Journal of Organometallic Chemistry, 51 (1973) 125–133
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

FLUXIONAL BEHAVIOR OF 5-(SILYL)CYCLOPENTADIENE AND 5-(SILYL)METHYLCYCLOPENTADIENE (1,2-ISOMER MIXTURE)

ARNULF P. HAGEN and PETER J. RUSSO*
Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73069 (U.S.A.)

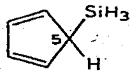
(Received August 21st, 1972)

SUMMARY

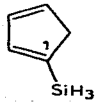
Variable temperature PMR spectra of the title compounds are analyzed in the −50 to +106° range. The limiting low-temperature spectrum of the methyl derivative shows that metal migration is retarded enough to identify individual nonequivalent configurations. The mode of metallotropic rearrangement for 5-(silyl)cyclopentadiene appears to be either 1,2 or random cavorts. Prototropic rearrangement proceeds much slower becoming increasingly evident at and above +66°. The AA′BB′X pattern at the slow exchange limit and the infrared spectrum (in the 3000 cm^{-1} region) of 5-(silyl)cyclopentadiene are consistent with a "static" σ-type bond between the H_3Si moiety and the unique carbon of the cyclopentadienyl ring.

INTRODUCTION

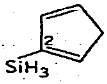
In a preliminary note[1] the "static" structures of (silyl)cyclopentadiene and (silyl)methylcyclopentadiene were briefly mentioned having been initially deduced from limiting low-temperature (−50°) proton magnetic resonance spectra; we also indicated that as the temperature was raised these silicon compounds exhibited fluxional behavior characteristically associated with stereochemically nonrigid, metal-olefinic ring systems[2–9]. We now report the variable temperature PMR spectra of the silyl derivatives of cyclopentadiene and methylcyclopentadiene in the entire rigid (static) to nonrigid (dynamic) behavior interval. Below −25° metal migration is slow enabling the behavior of semi-static isomer (I) to be studied. At and above +66° isomers (II) and (III) are formed via proton rearrangement. Spin-decoupling experiments performed at the slow exchange limit of 5-(silyl)methylcyclopentadiene revealed that an approximate 1/1 mixture of isomers (II′) and (III′) was present



(I)



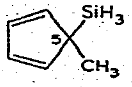
(II)



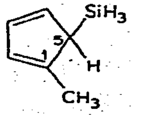
(III)

---

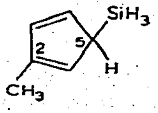
* Postdoctoral Research Associate.



(I′)



(II′)



(III′)

with none of isomer (I′) observed. Below −25° semi-static isomers (II′) and (III′) can be observed to undergo metallotropic migration; at and above +66° other stereochemically rigid isomers appear as a result of proton rearrangement. Davison and Rakita[6] studied 5-[$(CH_3)_3Si$]$C_5H_4CH_3$ from −4 to +135° and concluded that the three isomers analogous to (I′), (II′) and (III′) contributed to the low-temperature spectrum. Unfortunately, proton spin-decoupling measurements gave an unclear description of the methyl resonance behavior. In another report[9], the PMR spectrum of $(CH_3)_3SiC_9H_6CH_3$ gave no evidence for any amount of the isomer containing both indenyl ring substituents attached to the saturated carbon. It is therefore hoped that this article will clarify some of the complications arising in the low-temperature PMR spectra of compounds of the type, 5-$(R_3Si)C_5H_4CH_3$; R=H, CH_3.

EXPERIMENTAL

All manipulations were carried out either in an atmosphere of dry nitrogen or *in vacuo*. PMR spectra were obtained at 100 MHz using an XL-100 Varian Associates spectrometer equipped with a variable-temperature probe assembly calibrated with methanol and ethyleneglycol. All spectra were taken at −50° first on neat samples (TMS as internal standard) contained in evacuated, sealed tubes (5 mm o.d.). Infrared spectra were recorded on a Beckman IR-10 spectrometer using neat liquid between KBr disks. Mass spectra were taken at 75 eV energies on a Hitachi Perkin–Elmer RMU-6E mass spectrometer at ambient temperature. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

5-*(Silyl)cyclopentadiene*

Small pieces of potassium (0.4199 g, 0.01074 mole), cyclopentadiene (0.8216 g, 0.01243 mole), and ~15 ml of anhydrous diethyl ether, refluxed and vacuum distilled over $LiAlH_4$, were combined at −196° in a vacuum line receptacle fitted with a stopcock and open to a manometer. A vigorous reaction took place at −78°; after 12 h excess cyclopentadiene and solvent were separated slowly (at −30°) from the white residue (1.0891 g, 0.010448 mole) which was subsequently dried at +60° for 12 h. Silyl bromide (2.3566 g, 0.021227 mole) was combined at −196° with the pure, dry $K(C_5H_5)$. After being held at −78° for 30 min, most of the excess H_3SiBr was removed at −78° from the reaction vessel. Pure product (0.9092 g, 0.009450 mole; 89.01 % yield based on $K(C_5H_5)$; m.p. −94 to −96°; b.p. 59 to 61°; n_D^{25} 1.4750) was collected in a −60° trap after the volatile material removed from the vessel at ambient temperature was passed through −60 and −196° traps. (Found: C, 62.70; H, 8.62; Si, 28.81. C_5H_8Si calcd.: C, 62.42; H, 8.28; Si, 29.19 %.)

The PMR (neat, ambient temperature) spectrum had the following resonances: δ 2.95 (complex); δ 3.50 (singlet); δ 6.30 (broad). The gas-phase infrared spectrum showed bands at 3091 w, 2930 w, 2171 (sh), 2151 vs, 1101 w, 985 m, 921 vs, 911 vs, 781 w, 685 s, 630 w, 425 w cm^{-1}. The mass spectrum showed the molecular ion $C_5H_8{}^{28}Si$ at *m/e* 96.

5-(Silyl)methylcyclopentadiene (*1,2-isomer mixture*)

Small pieces of potassium (0.6095 g, 0.01559 mole), methylcyclopentadiene (1,2-isomer mixture; b.p. 73–74°) (2.0980 g, 0.026182 mole), and ~15 ml of anhydrous diethyl ether, refluxed and vacuum distilled over $LiAlH_4$, were allowed to react at −78°. After 12 h excess methylcyclopentadiene and solvent were separated slowly (at −30°) from the white residue (1.7414 g, 0.014730 mole) which was subsequently dried at +60° for 12 h. Silyl bromide (3.6825 g, 0.033178 mole) was combined at −196° with the dry $K(C_5H_4CH_3)$[10,11]. After being held at −78° for 30 min, most of the excess H_3SiBr was removed at −78° from the reaction vessel. Pure product (1.6061 g, 0.014570 mole; 98.99% yield based on $K(C_5H_4CH_3)$; m.p. −145 to −147°; b.p. 108 to 109°; n_D^{25} 1.4774) was collected in a −60° trap after the volatile material removed from the vessel at ambient temperature was passed through −60 and −196° traps. (Found: C, 65.17; H, 9.17; Si, 25.28. $C_6H_{10}Si$ calcd.: C, 65.38; H, 9.14; Si, 25.48%.)

The PMR (neat, ambient temperature) spectrum had the following resonances: δ 2.01 (singlet); δ 3.49 (singlet); δ 6.27 (broad). The gas-phase infrared spectrum showed bands at 3090 w, 2980 w, 2930 w, 2880 w, 2175 (sh), 2150 vs, 1095 w, 985 m, 920 vs, 913 vs, 785 w, 687 s, 648 m, 425 w cm^{-1}. The mass spectrum showed the molecular ion $C_6H_{10}{}^{28}Si$ at *m/e* 110.

RESULTS

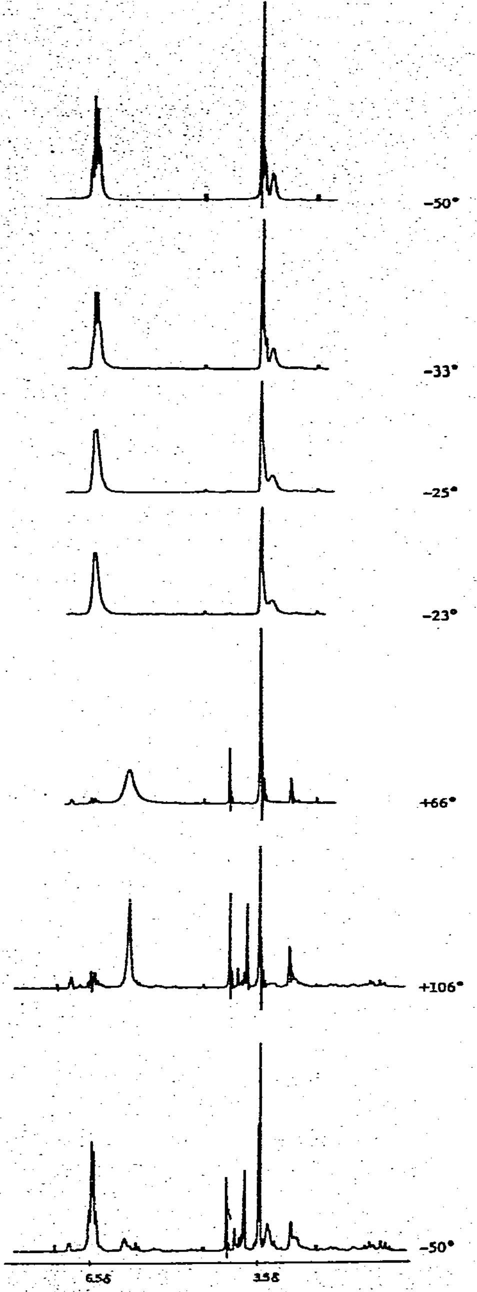
Preparation of compounds

It should be noted that $5\text{-}(H_3Si)C_5H_5$ and $5\text{-}(H_3Si)C_5H_4CH_3$ (1,2-isomer mixture) were synthesized *in vacuo* and in the absence of solvent at a low temperature of −78°. This method greatly simplifies the purification of the product since known methods employ an alkali or Grignard cyclopentadienide reacting with a substituted, mono- or polyhalide of silicon in the presence of a solvent which upon removal enhances isomer formation. As will be reported in a later article $5\text{-}(H_3Si)C_5H_5$ and $5\text{-}(H_3Si)C_5H_4CH_3$ (1,2-isomer mixture) react with potassium[10] (and methyllithium) rupturing the Si–C bond and forming the appropriate salt, $M'(C_5H_4\text{–}X)$: $M' = K, Li$; $X = H, CH_3$.

Uncracked methylcyclopentadiene dimer contains dicyclopentadiene (5–6.5% max)[12], and the PMR spectrum of $K(C_5H_4CH_3)$ contains some $K(C_5H_5)$[10]. It is therefore noteworthy that redistillation[8,13] of the cracked monomer, $C_5H_4CH_3$ (1,2-isomer mixture; b.p. 73–75°), is a necessary step in the synthetic procedure.

Analysis of the PMR spectra of 5-(silyl)cyclopentadiene

The variable temperature spectra are illustrated in Fig. 1. Clearly displayed at −50° are the resolved AA′BB′ portion of an AA′BB′X scheme for four olefinic protons (δ ~6.50), the complex multiplet of the X part for the methine proton (δ ~3.26), and a resolved doublet for the silyl protons (δ ~3.47) with silicon satellites ($|J(^{29}Si\text{–}H)|$ 102 Hz). These spectral observations are consistent with structure (I). As the temperature is raised the resonance signals diminish in intensity, show resonance



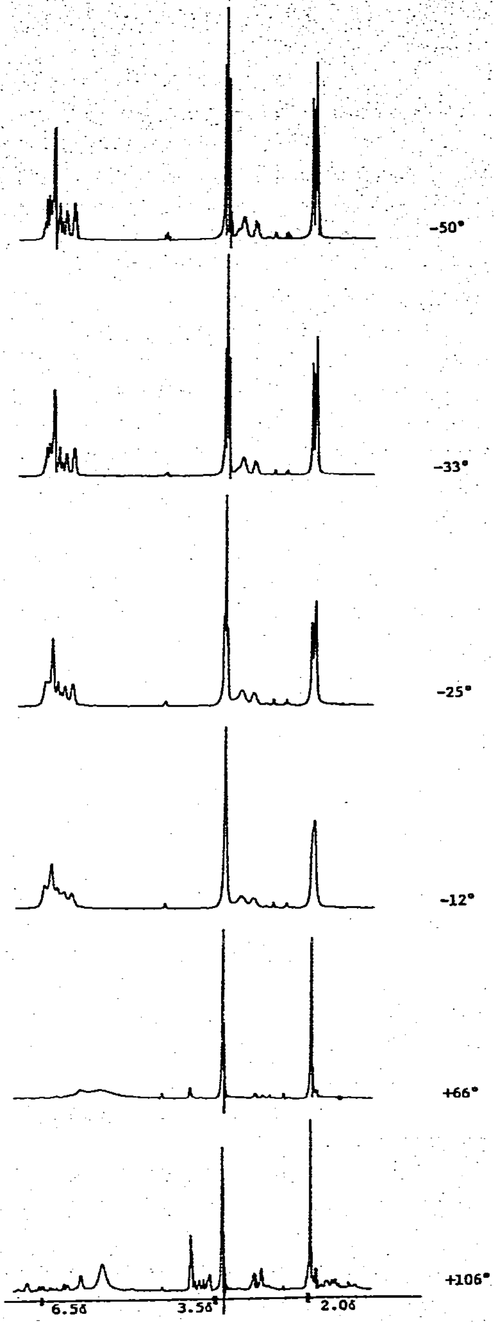


Fig. 1. Variable temperature PMR spectra of 5-(H_3Si)C_5H_5 in the δ 6.5–3.0 region at several temperatures. The complex −50° spectrum represents the +106° sample cooled to −50°.

Fig. 2. Variable temperature PMR spectra of 5-(H_3Si)$C_5H_4CH_3$ (1,2-isomer mixture) in the δ 6.5–2.0 region at several temperatures.

TABLE 1

CHEMICAL SHIFTS (ppm) OF 5-(H_3Si)C_5H_5 AT VARIOUS TEMPERATURES (°C)

Temperature	$\delta(H_2H_3, H_1H_4)$[a]	δ(*Si–H*)	$\delta(H_5)$	*J*(*Si–H*, H_5)
−50°	6.52 6.47	3.48 3.45 *J* (3.0 Hz)	3.26	(21.0 Hz)
−33°	6.53 6.48	3.49 3.46 *J* (3.0 Hz)	3.27	(23.0 Hz)
−25°	6.52 6.48	3.46	3.28	
−23°	6.50 6.50	3.47	3.27	
0°	6.50 6.50	3.48	—	
+39°	6.30 6.30	3.50	2.95	
+66°	6.93 6.56 6.50 5.87	4.06 3.50	2.94 2.80	
+106°	6.94 6.58 6.52 5.88	4.05 3.74 3.51	2.97 2.95	
−50°	6.94 6.52 6.48 5.92	4.08 3.75 3.50 3.47 *J* (3.0 Hz)	3.30 2.89	

[a] In accord with other assignments[20,25], the upfield signal is ascribed to H_1H_4.

broadening, and exhibit coalescence at −25, −23 and 0° for the silyl, vinyl, and tertiary hydrogen peaks respectively. Results of the PMR data are summarized in Table 1. At and above +66° new peaks appear simultaneously and irreversibly since on cooling from +106° to −50° the signals due to the presence of isomers (II) and (III) remain, with fine structure reappearing in the original (−50°) vinyl and silyl regions. It should be noted that the original (−50°) upfield olefinic resonances appear more structured; consequently, a small rise in temperature causes the resonance at the higher field to lose its fine structure. Above −45° the vinyl signals appear to broaden and coalesce at about the same rate.

Infrared spectrum of 5-(*silyl*)*cyclopentadiene* (*liquid film between KBr plates*)

Absorptions observed in the region above 3000 cm^{-1} were 3106 w, 3091 m, and 3075 m cm^{-1}. Other bands occurred at 2156 (sh), 2138 vs, 965 s, 933 vs, 908 vs, 890 vs, 812 w, 779 m, 686 vs, 635 s, 548 w, 420 m cm^{-1}.

Analysis of the PMR spectra of 5-(silyl)methylcyclopentadiene (*1,2-isomer mixture*)

The variable temperature spectra are displayed in Fig. 2. The −50° PMR spectrum exhibits multiple resonances with fine structure in the olefinic (δ ~6.50–6.00), silyl (δ ~3.50–3.40) with silicon satellites [$|J(^{29}\text{Si–H})|$ 102 Hz], tertiary (δ 3.20–3.00), and methyl (δ ~2.00–1.95) proton resonant regions. Spin-decoupling experiments performed at −50° (Fig. 3) resulted in the following changes in the fine structure of the methyl resonances: (1) Irradiation at 604 Hz downfield caused the upfield methyl triplet[14] to collapse into a doublet ($J = 1.5$ Hz). It was therefore assumed that in structure (III'), H(3) was decoupled from the protons of the methyl group; (2) Irradiation at 619 Hz downfield caused the downfield methyl doublet[14] to collapse into a singlet. It was thus concluded that in structure (II'), H(2) was decoupled from the methyl protons. Irradiations at 625, 630, 637, and 639 Hz downfield produced no changes in the −50° spectrum; likewise, irradiations at 201 and 195 Hz downfield produced no changes in the silyl resonances, and irradiations at 346 and 342 Hz downfield resulted in no differences in the methyl resonances. With a gradual rise in temperature (−33°), the pair of silyl doublets collapses into a triplet; at −25° the

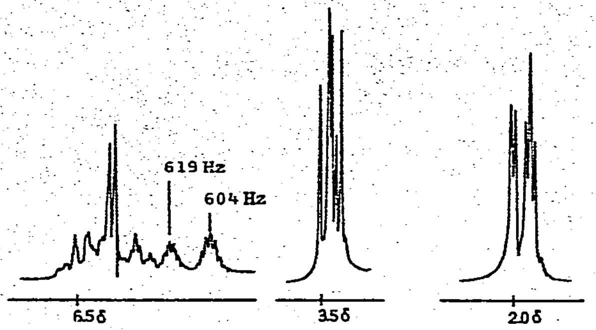


Fig. 3. Expanded (250 Hz sw) −50° PMR spectrum of 5-$(H_3Si)C_5H_4CH_3$ (1,2-isomer mixture) used during the proton spin-decoupling measurements.

methyl signals at the higher field collapse into a single peak with the methyl peak at the lower field appearing as a doublet, the silyl peak as a triplet, the olefinic and tertiary proton peaks appearing broad and unresolved. Resonance broadening and total fine structure collapse of the silyl and methyl resonances occur at ~ −12°; coalescence is complete at +39°. At and above +66° additional peaks in the silyl, tertiary, and methyl proton regions appear irreversibly due to isomers containing H_3Si attached to different double bond positions; however, at +106° numerous peaks complicate the spectrum. A summary of the PMR data is given in Table 2. For comparison purposes the PMR data of the carbon analogues are listed in Table 3.

TABLE 2

CHEMICAL SHIFTS (ppm) OF 5-(SILYL)METHYLCYCLOPENTADIENE (1,2-ISOMER MIXTURE) AT VARIOUS TEMPERATURES (°C)

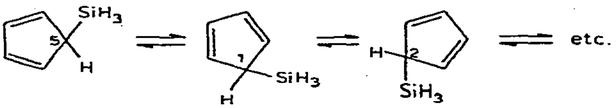
Temperature	$\delta(H_2H_3H_1H_4)^c$	$\delta(Si\text{–}H)$	$\delta(H_5)^c$	$\delta(CH_3)$
−50°	6.51 6.47 6.39 6.37 6.30 6.25 6.19 6.06 6.04 6.02	3.50 3.46 3.45 3.42 J(3.1 Hz)[a] J(3.1 Hz)[a]	3.19 2.99	2.01 2.00 1.97 1.95 1.94 J(1.2 Hz)[a] J(3.0 Hz)[b]
−33°	6.52 6.48 6.40 6.38 6.33 6.25 6.19 6.06 6.05	3.50 3.47 3.43	3.20 3.00	2.03 2.01 1.97 1.96 1.95 J(1.2 Hz)[a] J(3.0 Hz)[b]
−25°	6.52 6.48 6.40 6.31 6.25 6.19 6.04	3.51 3.47 3.44	3.21 3.00	2.03 2.02 1.97
−12°	6.52 6.40 6.31 6.19 6.06	3.48	3.21 3.01	1.98
+18°	6.40 6.28	3.48	— —	2.00
+39°	6.27	3.49	— —	2.01
+66°	5.88 5.52	4.05 4.03 3.50	2.95 2.82 2.70	2.01
+106°	6.77 6.57 6.51 6.29 6.15 5.87 5.51	4.02 3.95 3.91 3.89 3.88 3.80 3.49	2.85 2.83	2.01 1.93 1.91

[a] Doublet; [b] Triplet; Note that the silyl resonance (partially visible doublet) appearing at δ 3.44 in the −50° and −33° spectra and at δ 3.45 in the −25° spectrum is assigned to presence of 5-$(H_3Si)C_5H_5$[6]; see Fig. 3; [c] Complex multiplets observed for the vinyl and tertiary hydrogen resonances due to the isomeric mixture.

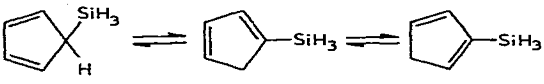
DISCUSSION

In general, intramolecular rearrangements sufficiently explain the observed spectral changes, *i.e.*, resonance broadening, silicon satellites at the slow and fast exchange limits, and additional peak formations at elevated temperatures, in the PMR spectra of 5-(silyl)cyclopentadiene and 5-(silyl)methylcyclopentadiene (1,2-isomer mixture). The variable temperature studies have shown that these compounds behave as fluxional molecules[8]. Metallotropic and prototropic migration are the two types of rearrangement which proceed at entirely different rates[18,19], because below ambient temperature metal migration predominates exclusively with the apparent mode of metal movement assumed to be either 1,2[8,20,25] or random shifts. Due to the close proximity of the H(5) and silyl resonances, the energy of metal migration is difficult to estimate.

The −50° spectrum of 5-(silyl)cyclopentadiene is consistent with instantaneous structure (I) whose behavioral processes undergo fast metal exchange below ambient temperature according to the scheme:

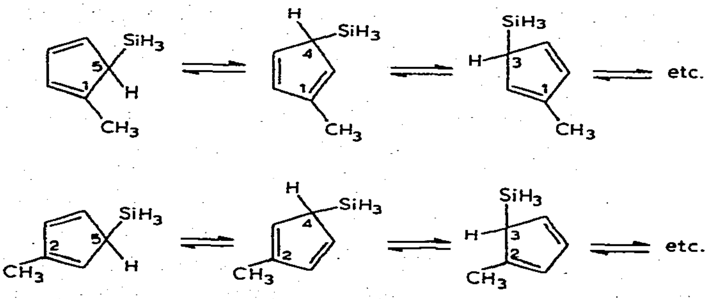


At elevated temperatures slow proton exchange[21] produces isomers (II) and (III) along with small amounts of dimeric species[22]. The downfield and upfield silyl proton signals are tentatively assigned to structures (II) and (III) respectively since isomer (II) appears first because a 1,2 proton shift is theoretically[23] and experimentally[15,17,24,25] verifiable. These assignments are at odds with those given to the isomers of 5-(trimethylsilyl)cyclopentadiene[18,21]. It can also be assumed that different barriers of proton migration exist[17,24] governing the path, *e.g.*[8,18,22],

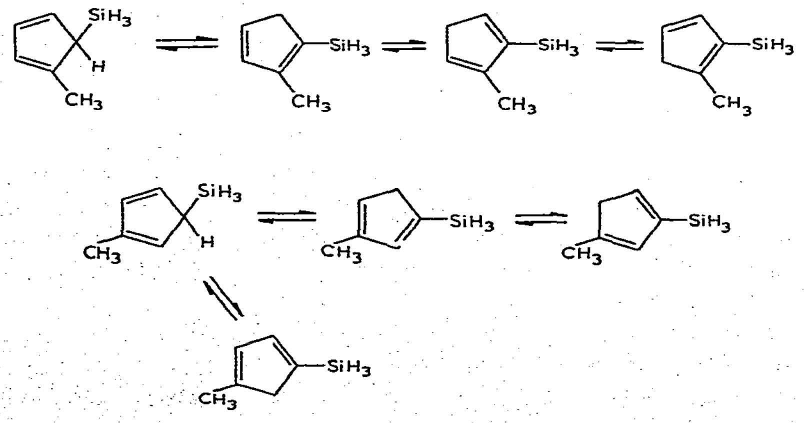


Multiple bands in the infrared region about 3000 cm^{-1} [8] and the well resolved AA'BB'X pattern of the slow exchange[7] PMR spectrum tend to support the assumption that the linkage in the compound 5-(H_3Si)C_5H_5 between silicon and the unique carbon of the cyclopentadienyl ring is a weak, labile σ-type bond. It is also assumed that similar bonding exists in the molecule 5-(H_3Si)$C_5H_4CH_3$.

The −50° spectrum of 5-(silyl)methylcyclopentadiene (1,2-isomer mixture) is indeed a superimposition of spectra[5] consistent with instantaneous structures (II') and (III') since proton spin-decoupling experiments clearly established the identity of each. It is assumed that $[\mathrm{III}']_{\text{initial}} = [\mathrm{II}']_{\text{initial}}$ since no equilibration of the isomers was permitted in the preparation of the sample. From Table 2, $J_{\mathrm{III}'}(\mathrm{Si{-}H}) = J_{\mathrm{II}'}(\mathrm{Si{-}H}) =$ 3.1 Hz. At −42° (spectrum not pictured) the upfield silyl doublet broadens (moves downfield) first. At −33° the partial disappearance of the upfield silyl doublet and the broadening of the upfield methyl triplet suggest that (1) the upfield silyl doublet belongs to isomer (III′) and (2) metal migration appears to occur more rapidly for isomer (III′). At −25° the total collapse of the upfield methyl resonance is quite obvious and supports the qualitative argument explaining the behavior of the upfield silyl doublet at the lower temperatures. Thus for this non-degenerate rearrangement isomer (III′) appears less stable and rearranges before isomer (II′). Davison and Rakita studied the variable temperature behavior of 5-[$(CH_3)_3Si$]-$C_5H_4CH_3$[6] and observed complex PMR spectra. There was little mention of additional peaks appearing at elevated temperatures especially in the τ 10 region. They assigned the low-temperature spectrum to a mixture of the three isomers analogous to (I′), (II′), (III′) rearranging slowly. In contrast to their assignment and our preliminary result[2], we are able to conclude due to the absence of a 5-methyl proton signal [$\delta \sim 1.6$ (ref. 9)–1.0 (ref. 14,16)] that the limiting low-temperature spectrum of 5-$(H_3Si)C_5H_4CH_3$ is clearly due to only structures (II′) and (III′) rearranging at a reduced rate, *viz.*:



The same conclusion seems to be applicable to the methylcyclopentadienyltrimethyl compounds[6,8] of silicon, germanium and tin as well as 5-$(H_3Ge)C_5H_4CH_3$[26]. At higher temperatures proton rearrangement takes place producing six possible isomers.



Those isomers with the methyl group situated at the 5-position and the silyl group attached at a vinyl site have been omitted from the above schemes since the 5-methyl isomers of dimethylcyclopentadiene are known to be the less stable structures at elevated temperatures[14].

TABLE 3

CHEMICAL SHIFTS (ppm) OF MONO- AND DIMETHYLCYCLOPENTADIENES[14]

Compound	δ(*tert-CH*$_3$)	δ(*vinyl-CH*$_3$)	δ(*tert-H*)	δ(*vinyl-H*)
1-methyl		1.96 (doublet)	2.70	6.40–6.00
2-methyl		1.95 (multiplet)	2.80	6.31–5.90
5-methyl	1.08 (doublet)			6.35
5,1-dimethyl	1.05 (doublet)	1.90 (doublet)	2.80	6.40–5.90
5,2-dimethyl	1.07 (doublet)	1.90 (multiplet)	2.80	6.40–5.90
5,5-dimethyl	1.38 (singlet)			6.26

ACKNOWLEDGEMENTS

This research was supported by the Petroleum Research Fund administered by the American Chemical Society. Special appreciation is extended to Dr. Pat Flanigan (Continental Oil, Ponca City, Okla.) for obtaining initial low-temperature spectra and Mr. Stan O. Sigle (Chemistry Dept., Oklahoma State Univ., Stillwater, Okla.) for producing the spectra appearing in this paper. Enjay Chemical Company supplied generous amounts of dicyclopentadiene and methylcyclopentadiene dimer.

REFERENCES

1 A. P. Hagen and P. J. Russo, *Inorg. Nucl. Chem. Letters*, 6 (1970) 507.
2 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 2 (1956) 32.
3 H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, 4 (1965) 313.
4 F. A. Cotton, *Accounts Chem. Res.*, 1 (1968) 257 and ref. therein.
5 Yu. A. Ustynyuk, A. V. Kisin and A. A. Zenkin, *J. Organometal. Chem.*, 37 (1972) 101 and ref. therein.
6 A. Davison and P. E. Rakita, *J. Amer. Chem. Soc.*, 90 (1968) 4479.
7 P. E. Rakita and A. Davison, *Inorg. Chem.*, 8 (1969) 1164.
8 A. Davison and P. E. Rakita, *Inorg. Chem.*, 9 (1970) 289.
9 A. Davison and P. E. Rakita, *J. Organometal. Chem.*, 23 (1970) 407.
10 P. J. Russo, *Ph.D. Dissertation*, University of Oklahoma (1970).
11 S. McLean and P. Haynes, *Can. J. Chem.*, 41 (1963) 1231.
12 *Tech. Data Sheet and Chemical Spec. Sheet*, Enjay Chemical Company.
13 L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 9 (1958) 86.
14 S. McLean and P. Haynes, *Tetrahedron*, 21 (1965) 2313.
15 S. McLean and P. Haynes, *Tetrahedron*, 21 (1965) 2329.
16 C. F. Wilcox, Jr. and M. Mesinov, *J. Org. Chem.*, 25 (1960) 1841.
17 V. A. Mironov, E. V. Sobolev and A. N. Elizarova, *Tetrahedron*, 19 (1963) 1939.
18 A. J. Ashe, III, *J. Amer. Chem. Soc.*, 92 (1970) 1233.
19 K. W. Egger and T. L. James, *J. Organometal. Chem.*, 26 (1971) 335.
20 N. M. Sergeyev, G. I. Avramenko, A. V. Kisin, V. A. Korenevsky and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 32 (1971) 55.
21 N. M. Sergeyev, G. I. Avramenko and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 22 (1970) 63.
22 G. I. Avramenko, N. M. Sergeyev and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 37 (1972) 89.
23 G. A. Shchembelov and Yu. A. Ustynyuk, *Doklady Akad. Nauk SSSR*, 173 (1967) 847; *Proc. Acad. Sci. U.S.S.R.*, 173 (1967) 323.
24 V. A. Mironov, E. V. Sobolev and A. N. Elizarova, *Doklady Akad. Nauk SSSR*, 146 (1962) 1098; *Proc. Acad. Sci. U.S.S.R.*, 146 (1962) 898.
25 N. M. Sergeyev, G. I. Avramenko and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 22 (1970) 79; (Erratum) *ibid.*, 24 (1970) C39.
26 S. R. Stobart, *J. Organometal. Chem.*, 43 (1972) C26.