene. In general, the process is described by ten rate constants (see the routes, Fig. 8). Theoretical estimations rule out all the routes that relate to the 1,3-shift, because the latter require too high an activation energy. Also, the ratio of the equilibrium concentrations, (I):(II):(III)=10:10:1, suggests that k_{12} (I, II) \gg k_{23} (II, III). The characteristic lifetime of a hydrogen is $10^5\text{--}10^6$ sec; thus this process is by six to seven orders slower than the metal migration. The kinetics of the prototropic rearrangement are obscured by the fact that isomers (II) and (III) undergo a Diels-Alder dimerization. Kinetic curves which show in detail hydrogen migration accompanied by dimerization will be published shortly*.

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* Note added in proof: Recently we have studied the dynamic behaviour of the series $\text{C}_5\text{H}_5\text{Si(CH}_3)_n\text{Cl}_{3-n}$ ($n=0\text{--}3$), which give similar results (to be published).

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