Stereochemically Non-rigid Silanes, Germanes, and Stannanes. Part 2.[1] Silylcyclopentadienes

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Reactions of chlorosilanes with cyclopentadienyl or related anions have been used to synthesize 5-silyl-, 5-chlorosilyl-, 5-dichlorosilyl-, 5-trichlorosilyl-, 5-methylsilyl-, and methyl-5-silyl-cyclopenta-1,3-diene (1)—(6), respectively, and 1-silylindene (7). Infrared and mass-spectral data have been obtained and assigned. Intramolecular rearrangements in compounds (1)—(7) have been investigated using ^{13}C as well as ^{1}H n.m.r. spectroscopy. Compounds (1)—(3) and (5) undergo degenerate metallotropism above −25 °C, (6) exhibits ready non-degenerate rearrangement, while for (4) and (7) slow-limiting spectra are observed below 50 °C. The effect of increasing Cl substitution at the Si atom on the olefinic carbon resonances in the ^{13}C n.m.r. spectra for (1)—(4) has been examined, leading to an assignment which when related to temperature-dependent non-symmetrical collapse in this region provides new and compelling evidence for a 1,2-metallotropic shift as the mechanism for intramolecular non-rigidity. Slow formation of stereochemically rigid '2-' and '3-'isomers by prototropic shifts has been fully characterized for compounds (1) and (5) using ^{1}H n.m.r. spectroscopy.

INVESTIGATION of the stereochemically non-rigid behaviour of germylcyclopentadiene and some related derivatives of monogermane was reported in an earlier paper.[1] As well as the well established temperature-dependent coalescence phenomena which have been found in the n.m.r. spectra of similar molecules, we observed spin coupling between ^{1}H nuclei located respectively on the substituent metal hydride group and the supporting ring system at the fast limit of intramolecular exchange.[1-3] This observation represents unequivocal proof that migratory behaviour of the substituent metal atom is responsible for the fluxional character of these species. We have subsequently undertaken a detailed study of some silane analogues which has included extensive use of variable-temperature ^{13}C n.m.r. spectroscopy, a technique so far applied to rather few dynamic systems of this type.

During the course of the study discussed in this paper the synthesis of 5-silylcyclopenta-1,3-diene (1) and methyl-5-silylcyclopenta-1,3-diene (6) has been described together with some ^{1}H n.m.r. data.[4] A preliminary account of the determination by electron-diffraction methods of the structure of (1) in the vapour phase was published[5] in 1971. Much more recently, efforts have been made to elucidate the electronic properties of these systems[6] through *ab initio* calculations for (1) and valence-shell photoelectron spectroscopy applied to (1) and to 5-trichlorosilylcyclopenta-1,3-diene (4).

(1) R=Q=H
(2) R=Cl,Q=H
(3) R=H,Q=Cl
(4) R=Q=Cl
(5) R=Me,Q=H

TABLE 1

Synthesis of compounds

	Product [a]	Reactants (amount/mmol)	θ_c/°C (*t*/h)	Yield (%) [b]
(1)	5-Silylcyclopenta-1,3-diene	$K(C_5H_5)$ (77), $SiBrH_3$ (58)	−78 (1.0)	78
(2)	5-Chlorosilylcyclopenta-1,3-diene	$K(C_5H_5)$ (92), $SiCl_2H_2$ (120)	−78 (20.0)	31
(3)	5-Dichlorosilylcyclopenta-1,3-diene	$K(C_5H_5)$ (74), $SiCl_3H$ (38)	−35 (1.0)	6
(4)	5-Trichlorosilylcyclopenta-1,3-diene	$K(C_5H_5)$ (77), $SiCl_4$ (38)	−78 (1.0)	35
(5)	5-Methylsilylcyclopenta-1,3-diene	$K(C_5H_5)$ (5.5), $SiMe(Cl)H_2$ (5.4)	−78 (1.0)	95
(6)	Methyl-5-silylcyclopenta-1,3-diene	$K(C_5H_4Me)$ (37), $SiBrH_3$ (15)	−78 (0.5)	46
(7)	1-Silylindene	$K(C_9H_7)$ (10), $SiBrH_3$ (26)	−78 (1.0)	62

[a] Separated by fractional condensation; held in a trap at −63 [compounds (1)—(3), (5), and (6)], −45 [(4)], or at −78 °C [(7)]. Trace amounts of parent hydrocarbon were isolated together with unchanged halide at −196 °C. [b] Based on halogenosilane consumed.

EXPERIMENTAL

Experimental methods have been detailed previously.[1] Infrared, Raman, and mass-spectroscopic data were obtained as before [1] or by using Beckman IR20 or Perkin-Elmer–Hitachi RMU 7E units. Perkin-Elmer R32 and

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[1] Part 1, P. C. Angus and S. R. Stobart, *J.C.S. Dalton*, 1973, 2374.

[2] S. R. Stobart, *J. Organometallic Chem.*, 1971, **33**, C11; 1972, **43**, C26.

[3] S. R. Stobart, *Abs. 6th Internat. Conf. Organometallic Chem.*, Amherst, 1973, Paper no. 164.

[4] A. P. Hagen and P. J. Russo, *J. Organometallic Chem.*, 1973, **51**, 125.

[5] J. E. Bentham and D. W. H. Rankin, *J. Organometallic Chem.*, 1971, **30**, C54.

[6] S. Cradock, R. H. Findlay, and M. H. Palmer, *J.C.S. Dalton*, 1974, 1650; S. Cradock, E. A. V. Ebsworth, H. Moretto, and D. W. H. Rankin, *ibid.*, 1975, 390.

Nicolet TT-14 Fourier-transform spectrometers were used throughout for variable-temperature ^1H and ^{13}C n.m.r. measurements at 90.0 and 15.09 MHz respectively. Pure products were obtained by fractional condensation and characterized by the spectral data.

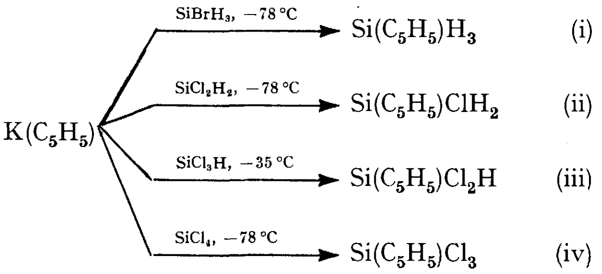
Solvents were distilled directly from lithium tetrahydridoaluminate. Bromosilane was prepared through reaction of phenylsilane with HBr at −78 °C.[7] Chloro(methyl)silane was synthesised by reaction of $SiMeH_3$ with $SnCl_4$.[8] Dichlorosilane was a generous gift of the Union Carbide Corporation, Sistersville, W. Virginia. Commercial trichloro- and tetrachloro-silane were fractionated before use. Syntheses of potassium salts of cyclopentadiene, methylcyclopentadiene, and indene have been described.[1]

Preparative details for complexes (1)—(7) are shown in Table 1. Infrared data for (1) and (6) have been listed elsewhere,[4] and for the remaining compounds were recorded as follows [gas phase except for (7) as liquid film]: (2) 3 120w (sh), 3 005m, 2 910w,br, 2 216s, 2 193*R*, 2 182*P*,vs, 1 845w,br, 1 625w,br, 1 380w, 1 290vw, 1 195w, 1 110m, 1 080w (sh), 995vs, 945*R*, 934*Q*, 925*P*,vs, 887m, 864*R*, 859*Q*, 855*P*,vs, 834*R*, 829*Q*, 823*P*,s, 790m (sh), 720s, 690s (sh), 576w (sh), 540vs,br, 433m; (3) 3 120vw (sh), 3 095w, 2 245*R*, 2 237*Q*, 2 230*P*,m, 1 390vw, 1 300vw, 1 205vw, 1 125w,br, 995s, 949m, 905w, 815s, 795*R*, 788*P*,s, 744m, 710vs, 580s, 530s, 420w; (4) 3 122vw, 3 102w, 2 920vw,br, 1 190w, 1 126w, 1 090w, 1 032m, 952m, 918w, 775m, 700vs, 600vs, 552m, 520s; (5) 3 111m (sh), 3 100m, 2 980w, 2 921w, 2 173s, 2 150vs, 1 450vw, 1 425w,br, 1 385w,br, 1 265*R*, 1 260*Q*, 1 255*P*,m, 1 204vw, 1 110w (sh), 1 085w,br, 998*R*, 995*Q*, 990*P*,s, 953*R*, 948*Q*, 943*P*,s, 896vs, 828w, 790w, 740vs (sh), 720*R*, 714*Q*, 708*P*,vs, 682m (sh), 495w, 430w; and (7) 3 076w, 3 060vw, 3 025vw, 2 980w,br, 2 160s, 1 465w, 1 456m, 1 365vw, 1 316vw, 1 226w, 1 195w, 1 115vw, 1 048m,br, 1 022vw, 936m,br, 910vs, 880m, 808m, 764s, 739m, 727m, 712m, 641m,br, 618w, 558w, 550w, 527w, and 458m,br cm^{-1}.

Raman spectra were measured for liquid samples of compounds (1) and (5), and showed the following shifts (p = polarized, dp = depolarized): (1) 3 055m,p, 3 015s,p, 2 859m,p, 2 827w, p, 2 190m (sh), dp, 2 148vs,p, 1 600vw, 1 502vw, 1 485m,p, 1 465vw,p, 1 431w,p, 1 383vw,dp, 1 368vw,p, 1 115m,p, 1 017m,p, 1 008m,p, 992m,p, 947m,dp, 930m,dp, 904w,dp, 846vw,p, 828m,p, 797m,p, 707m,p, 657w,dp, 570w,dp, 440vs,p, 360vw, 206m,dp, 133m,p; (5) 3 110 (sh), 3 105m,p, 3 065m,p, 2 960w,dp, 2 902s,p, 2 140vs,p, 1 481w,p, 1 466vs,p, 1 430w,br,p, 1 381w,dp, 1 366vw, 1 257w,p, 1 118m,p, 1 096w,dp, 1 021w,p, 995m,p, 961w,dp, 952w,dp, 943w,dp, 917w,dp, 893w,p, 890vw,p, 830w,p, 800w,p, 741w,p, 715w (sh), 693m,p, 660w, 437s,p, 250w,dp, 238vw,p, 203vw,dp, and 110w,p cm^{-1}.

RESULTS AND DISCUSSION

Reaction between halogenosilanes and the cyclopentadienyl anion under conditions established earlier by us [1-3] and other workers [4,6] afforded monocyclopentadienyl-substituted silanes (1)—(4) according to equations (i)—(iv). Repetition of reactions (ii) and (iii) using different conditions has produced in low yield three polycyclopentadienyl silanes [9] as well as compounds (2) and (3). The isomeric derivatives 5-methylsilylcyclopenta-1,3-diene (5) and methyl-5-silylcyclopenta-1,3-diene (6),[4] as well as silylindene (7), have been isolated



similarly. All these compounds are colourless low-melting liquids which are sufficiently volatile to allow convenient manipulation and purification using standard high-vacuum techniques. For compounds embodying the SiH_3 group, (1), (6), and (7) are unusually insensitive to oxidation; they decompose only slowly on exposure to air unlike silane or silyl halides which explode or inflame under such conditions.

Like those of the related germanes,[1] at ambient temperature the ^1H n.m.r. spectra of newly formed (1)—(3), (5), and (6) were deceptively simple, indicative of existence as dynamic ' 1-isomers '. By contrast, under the same conditions, compounds (4) and (7) exhibited more extensively coupled spectra interpretable as those of stereochemically rigid 1-isomers. The rate of prototropic rearrangement of (1)—(3) and of (5) and (6) to rigid [1,10] 2- and 3-substituted isomers was significant at ambient and higher temperatures; the equilibrium between the fluxional 1-isomer and the non-fluxional 2- and 3-isomers was identified for (5). As was found for the corresponding germanium species,[1] these compounds are remarkably resistant to intermolecular dimerization when compared with cyclopentadiene or methylcyclopentadiene. A complete investigation of their intramolecular-rearrangement properties by variable-temperature ^1H and ^{13}C n.m.r. spectroscopy is presented below.

Vibrational Spectra.—Assignment of observed i.r. and Raman bands for compound (1) (see Experimental section) parallels that proposed [1] for the germanium analogue and corresponds to the C_s symmetry expected for an η^1-metallocyclopentadienyl structure. Strong features at 2 150—2 200 cm^{-1} are due to Si–H stretching ($2a' + a''$), while the intense i.r. absorption at 921 and 929 cm^{-1} arises mainly from SiH_3 deformation modes (also $2a' + a''$).

The single prominent Raman shift in the low-wavenumber region is at 440 cm^{-1} and is polarized (a'). This can be attributed to Si–C(ring) stretching and may be compared with a value of 413 cm^{-1} for the same motion [11] in $SiMe_3(C_5H_5)$ and with ν[Ge–C(ring)] at 369 cm^{-1} for $Ge(C_5H_5)H_3$.[1] In the Raman spectrum of (5) two strong

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[7] L. G. L. Ward, *Inorg. Synth.*, 1968, **11**, 161.

[8] S. Cradock, E. A. V. Ebsworth, and N. Hosmane, *J.C.S. Dalton*, 1975, 1624.

[9] A. Bonny and S. R. Stobart, unpublished work.

[10] E. W. Abel and M. O. Dunster, *J. Organometallic Chem.*, 1971, **33**, 161.

[11] H. P. Fritz, *Adv. Organometallic Chem.*, 1964, **1**, 239.

polarized features are present and can be identified as ν[Si–C(Me)] (693 cm^{-1}) and ν[Si–C(ring)] (437 cm^{-1}). Analogous stretching vibrations involving germanium in 5-methylgermylcyclopenta-1,3-diene were found[1] at 603 and 371 cm^{-1} respectively. In both cases this represents a *ca.* 40% drop in energy between ν[M–C(Me)] and ν[M–C(ring)] which appears to correlate with the low energies of activation for metallotropic migration of the metal-containing group.

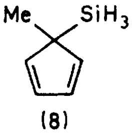
Infrared data for compounds (2)—(7) are listed in the Experimental section. All the compounds apart from (4) show strong i.r. absorption in the 2 200 cm^{-1} region confirming the presence of Si–H bonds. For (1)—(3) a monotonic increase in ν(Si–H) (strongest component centred at 2 165, 2 188, and 2 237 cm^{-1} respectively) can be identified with the degree of substitution of H by the more electron-withdrawing Cl. In the ν(Si–Cl) region, (2), (3), and (4) give rise respectively to one (540 vs), two (580s and 530s), and three i.r. bands (600vs, 552m, and 520s cm^{-1}) in agreement with low molecular symmetry (C_s).

Mass Spectra.—Electron-impact fragmentation data are available as Supplementary Publication No. SUP 22251 (2 pp.).* Coincident nominal mass for ^{28}Si and the C_2H_4 unit (*m/e* 28) leads to limited ambiguity for certain ion families, but a number of firm conclusions can be drawn. For compound (1) over half the ion current was carried by the parent-ion family $[C_5H_xSi]^+$. The next most abundant family corresponds to fragmentation of the C_5 ring without Si–C cleavage by loss of neutral ethylene, a metastable-supported process (v).

$$[C_5H_8Si]^{+\cdot} \longrightarrow [C_3H_4Si]^{+\cdot} + C_2H_4 \qquad m^* = 48.2 \quad \text{(v)}$$

Intense parent-ion and $[C_5H_xSi]^+$ peaks were present in the spectrum of (5), the latter probably due to Si–C bond cleavage as postulated for the germanium analogue.[1] In contrast, for (2)—(4) the parent-ion families rapidly diminish in importance with increasing chlorine content, probably due to fragmentation of the polar Si–Cl bond with Cl$^{\cdot}$ elimination. Differences between the data in SUP 22251 and those for germanium analogues are attributable to the greater strength of Si–C over Ge–C bonds.[1,12] The effect of this is particularly noticeable for (7), where a very weak parent ion is found and the abundant fragments are $[C_6H_x]^+$, $[CH_xSi]^+$, and $[C_3H_x]^+$ corresponding to rupture of the indene framework; for germylindene, intense parent peaks and $[C_9H_x]^+$ fragments[1] suggest more ready cleavage of the germanium–hydrocarbon linkage.

N.M.R. Spectra (^{1}H *and* ^{13}C) *and Intramolecular Non-rigid Behaviour.*—Variable-temperature n.m.r. spectroscopy establishes that compounds (1)—(7) all undergo intramolecular rearrangement, but that they show three different types of behaviour. As established earlier,[4] (1) is fluxional with an energy of activation sufficiently low that significant broadening of ^{1}H signals in the low-field region occurs at > -25 °C and (2), (3), and (5) behave similarly. Like its germanium analogue,[1] (6) is *quasi-fluxional*,† undergoing ready non-degenerate rearrangement involving exchange between the 1-silyl isomers (8)—(10). In contrast, at 28 °C slow-limiting characteristics are observed for (4) and (7), effects of exchange being distinguishable only at a much higher temperature. It is convenient to simplify discussion of the results by maintaining these distinctions. Observed data are condensed into Tables 2 and 3, in which the term coalescence refers to collapse of the slow-limiting aa'bb'x pattern (11) for ring nuclei. In this process the most obvious change is the disappearance of the high-field (x) resonance.



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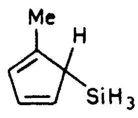

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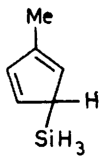

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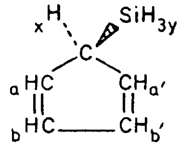

(11)

Compounds (1)—(3) *and* (5). As reported previously,[4] a ^{1}H spectrum corresponding to the 'static' or slow-limit configuration (11) is observed for (1) below −25 °C although the chemical-shift difference between a,a′ and b,b′ protons [see (11)] is very small as was found for the corresponding germane.[1] Coalescence occurs on increasing the temperature, giving a broad olefinic resonance, and although not noted by Hagen and Russo,[4] at 50 °C the Si*H* resonance splits into a beautifully resolved sextet as equivalence between the five ring protons becomes fully established. Similar behaviour is shown by the 'satellite' resonances (Figure 1) arising through coupling with the magnetically active ^{29}Si isotope (4.70% abundant, $I = \frac{1}{2}$). Averaged fast-limiting coupling was first detected by us[1] between germyl and ring hydrogen atoms in $C_5H_5(GeH_3)$ and $C_5H_4Me(GeH_3)$ and has since been observed in metal magnetic-resonance signals for cyclopentadienyl-mercury and -tin derivatives through use of the heteronuclear magnetic double-resonance technique.[13] The coupling constant $^1J(^{29}Si\text{–}H)$ for (1) and also that for (6) were given incorrectly earlier[4] as half the true values. A marked increase in this parameter is associated with electron withdrawal from

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

† By this expression we imply intramolecular exchange between non-degenerate states (here *isomers*) of similar mechanism and energy of activation to that found in *fluxional* molecules of closely related structure.

[12] F. Glockling, M. A. Lyle, and S. R. Stobart, *J.C.S. Dalton*, 1974, 2537.

[13] R. J. Goodfellow and S. R. Stobart, *J. Magnetic Resonance*, 1977, **27**, 143.

the silicon atom by successive chlorine substitution along the series (1)—(3), comparable with results obtained from chlorination of a variety of silyl compounds.[14] Corresponding increased deshielding of the tertiary ring proton is also evident (Table 2). For compound (5) the methyl resonance at high field (τ 9.92) remains a well resolved triplet (J 4.0 Hz) throughout the temperature range investigated; re-examination of the ^{1}H spectrum of $C_5H_5(GeMeH_2)$ has established identical CH_3 characteristics, correcting our earlier unaccountable claim that the triplet structure collapsed on increasing the temperature.[1] We attribute the latter observation

TABLE 2

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

		Chemical shifts (τ [b])					Coupling constants (Hz)		
T/K	Compound	$H_{aa'bb'}$	H_x	H_y	H_z		$J(H_xH_y)$	$J(H_yH_z)$	$J(^{29}SiH_y)$
213	(1)	3.52 [c]	6.73 [d]	6.55			3.20		203.5
	(2)	3.2—3.27 [c] 3.37—3.43 [c]	6.24 [d]	5.89			2.8		249.6
	(3)	3.17—3.24 [c] 3.43—3.51 [c]	6.15 [d]	6.05			2.8		311.6
223	(5)	3.33 [c]	7.0 [d]	6.41	9.92		2.6	4.0	199.8
		$H_{aa'bb'x}$	H_y	H_z			$J(H_{aa'bb'x}H_y)$	$J(H_yH_z)$	$J(^{29}SiH_y)$
343	(2)	3.96	5.82				0.5		248.4
	(3)	3.93	5.78				0.5		311
368	(5)	4.05	6.3	9.92			0.58	4.0	
		H_{phenyl}	H_a	H_b	H_x	H_y	$J(H_xH_y)$		$J(^{29}SiH_y)$
308	(7)	3.03—3.2 [c] 3.24—3.35 [c]	3.65 [e]	4.05 [f]	7.18 [d]	6.03	3.3		228.2

[a] Recorded for $CDCl_3$ solutions of (1)—(3) and (5), and for a neat sample of (7). A $CDCl_3$ solution of (7) exhibited only one resonance in the τ 6—7 region [τ 6.46, corresponding to both τ(SiH) and $\tau(CH_x)$]. [b] Proton environments are distinguished as follows: aa'bb', olefinic C_5-ring hydrogen atoms; x, aliphatic C_5-ring hydrogens; y, substituent SiH hydrogens; z, substituent methyl hydrogens. Integrations gave relative intensities consistent with proposed assignments throughout. [c] Multiplet, J values not determined. [d] Broad. [e] Doublet of doublet of doublets: $J(H_aH_b)$ 5.3, $J(H_aH_x)$ 1.7, $J(H_aH_{Ph})$ 0.7 Hz. [f] Doublet of doublets: $J(H_aH_b)$ 5.2, $J(H_bH_x)$ 1.7 Hz.

TABLE 3

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

		Chemical shift/p.p.m.[b]		Coupling constants/Hz	
Compound	T/K	C(olefinic)	C(aliphatic)	$^2J[^1H-^{13}C(olefinic)]$	$^2J[^1H-^{13}C(aliphatic)]$
C_5H_6	263	133.3 (90) [c] 132.4 (100)	41.7 (49)	170.5	126.0
(1)	223	134.8 (95) 130.8 (100)	42.6 (40)	n.o.	135.8
$C_5H_5(GeH_3)$		135.1 (83) 129.1 (100)	42.4 (36)	n.o.	n.o.
(2)		133.9 (100) 130.7 (90)	49.0 (34)	167.2,[d] 170.3 [e]	140.4
(3)		135.3 (100) 129.2 (86)	53.0 (39)		
(4)	308	136.2 (100) 129.6 (89)	54.1 (39)	96.2,[d] 102.1 [e]	131.6
(6)	233 [f]	145.3 (21) 141.0 (25) 135.0 (99) 133.9 (100) 131.5 (88) 131.3 (92) 129.0 (99) 126.9 (84)	44.8 (67) 41.3 (83)	n.o.	137.9
(7)	308	145.3 (12) 143.6 (12) 135.7 (89) 130.1 (78) 125.8 (100) 124.6 (92) 123.0 (85) 121.7 (87)	37.1 (81)	n.o.	132.7

n.o. = Not measured.

[a] $CDCl_3$ used as solvent and internal reference throughout. [b] High frequency relative to δ 77.2 p.p.m. for $CDCl_3$ (central component of triplet); high frequency corresponds to low field and *vice-versa*. [c] Numbers in parentheses indicate relative peak heights (pulse interval 1.36 s, pulse width 8 μs). [d] Higher-frequency olefinic ^{13}C resonance. [e] Lower-frequency olefinic ^{13}C resonance. [f] $\delta[^{13}C(Me)]$ observed at 15.5 (47) and 15.3 (51) p.p.m.

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[14] E. A. V. Ebsworth, 'Volatile Silicon Compounds,' Pergamon, New York, 1963.

to inhomogeneity possibly associated with thermal ' bumping ' of the sample at 100 °C.

Much controversy has surrounded the mechanism of sigmatropic migration in the class of compounds to which (1)—(5) belong. While a 1,2 rearrangement * is more compatible with both least-path and symmetry considerations [16] than the proposed alternative 1,3 route,[17] the latter has never been categorically ruled out. A random shift has been eliminated since unsymmetrical collapse invariably occurs in the olefinic aa′bb′ region. Careful scrutiny of the present ^{13}C n.m.r. data provides new and compelling evidence for a 1,2 shift. By analogy with related cyclic systems, notably substituted benzenes and pyridines,[18] an increase in electron-withdrawing character of the substituent at the 1-position on the cyclopentadiene ring would be predicted to generate a paramagnetic shift in C^1 and $C^{3,4}$ but a diamagnetic shift in $C^{2,5}$. Assignments based on this expectation are set out in Table 4 for compounds (1)—(4), the analogous chloro(methyl)silanes,[19] and two related germanes. In every case the higher-frequency carbon resonance collapsing first on increasing the temperature is that attributed to $C^{2,5}$.

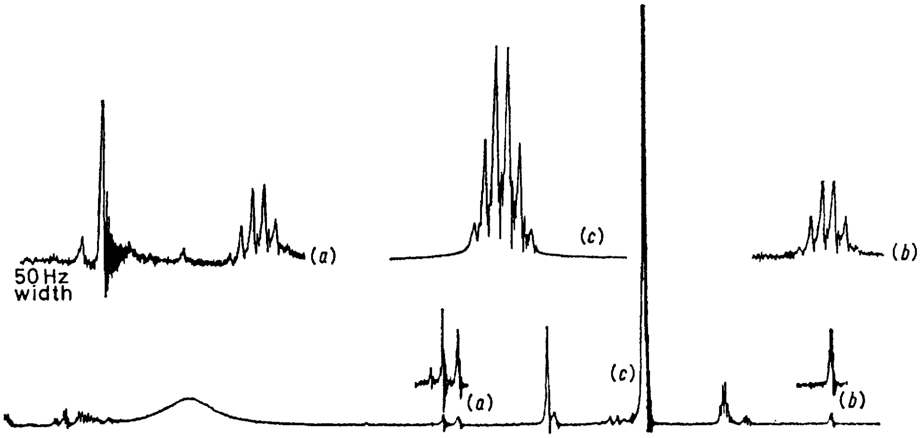

FIGURE 1 Hydrogen-1 n.m.r. spectrum (500 Hz width) of compound (1) at 50 °C (neat liquid). For chemical-shift values and assignments see Table 2. Inset spectrum at 50 Hz width: regions (a) and (b), $^{29}Si-H$ ' satellite;' (c) main $Si-H$ resonances

TABLE 4

Assignment of ^{13}C resonances [a] in compounds (1)—(4) and related species

Compound	C^1	$C^{2,5}$	$C^{3,4}$
$C_5H_5(GeH_3)$	42.4	135.1	129.1
(1)	42.6	134.8	130.8
(2)	49.0	133.9	130.7
(3)	53.0	129.2	135.3
(4)	54.1	129.6	136.2
$C_5H_5(GeMe_3)$ [b]	52.1	133.9	129.8
$C_5H_5(SiMe_3)$ [b]	52.5	134.0	131.3
$C_5H_5(SiMe_2Cl)$ [b]	54.0	133.0	133.7
$C_5H_5(SiMeCl_2)$ [b]	53.3	131.9	135.6

[a] Measured as described in Table 3. [b] Values from ref. 18.

Compound (6). Proton data have been reported for this compound in detail by Hagen and Russo.[4] At the slow limit of non-degenerate rearrangement these workers detected only the two non-*gem* isomers (9) and (10), in agreement with our findings for the analogous germane.[1] They were also able to distinguish between these two species by use of proton-decoupling techniques. At ⩽−30 °C in the ^{13}C n.m.r. spectrum we observe only two resonances due to CH_3 nuclei, and 10 other lines clearly attributable to two superimposed abcdx patterns belonging to ring carbon atoms (Table 3). This confirms the presence of a mixture of equal proportions of the two isomers (9) and (10), each of which shows complete non-equivalence for the five ring-carbon atoms due to unsymmetrical substitution, in *ca.* equimolar ratio as suggested by the ^1H data.[1,4] On warming above 10 °C resonances other than the CH_3 signal (which collapses to a sharp singlet) coalesce into a broad envelope in the olefinic region (130—132 p.p.m.), in accordance with the establishment of equivalence due to ready non-degenerate rearrangement *via* 1,2-metallotropic shifts.

Compounds (4) *and* (7). The resistance of compound (4) towards degenerate rearrangement has been estab-

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* Considerable confusion surrounds the numbering of the C_5 ring positions in compounds of the type under discussion. According [15] to both I.U.P.A.C. nomenclature and that adopted by Chemical Abstracts, the monocyclic hydrocarbon is termed cyclopenta-1,3-diene rendering the saturated carbon position 5. On the other hand, the corresponding cyclic hydrocarbon radical is named cyclopenta-2,4-dien-1-yl conferring the number 1 on the (previously) saturated carbon atom. We prefer to adopt the latter scheme, thereby tacitly regarding compounds (1)—(5) as cyclopentadienylsilanes although for convenience and consistency [1] we refer to them as silylcyclopentadienes.

[15] ' Nomenclature of Organic Chemistry,' 3rd edn., I.U.P.A.C., Butterworths, London, 1971; ' Naming and Indexing of Chemical Substances,' Chemical Abstracts, 1973, vol. 76 Index Guide, Section IV.

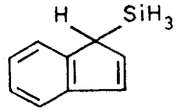
[16] R. B. Larrabee, *J. Organometallic Chem.*, 1974, **74**, 313; Chan-Cheng Su, *J. Amer. Chem. Soc.*, 1971, **93**, 5653.

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

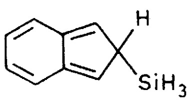
[18] J. B. Stothers, ' Carbon-13 NMR Spectroscopy,' in ' Organic Chemistry,' vol. 24, 1972; G. C. Levy and G. L. Nelson, ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley, New York, 1972.

[19] Yu. K. Grishin, N. M. Sergeyev, and Yu. A. Ustynyuk, *Org. Magnetic Resonance*, 1972, **4**, 377.

lished elsewhere [6,20] using ^{1}H n.m.r. spectroscopy. The ^{13}C data (Table 3) concur with this conclusion, an a_2b_2x pattern persisting up to 50 °C. The ease with which prototropic migration and dimerization occur for compound (4) and its germanium analogue [21] precluded measurements at higher temperatures. The reasons for the non-fluxional character of these species remain unclear,[6] but the rigidity of the indene (7) as revealed by both ^{1}H and ^{13}C n.m.r. spectra (Tables 2 and 3) can be attributed [1] to the generation by a 1,2-metallotropic shift from (12) of the energetically much less favourable *iso*-indene (13).

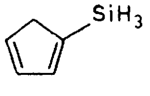


(12)

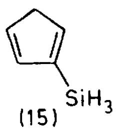


(13)

Prototropic rearrangement in compounds (1)—(5): *formation of non-fluxional* 2- *and* 3-*isomers*. Isomerization *via* hydrogen shifts to stereochemically rigid 2- and 3-substituted derivatives has been characterized for cyclopentadienyl-silanes and -germanes,[1,4,21] most thoroughly [22] for $C_5H_5(SiMe_3)$ for which hydrogen migration is reversible and reaches equilibrium. A similar conclusion has been reached for 5-germylcyclopenta-1,3-diene.[1] Such rearrangement occurs very much more slowly than the metallotropic behaviour of the 1-isomers but is more ready for silane derivatives than for germanes.[1] The result of this process is evident in Figure 1: in a very short time at ambient temperature new singlets appear at low field from the Si*H* resonance of compound (1), attributable to the corresponding signals for the 2- and 3-isomers (14) and (15). This is confirmed unequivocally for compound (5) owing to the spin-coupled structure of the Si*H* line; the τ 5—7 region at 50 °C is illustrated in Figure 2 and consists of three well resolved quartets. The most abundant, which is that at highest field, is further split into sextets through averaged fast-limiting coupling [1,13] with the five cyclopentadienyl protons in the fluxional isomer (5). The middle quartet is of intermediate intensity showing a small olefinic coupling and is assigned to the 2-isomer, analogous to structure (14). Since the lowest-energy path to the 3-isomer is presumably by prototropic rearrangement of the 2-isomer, we assign the weakest signal at lowest field to this species. Chemical-shift data are collected in Table 5 and constitute a consistent pattern with earlier assignments.[1,22] Corresponding isomer formation was observed for compounds (2)—(4) but was not analysed in detail.



(14)



(15)

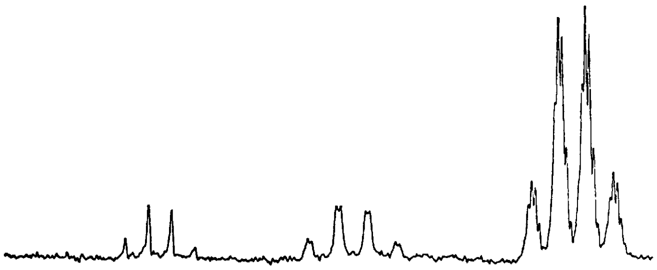


FIGURE 2 Hydrogen-1 n.m.r. spectrum of compound (5), τ 5—6.5 region, 100 Hz width. Chemical-shift data are given in Table 5

TABLE 5

Hydrogen-1 n.m.r. parameters [a] for silylcyclopentadiene and methylsilylcyclopentadiene isomers

	τ			
Compound [b]	H^{2-5}	H^1	SiH_3	CH_3
$C_5H_5(SiH_3\text{-}1)$	4.02		6.49	
$C_5H_5(SiH_3\text{-}2)$	3.50	6.92	6.32	
$C_5H_5(SiH_3\text{-}3)$	3.28	7.02	6.13	
$C_5H_5(SiMeH_2\text{-}1)$	3.87		6.32	9.95
$C_5H_5(SiMeH_2\text{-}2)$	3.33	6.93	5.79	9.70
$C_5H_5(SiMeH_2\text{-}3)$	3.21	7.04	5.27	*c*

[a] In $CDCl_3$ solution relative to internal $SiMe_4$ at 35 °C. [b] For numbering system see footnote on p. 942. [c] Not distinguished due to overlapping resonances.

Throughout this work chemical shifts of compounds (1)—(7) were found to be concentration dependent, changing by as much as 0.5 p.p.m. to low field between neat liquid samples and 10% v/v deuteriochloroform solutions.

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[7/1134 *Received, 29th June,* 1977]

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[20] N. M. Sergeyev, G. R. Avramenko, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1970, **22**, 63.

[21] V. S. Shriro, Yu. A. Strelenko, Yu. A. Ustynyuk, N. N. Zemlyansky, and K. A. Kocheshkov, *J. Organometallic Chem.*, 1976, **117**, 321.

[22] E. W. Abel and M. O. Dunster, *J. Organometallic Chem.*, 1971, **33**, 161; A. J. Ashe, *J. Amer. Chem. Soc.*, 1970, **92**, 1233.