Stereochemically Non-rigid Silanes, Germanes, and Stannanes. Part 6.[1] Poly(cyclopentadienyl)silanes. A Comparison of Thermodynamic Parameters derived from Approximate Methods with those obtained using Full Lineshape Analysis of Carbon-13 Nuclear Magnetic Resonance Data

By **Alan Bonny** and **Stephen R. Stobart**,* Department of Chemistry, University of Victoria, Victoria, B.C., Canada V8W 2Y2

Reaction of dichloro- or trichloro-silane with the cyclopentadienide anion yields bis(cyclopenta-1,3-dien-5-yl)-silane, (1), chlorobis(cyclopenta-1,3-dien-5-yl)silane, (2), and tris(cyclopenta-1,3-dien-5-yl)silane, (3), for which i.r. and mass spectral data are reported. The activation parameters for degenerate metallotropic rearrangement in compounds (1)—(3) and in $Si(C_5H_5)H_3$, $Si(C_5H_5)ClH_2$, and $Si(C_5H_5)Cl_2H$ have been calculated from (*i*) the temperature dependence of coalesced linewidth in variable-temperature ^1H n.m.r. spectra using an established approximation, and (*ii*) full lineshape analysis of corresponding proton-noise decoupled ^{13}C n.m.r. data. Both methods give $\Delta G^‡$ of 55—60 kJ mol^{-1} as the range for the compounds investigated with no evidence for a dependence on chlorine substitution or the number of C_5 rings attached at the Si. Derived $\Delta S^‡$ and $\Delta H^‡$ values are subject to large errors, the implications of which in relation to previously reported data are discussed. Compound (2) exhibits anisochronous character between two ring carbon atoms, and the temperature dependence of the diastereotopically shifted ^{13}C resonances is interpreted as further evidence for a 1,2 metallotropic migration.

PREVIOUS papers in this series have been concerned with the qualitative description of stereochemically non-rigid characteristics exhibited by monohapto-cyclopentadienyl derivatives of silicon, germanium, and tin. In particular, it has been possible to confirm the intramolecular nature of the rearrangements involved,[2,3] to obtain new evidence for a 1,2 (symmetry-allowed, least-motion) shift,[3,4] and to identify[5] corresponding behaviour in larger-ring analogues. Quantitatively, however, this type of dynamic behaviour is still rather poorly defined although its existence was first recognized over 20 years ago.[6] Various estimates of activation energies E_a are available[7,8] covering a substantial range of appropriate compounds including monohapto-cyclopentadienyl derivatives of both transition and non-transition metals. Nevertheless, almost without exception these values have been determined using approximate methods which derive rates from the temperature dependence of the linewidth of the averaged n.m.r. signal resulting after coalescence of the *aa'bb'x* array upon rapid exchange. All the approximations which have been used fail to take account of variation in natural linewidth and of contribution to the latter from spin–spin coupling. Moreover, while some results[7] have been obtained using Arrhenius plots for data measured over a range of temperature, others[8] have been derived by substitution of a single measurement at one temperature into an Eyring expression. To our knowledge, for only one compound, $[Fe(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)(CO)_2]$ has a more reliable method been applied: full lineshape analysis of ^{13}C n.m.r. data in the range −88 to 52 °C was used to obtain a value for $E_a = 10.7 \pm 0.5$ kcal mol^{-1} † which was considered by the authors[9] to be more reliable than those determined earlier from ^1H n.m.r. spectroscopy.

The computational difficulties inherent in full lineshape calculations directed towards simulation of the temperature dependence of ^1H n.m.r. spectra for these systems result from the need to include coupling (^1H–^1H) terms between a large number of nuclear spins. This complication disappears, however, for ^{13}C n.m.r. data which are obtained in the proton-decoupled Fourier-transform mode and the calculation reduces to that of a trivial three-site exchange. We felt it would be useful to generate a comparison of activation parameters derived in this way from ^{13}C measurements with those calculated using the standard approximations from corresponding ^1H results. This has been incorporated into an investigation of the properties of some poly(cyclopentadienyl)silanes, a development of an earlier study.[4]

EXPERIMENTAL

General synthetic and spectroscopic methods have been described in earlier papers.[2,4] Dichlorosilane was provided as a gift by the Union Carbide Corporation, Sisterville, W. Virginia. The new compounds were purified by repeated vacuum distillation and characterized by i.r., n.m.r., and mass spectroscopy as described below; satisfactory microanalytical data were also obtained in each instance.

Bis(*cyclopenta*-1,3-*dien*-5-*yl*)*silane* (1).‡—Onto dry $K[C_5H_5]$ (82 mmol) was condensed dichlorosilane (55 mmol). After 1 h at −78 °C, fractional condensation afforded the *product* (44%) held as a colourless liquid at 0 °C. Infrared spectrum (liquid film): 3 935vw, 3 910w, 3 123w, 3 100w, 3 080m, 3 027vw, 3 003vw, 2 928w(br), 2 905vw(sh), 2 885vw(sh), 2 152vvs(br), 1 840mw(br), 1 635m(br), 1 573vw, 1 488vw, 1 474m, 1 469m, 1 465m, 1 386m, 1 372w, 1 350w, 1 294m, 1 225w(sh), 1 210m, 1 115m, 1 091m, 1 073m, 990vs(br), 951s, 931ms, 922m, 908s, 897w(sh), 868ms, 846vs, 822vs, 816vs, 800w(sh), 783w, 745vs, 700vvs(br), 656w, 585w(sh), 577mw, 562w, 535w, 525m, 455ms, and 416m cm^{-1}. Raman spectrum (neat liquid): 3 118ms, 3 078s, 2 962mw, 2 925m, 2 911m, 2 879m, 2 142vs(br), 1 593w, 1 565w, 1 485s, 1 465s, 1 383w, 1 117s, 1 102w, 1 094w, 1 018m, 983s(br), 953w, 930mw, 908mw,

---

† Throughout this paper: 1 cal = 4.184 J; 1 mmHg ≈ 13.6 × 9.8 Pa.

‡ I.U.P.A.C. names for compounds (1)—(3) are bis(cyclopenta-2,4-dien-1-yl)silane, chlorobis(cyclopenta-2,4-dien-1-yl)silane, and tris(cyclopenta-2,4-dien-1-yl)silane respectively.

826mw, 802w, 712w, 690mw, 660w, 442w, 420s, and 261w cm^{-1}.

*Chlorobis(cyclopenta-*1,3-*dien-*5-*yl)silane* (2).—In the reaction between K[C_5H_5] (130 mmol) and trichlorosilane (65 mmol) for 30 h at −78 °C, in addition to 5-dichlorosilylcyclopenta-1,3-diene,[4] *compound* (2) (1.2 mmol), condensing at 0 °C, was produced. Infrared spectrum (liquid film): 3 128vw, 3 107vw, 3 083w, 3 060w(sh), 2 975m, 2 938m, 2 910mw(sh), 2 860mw, 2 184ms(br), 1 720w(br), 1 625w(br), 1 582w, 1 550w(br), 1 450w(br), 1 390w, 1 370w, 1 347w, 1 312vw, 1 294w, 1 254w, 1 228w, 1 202w, 1 145m(sh), 1 085s(vbr), 1 045m(sh), 977w, 954w, 913w, 900vw, 845ms, 822s, 752m, 707m, 686w(sh), 640vw, 560mw, and 520m cm^{-1}.

*Tris(cyclopenta-*1,3-*dien-*5-*yl)silane* (3).—After reaction between K[C_5H_5] (33 mmol) and trichlorosilane (8.1 mmol) in dry pentane (10 cm^3) over 26 h at −78 °C, slow warming of the mixture was followed by removal of material volatile at 10^{-3} mmHg (25 °C). Extraction of the residue with dry dichloromethane followed by evaporation of this solvent left the *product* (30%) as a clear viscous oil. Infrared spectrum (liquid film): 3 126vw, 3 104w, 3 083m, 3 027vw, 3 010vw, 2 962vw, 2 930mw, 2 910w, 2 860w, 2 145ms, 1 840w(br), 1 638mw(br), 1 488w, 1 470mw, 1 385mw, 1 368w, 1 350w, 1 293w, 1 232vw, 1 203w, 1 115mw, 1 100vw(sh), 1 090mw, 1 069m, 996vs(br), 952s, 910s, 862w, 853w, 838w, 825ms, 808ms, 775w, 742vvs, 690vs, 650w, 563w(br), 545vvw, 520vw, 480m(sh), 457ms, 425vw, and 402w cm^{-1}.

RESULTS AND DISCUSSION

Reaction of dichloro- or trichloro-silane with the appropriate molar excess of potassium cyclopentadienide yielded bis(cyclopenta-1,3-dien-5-yl)silane, (1), and tris(cyclopenta-1,3-dien-5-yl)silane, (3), respectively. A third poly(cyclopentadienyl)silane, chlorobis(cyclopenta-1,3-dien-5-yl)silane, (2), was isolated as a minor product during the preparation[3] of Si(C_5H_5)Cl_2H. While compounds (1) and (2) are colourless liquids which can be manipulated using standard high-vacuum methods, (3) is involatile at ambient temperature and was extracted into dichloromethane whence it was recovered as a colourless viscous oil. Compound (2) was found to be substantially more air-sensitive than (1) or (3) or monocyclopentadienylsilanes:[4] during exposure for *ca.* 0.3 h it reacted to produce an unidentified yellow-brown solid. Over 24 h *in vacuo* at ambient temperature, liquid (3) slowly solidified to a polymeric gum which could not be redissolved in common organic solvents.

The ^{1}H n.m.r. spectra of compounds (1)—(3) at ambient temperature are consistent with rapid degenerate intramolecular rearrangement and are discussed further below, in relation to the calculation of activation parameters for such a migration. Minor signals attributable to the presence of stereochemically rigid vinylic isomers formed by prototropic shifts were also observed. This parallels the behaviour of monocyclopentadienyl derivatives,[2,4] and appeared to be particularly ready for compound (3).

Infrared spectra (see Experimental section) contain absorptions near 2 100 cm^{-1} substantiating the presence of Si–H bonds. An increase in ν(Si–H) from 2 152 to 2 184 cm^{-1} between compounds (1) and (2) accompanies chlorine substitution at silicon as discussed earlier.[4] A smaller but monotonic trend occurs in the opposite sense as the number of cyclopentadienyl groups attached to Si increases: for Si(C_5H_5)H_3 the main ν(Si-H) band is found[4] at 2 165, for compound (1) at 2 152, and for (3) at 2 145 cm^{-1}, consistent with increasing electron release towards silicon. Of more significance is the situation observed in the ν(C–H) region for all three compounds: the resolution of eight [(1) and (2)] or nine [(3)] distinct components is very clear evidence for low-symmetry structures involving monohapto-bonding between the C_5 rings and the Si atom. Below 2 000 cm^{-1} the spectra are complex with overlapping vibrations and will not be discussed further.

Mass spectra of compounds (1)—(3) were mainly useful for definitive characterization but certain features of the fragmentation are worthy of brief comment. Molecular ion abundances were 5.8, 1.4, and 1.5% respectively, the decrease on Cl substitution between compounds (1) and (2) again parallelling earlier observations.[4] The most intense ions resulted from loss of C_5 units to give [SiC_5H_x]$^+$ [42.4% for (1), 27.8% for (2)] accompanied in the case of compound (2) by a series of peaks corresponding to fracture of the C_5 groups.

TABLE 1

Pre- and post-coalescence ^{1}H n.m.r. data [a]

T/K	Compound	Chemical shifts (τ) [b]			$^1J(^{29}SiH_y)$/Hz
		$H_{aa'bb'}$	H_x	H_y	
233	(1) [c]	3.49 [d]	6.51	6.70	214.6
213	(2)	3.41 [d] 3.24 [d]	6.42	6.52	n.o.
223	(3)	3.52 [d] 3.66 [d]	7.15	6.33	216.8
		$H_{aa'bb'x}$		H_y	$J(^{29}SiH_y)$
303	(1)	4.05 [g]		6.73 [h]	214.0
308	(2)	3.94 [g]		6.49	n.o.
313	(3) [i]	4.10 [g]		6.37	217.6

[a] Spectra recorded for $CDCl_3$ solutions of (1) and (2), and for a CS_2 solution of (3). A neat sample of (1) exhibited only one resonance in the τ 6—7 region at 213 K [τ 6.97, corresponding to both τ (SiH) and τ (CH_x)]. n.o. = Not observed. [b] Proton environments distinguished as follows: *aa'bb'*, olefinic C_5-ring hydrogen atoms; *x*, aliphatic C_5-ring hydrogens; *y*, substituent SiH hydrogens. Integrations gave relative intensities consistent with proposed assignments throughout. [c] Resonances observed at τ 5.94 (doublet, J_{xy} = 2.7 Hz) and 6.85 are attributed to the 1,2 isomer. [d] Multiplet, J value not determined. [e] Resonances observed at τ 6.18, 6.71, and 7.39 are attributed to the 1,1,2 isomer. The olefinic signals from this isomer were not resolved. [f] Resonances observed at τ 3.08, *ca.* 3.48, 6.06, and 7.03 (multiplet) are attributed to the 1,2 isomer. [g] Broad. [h] Observed as a multiplet at 348 K [at least seven lines with $J_{(aa'bb'x)y}$ = 0.5 Hz]. [i] Resonances observed at τ 3.15, 3.50, 6.08 [$^1J(^{29}SiH)$ = 213.6 Hz], and 7.18 (multiplet) are attributed to the 1,1,2 isomer.

Variable-temperature N.M.R. Data (^{1}H *and* ^{13}C).—The data are summarized in Tables 1 and 2. Coalescence phenomena accompanying warming parallelled those observed for mono(cyclopentadienyl)silanes:[4] collapse of the *aa'bb'x* spectrum led to disappearance of the aliphatic (*x*) signal at high field and to establishment of a broad averaged resonance in the olefinic region. No anomalies arising from the presence on the silicon atom of more than one C_5 ring were detected and the following discussion therefore assumes that in each of the compounds (1)—(3) individual cyclopentadienyl groups behave in such a way as to be indistinguishable from one another.

In ^1H spectra at the slow limit, while for compound (1) there was no clear separation between (a,a') and (b,b') proton resonances, for (2) and (3) two multiplets of equal intensity were chemically shifted from one another (Table 1) and in both cases unsymmetrical collapse occurred, as expected for a non-random metallotropic migration.[4] Slower prototropic rearrangement like that encountered previously for mono(cyclopentadienyl)-silanes [4] resulted in the accumulation of minor resonances (Table 1) attributable to isomers with one ring bound to silicon at a vinylic position. We designate these species 1,2 for compound (1) and 1,1,2 for compound (3), in terms of a numbering system discussed earlier,[4] but have not pursued their characterization further. Although formation of these isomers led to deterioration of n.m.r. samples especially above ambient temperature, for compound (1) at 75 °C we were able to resolve multiplet structure in the SiH_2 resonance (τ 6.73). At least seven lines having a unique central component were observed, $J = 0.5$ Hz. This corresponds to the major portion of an 11-line spectrum, generated through averaged fast-limiting coupling,[3,10,11] in a situation whereby equivalence has been established among all 10 protons of the two cyclopentadienyl groups.

TABLE 2

Pre-coalescence ^{13}C n.m.r. spectra [a]

		Chemical shift/p.p.m.[b]		Coupling constant/Hz	
Compound	T/K	C(olefinic)	C(aliphatic)	$^1J[^1H-^{13}C(\text{olefinic})]$	$^1J[^1H-^{13}C(\text{aliphatic})]$
(1)	213	133.3 (95) [c]	47.1 (40.2)	170.5	135.5
		131.3 (100)		165.9	
(2)	218	133.5 (100)	50.1 (35)	163.8	135.8
		132.0 (42)			
		131.0 (42)			
(3) [d]	223	133.3 (100)	45.9 (45)		
		131.4 (100)			

[a] $CDCl_3$ was used as solvent and internal reference. [b] High frequency relative to δ 77.2 p.p.m. for $CDCl_3$ (central component of triplet). [c] Numbers in parentheses indicate relative peak heights (pulse interval 1.36 s, pulse width 8 μs). [d] Weak resonances at 145.5, 138.9, 132.5, and 48.4 p.p.m., which were observed to increase in intensity with time at ambient temperature, are assigned to the 1,1,2 isomer of (3).

Coalescence of the ^{13}C n.m.r. spectra was examined in detail between −50 and +30 °C. Data obtained in this way provided the basis for the lineshape fitting described below.

Energies of Activation and Thermodynamic Parameters.—Because of rather marked intensity differences arising from Overhauser effects in the ^{13}C spectra of compound (2) as well as the anisochronous characteristics discussed below, a full line fit for this system was not attempted. Thus, activation parameters were calculated using experimental results for compounds (1), (3), and three others described earlier:[4] silylcyclopentadiene, (4), chlorosilylcyclopentadiene, (5), and dichlorosilylcyclopentadiene, (6). Determination of such data by dynamic n.m.r. spectroscopy is subject to a variety of errors which has led to drastic discrepancies in the literature, a situation recently critically appraised in an excellent article by Binsch [12] in which emphasis was placed on the need for use of rigorous statistical methods. Our approximate calculations from the ^1H measurements used equation (1), which has been shown [13-15] to pertain satisfactorily to post-coalescence (fast-exchange) data, to evaluate the dependence of rearrangement rate $k_{\text{eff.}}$ on temperature. In this expression $\delta\nu_e$ is the separation (Hz) between (a,b) and x proton resonances in the slow-limiting spectrum, W^* is the half-height linewidth of the coalesced envelope, and W'' is the linewidth in the absence of exchange contributed by the relaxation mechanism. When $W^* \gg W''$, W'' can be neglected;[14]

$$k_{\text{eff.}} = 1.6085\, \delta\nu_e^{\,2}/(W^* - W'') \qquad (1)$$

thus we have assumed $W'' = 0$ in our calculations. The constant term in equation (1) accounts for relative state probabilities in the three-position (a,b,x) approximation.[14,15] With a minimum of 40 measured data points,† least-squares regression analysis [16] was used to determine an Arrhenius line for each compound, giving excellent straight-line agreement in every case and uncertainties defining 95% confidence intervals derived from the standard errors.[16]

The exact lineshape treatment matched experimental ^{13}C spectra *visually* with computer simulations generated using a locally written program based on a three-site exchange model,[13] to give the lifetime τ and thence rate k at a series of temperatures T. The free energy of activation $\Delta G^{\ddagger}$ at each T was computed using the Eyring relationship [12] (2); regression analysis of the temperature dependence of $\Delta G^{\ddagger}$, $(\partial\Delta G^{\ddagger}/\delta T)_P$ gave corresponding $\Delta S^{\ddagger}$ values.

$$(1/2\tau) = k = \kappa(\boldsymbol{k}_B T/\boldsymbol{h})\exp(-\Delta G^{\ddagger}/RT) \qquad (2)$$

Calculated $\Delta G^{\ddagger}$ values are collected in Table 3. We estimate that the errors in these will be of the order of ±2 kJ mol^{-1}, corresponding to an uncertainty of ±1° in our temperature measurements; the uncertainties defining 95% confidence intervals from the regression analy-

---

† Typically, four independent measurements at each of 10 different temperatures in the range 25—70 °C.

sis are also shown in parentheses. Within these bounds, it is clear that values derived from the approximate method lie very close to those obtained using a full lineshape analysis. This provides solid support for $\Delta G^\ddagger$ parameters reported earlier for related systems, and in the present case establishes that: (*a*) free energies of activation for metallotropic migration in cyclopentadienyl silanes are of the order of 50—60 kJ mol^{-1}, or about half that established[17] for hydrogen migration in C_5H_6 (E_a = 101.3 kJ mol^{-1}); and (*b*) there is no indication of a measurable dependence of $\Delta G^\ddagger$ on chlorine substitution at silicon * (contrary to an earlier conclusion[8]) or on poly(cyclopentadienyl) substitution.

TABLE 3

Values * for $\Delta G^\ddagger$ for metallotropic shifts in cyclopentadienylsilanes

	Compound	(A)	(B)
(1)	$Si(C_5H_5)_2H_2$	57.9 (1.2)	55.3 (0.3)
(3)	$Si(C_5H_5)_3H$	60.7 (0.6)	58.1 (0.3)
	$Si(C_5H_5)H_3$	59.4 (1.0)	57.7 (0.1)
	$Si(C_5H_5)ClH_2$	not measured	54.0 (0.2)
	$Si(C_5H_5)Cl_2H$	57.7 (1.2)	56.6 (0.1)

* kJ mol^{-1}: values under (A) are derived from full treatment of ^{13}C data, those under (B) result from approximate treatment of ^1H data. Error estimated to be ± 2 kJ mol^{-1}, see text.

By contrast, further numerical manipulation of data from either the approximate or lineshape calculations convincingly illustrates the arguments advanced by Binsch:[12] we find errors in $\Delta S^\ddagger$ and thence in $\Delta H^\ddagger$ which are much larger than those in $\Delta G^\ddagger$ and do not allow the results to be taken seriously. This reinforces doubts as to the validity of the large number of E_a and log *A* data which have been reported[7,8,18] for related compounds. A possible exception is the iron complex investigated by Cotton and co-workers where a lineshape fit was achieved over an unusually long temperature range (—69 to +52 °C).

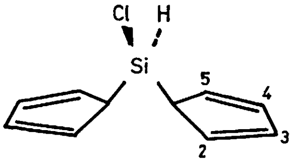

FIGURE 1 Chlorobis(cyclopentadienyl)silane. The arrangement at the silicon centre renders carbons 2 and 5 (and also 3 and 4) anisochronous

Anisochronous (*Diastereotopic*) *Effects in Compound* (2). —As in the chiral silylcyclopentadienes we have discussed elsewhere,[3] the arrangement at the silicon atom in compound (2) establishes a diastereotopic relationship between the pairs of (2,5) and (3,4) nuclei (Figure 1). The effect of this is observable experimentally in the proton-decoupled ^{13}C n.m.r. spectrum at 218 K (Table 2, Figure 2) where three resonances are present in the olefinic region, in ratio 2 : 1 : 1. This corresponds to a measurable chemical-shift difference between the pair of anisochronous carbon atoms adjacent to the origin of non-equivalence ($C_{2,5}$) with no resolvable splitting of the more distant pair ($C_{3,4}$). On raising the temperature the two resonances thus distinguished as belonging to the $C_{2,5}$ nuclei are those which collapse first in an unsymmetrical coalescence (Figure 2), convincing evidence for a 1,2 shift as the mechanism for rearrangement.[3]

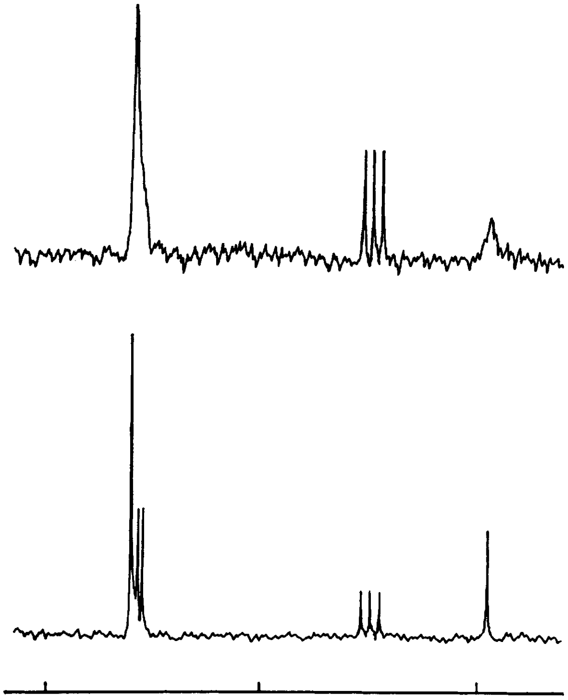

FIGURE 2 Carbon-13 n.m.r. spectrum of compound (2) at 218 (lower); and 243 K (upper). The central triplet is due to $CDCl_3$ solvent and chemical-shift data are listed in Table 2

We thank the National Research Council, Canada, and the University of Victoria for financial support.

[8/2145 *Received*, 12*th December*, 1978]

REFERENCES

[1] Part 5, S. R. Stobart and R. D. Holmes-Smith, *J.C.S. Dalton*, 1980, 159.

[2] P. C. Angus and S. R. Stobart, *J.C.S. Dalton*, 1973, 2374.

[3] A. Bonny and S. R. Stobart, *J. Amer. Chem. Soc.*, 1979, **101**, 2247.

[4] A. Bonny, S. R. Stobart, and P. C. Angus, *J.C.S. Dalton*, 1978, 938.

[5] A. Bonny and S. R. Stobart, *J.C.S. Dalton*, 1979, 786.

[6] G. Wilkinson and T. S. Piper, *J. Inorg. Nuclear Chem.*, 1956, **2**, 32; F. A. Cotton, *J. Organometallic Chem.*, 1975, **100**, 29.

[7] N. M. Sergeyev, G. I. Avramenko, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1970, **22**, 79; A. V. Kisin V. A. Korenevsky, N. M. Sergeyev, and Yu. A. Ustynyuk, *ibid.*, 1972, **34**, 93; G. I. Avramenko, N. M. Sergeyev, and Yu. A. Ustynyuk, *ibid.*, 1972, **37**, 89.

[8] N. M. Sergeyev, G. I. Avramenko, A. V. Kisin, V. A. Korenevsky, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1971, **32**, 55; Yu. K. Grishin, N. M. Sergeyev, and Y. A. Ustynyuk, *Org. Magn. Reson.*, 1972, **4**, 377.

[9] D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organometallic Chem.*, 1972, **42**, 159.

[10] R. J. Goodfellow and S. R. Stobart, *J. Magn. Reson.*, 1977, **27**, 143.

[11] A. Bonny, A. D. McMaster, and S. R. Stobart, *Inorg. Chem.*, 1978, **17**, 935.

[12] G. Binsch, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, ch. 3.

---

* The slow rearrangement behaviour of $Si(C_5H_5)Cl_3$ thus remains anomalous.

[13] G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, 1967, **89**, 2855.

[14] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, 1966, **88**, 3185.

[15] Yu. N. Luzikov, N. M. Sergeyev, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1974, **65**, 303.

[16] G. W. Snedecor and W. G. Cochran, 'Statistical Methods,' 6th Edn., Ames Iowa State University Press, 1973.

[17] W. R. Roth, *Tetrahedron Letters*, 1964, 1009.

[18] R. B. Larrabee, *J. Organometallic Chem.*, 1974, **74**, 313; F. A. Cotton, ch. 10 in ref. 10.