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Fluxional Behavior of Cyclopentadienyl, Methylcyclopentadienyl, and Pentamethylcyclopentadienyl Compounds of Silicon, Germanium, and Tin

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Received August 14, 1969

The variable-temperature proton magnetic resonance spectra of cyclopentadienyl, methylcyclopentadienyl, and pentamethylcyclopentadienyl compounds of the group IV metals have been investigated and they have been shown to be fluxional molecules. The infrared spectra of the cyclopentadienyltrimethyl compounds of silicon, germanium, and tin (in the 3000-cm^{-1} region) provide a clear diagnostic test for the identification of a σ-cyclopentadienyl group.

Introduction

In a previous communication[1] we reported some initial observations on several methyl-substituted σ-cyclopentadiene compounds of silicon and tin. Contrary to earlier reports it was shown that ring substitution does not significantly alter the fluxional character of the metal-to-ring bond. We report here the details of the studies on the silicon and tin compounds, as well as the corresponding germanium compounds which, as expected, exhibit intermediate behavior. This represents the first systematic study of fluxional behavior in a closely related series of substituted σ-cyclopentadienylmetal compounds.

Experimental Section

General Data.—Unless otherwise indicated, all manipulations were carried out in an atmosphere of dry nitrogen or *in vacuo*. Infrared spectra were recorded using liquid films between NaCl plates on a Perkin-Elmer 337 spectrometer. Nmr spectra were obtained at 60 and 100 MHz utilizing spectrometers (A-60, HA-100) by Varian Associates equipped with variable-temperature probes. Temperature calibrations were made with methanol or ethylene glycol. High-temperature spectra were recorded on neat liquids; those at low temperature, in CS_2 or $CDCl_3$ solution. Benzene was used as an internal reference.

Preparation of Cyclopentadienyltrimethylsilane.—A modification to the published procedure[2] was used to obtain $(CH_3)_3SiC_5H_5$. To avoid contamination by the isomers containing vinyl trimethylsilyl groups, samples for spectral studies were freshly prepared or distilled immediately prior to use. Even at −15° isomerization was significant after several days, as evidenced by the appearance of extraneous peaks in the proton nmr in the trimethylsilyl, olefin, and tertiary proton region.[3]

Preparation of Methylcyclopentadienyltrimethylsilane.—To a solution of 65 ml (0.104 mol) of *n*-butyllithium in hexane (1.6 *M*) and 500 ml of anhydrous ether was added dropwise with stirring 10 ml (0.10 mol) of methylcyclopentadiene monomer (from the 70–75° fraction obtained by distilling freshly cracked methylcyclopentadiene monomer[4]). The resulting white suspension was treated dropwise with 13 ml (0.101 mol) of chlorotrimethylsilane in 20 ml of ether and the mixture was refluxed for 12 hr. Lithium chloride was removed by filtration in air and the ether and hexane were distilled at atmospheric pressure followed by vacuum distillation at 52° (20 mm). Fractionation on a Nester-Faust annular Teflon spinning-band column (7200 rpm) gave a small forerun of $(CH_3)_3SiC_5H_5$ at 42–44° (16 mm), identified by its proton nmr spectrum. The product was collected at 54–56° (16 mm) and could be kept without apparent decomposition for several days at −15°. Decomposition was evidenced by the appearance in the nmr of multiplets at τ 3.3, 3.8, 7.1, and 7.2.

The infrared spectrum showed 3094 (m), 3060 (m), 3045 (m), 2955 (s), 2919 (m), 2892 (m), 2860 (m), 2730 (w), 1585 (m), 1488 (w), 1440 (m), 1400 (w), 1314 (w, br), 1290 (w), 1262 (w, sh), 1250 (vs), 1212 (w), 1194 (m), 1146 (w), 1105 (w), 1082 (w), 1036 (w), 1017 (m), 988 (s), 971 (s), 954 (s), 915 (m), 903 (m), 866 (vs), 834 (vs, br), 825 (sh), 812 (w), 795 (vs), 750 (s), 709 (s), 693 (m), 680 (sh), 611 (m), and 584 (m) cm^{-1}.

Anal. Calcd for $C_9H_{16}Si$: C, 70.97; H, 10.59. Found: C, 70.44; H, 10.68.

Preparation of Cyclopentadienyltrimethylgermane.—A solution of 13.5 ml (0.02 mol) of *n*-butyllithium (1.6 *M*) in hexane and 40 ml of anhydrous ether chilled in an ice bath was treated dropwise with 1.65 ml (0.02 mol) of freshly cracked cyclopentadiene monomer in 10 ml of ether over 45 min. The resulting white suspension then was allowed to warm to room temperature with stirring. To this was added over 1 hr 2.46 ml (0.02 mol) of $(CH_3)_3GeCl$ in 10 ml of ether and the mixture was refluxed for 6 hr. The LiCl was removed by filtration and the ether–hexane was removed by distillation at atmospheric pressure. Vacuum distillation yielded the product at 47° (14 mm) which was redistilled at 48° (13.5 mm); $n^{28}{}_{\mathrm{D}}$ 1.4805. The infrared spectrum showed 3110 (w), 3090 (s), 3070 (s), 2975 (vs), 2910 (vs), 2870 (w), 2855 (w), 2800 (w), 1800 (w), 1617 (w), 1458 (s), 1402 (m), 1378 (m), 1295 (w), 1238 (vs), 1110 (w), 1087 (m), 1015 (w), 995 (w), 960 (m), 944 (vs), 900 (m), 826 (vs), 817 (vs), 795 (w, sh), 770 (w), 748 (w, sh), 729 (vs), 650 (vs), 597 (s), and 561 (m) cm^{-1}.

Anal. Calcd for $C_8H_{14}Ge$: C, 52.57; H, 7.72. Found: C, 51.96; H, 7.50.

Preparation of Methylcyclopentadienyltrimethylgermane.—The compound $(CH_3)_3GeC_5H_4CH_3$ was prepared in a similar manner to cyclopentadienyltrimethylgermane with the precaution of fractionating the methylcyclopentadiene monomer to remove cyclopentadiene.[4] The product was obtained as a colorless liquid, bp 58–59° (10 mm), $n^{23}{}_{\mathrm{D}}$ 1.5605. The infrared spectrum showed 3093 (m), 3060 (m, br), 2975 (vs), 2913 (vs), 2865 (w), 1798 (w), 1613 (w), 1585 (m), 1481 (m), 1445 (m), 1406 (m), 1373 (m), 1293 (w), 1237 (vs), 1199 (m), 1155 (m), 1100 (w), 1079 (w), 1032 (w), 1014 (w), 953 (vs), 900 (m), 820 (vs, br), 795 (m), 748 (m), 720 (m), 663 (s), 597 (s, br), and 562 (m) cm^{-1}.

Anal. Calcd for $C_9H_{16}Ge$: C, 54.92; H, 8.20. Found: C, 54.19; H, 8.11.

Preparation of Pentamethylcyclopentadienyltrimethylgermane.—Pentamethylcyclopentadienyllithium was prepared by adding a solution of 2.72 g (0.02 mol) of pentamethylcyclopentadiene[5,6] in 25 ml of ether to 13.5 ml (0.02 mol) of butyllithium (1.6 *M*) in hexane and 50 ml of ether at 0° with stirring. The mixture was then allowed to warm to room temperature. To the re-

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(1) A. Davison and P. E. Rakita, *J. Am. Chem. Soc.*, **90**, 4479 (1968).

(2) G. Wilkinson, and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956).

(3) The isomerization (by hydrogen migration) of cyclopentadienyltrimethylsilane has been carefully studied and shown to be 10^6 times slower than the trimethylsilyl migration: A. J. Ashe, personal communication.

(4) G. Wilkinson and L. T. Reynolds, *J. Inorg. Nucl. Chem.*, **9**, 86 (1959).

(5) L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960).

(6) R. B. King and M. Bisnette, *J. Organometal. Chem.* (Amsterdam), **8**, 287 (1967).

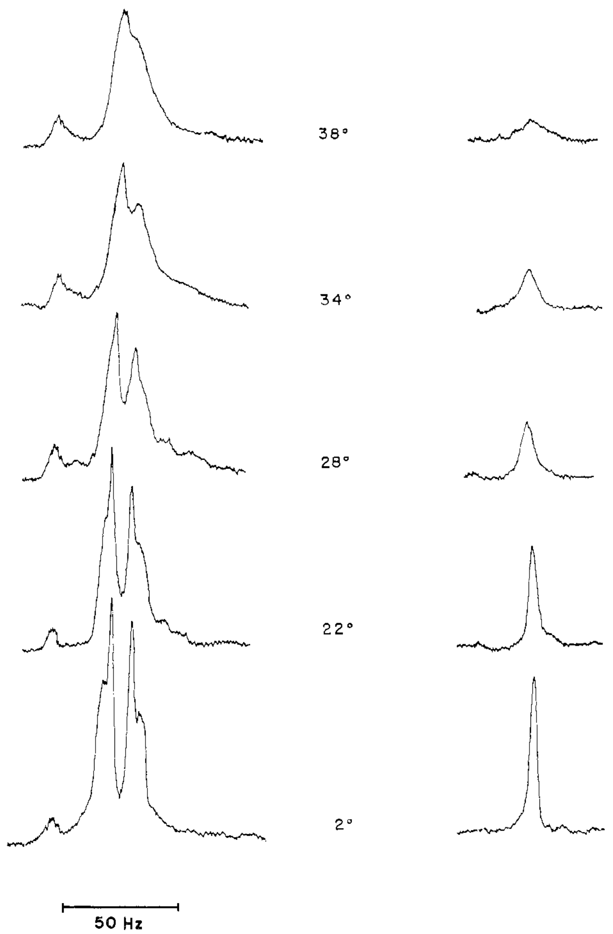

Figure 1.—The proton magnetic resonance spectra of cyclopentadienyltrimethylsilane (100 MHz) at several temperatures in the regions τ 3–4 and 6.7 (see text).

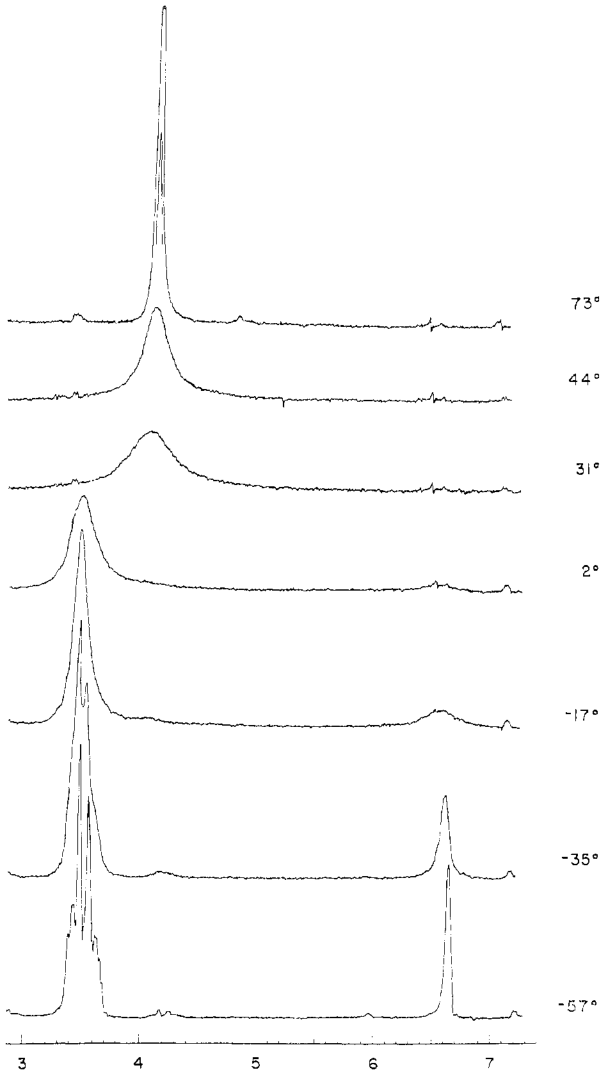

Figure 2.—The proton magnetic resonance spectra of cyclopentadienyltrimethylgermane, $(CH_3)_3GeC_5H_5$, in the region τ 3–7 at several temperatures.

sultant white suspension was added 2.5 ml (0.02 mol) of chlorotrimethylgermane in 15 ml of ether and the mixture was stirred at reflux for 8 hr. Lithium chloride was removed by filtration and the ether and hexane were distilled at atmospheric pressure. Vacuum distillation yielded a brief forerun followed by the product, a golden yellow liquid, at 74° (2.1 mm). The infrared spectrum showed 2978 (vs), 2915 (vs), 2865 (m), 2737 (w), 1702 (m), 1650 (w), 1625 (w), 1550 (w), 1520 (w), 1440 (s), 1401 (w), 1375 (s), 1355 (sh), 1240 (sh), and 1232 (s) cm^{-1}.

Anal. Calcd for $C_{13}H_{24}Ge$: C, 61.73; H, 9.56. Found: C, 62.02; H, 9.34.

Preparation of Cyclopentadienyltrimethylstannane.—The compound was obtained by a modification of the published synthesis[7] using cyclopentadienyllithium as described above. The product was obtained as a pale yellow liquid at 54° (2.9 mm); $n^{26}{}_D$ 1.5189. The infrared spectrum showed 3065 (sh), 3052 (s), 3042 (m, sh), 3014 (vw), 2958 (sh), 2935 (vs), 2890 (vs), 2855 (sh), 2370 (w), 1820 (w), 1803 (w), 1721 (w), 1705 (w), 1625 (w), 1438 (s), 1408 (w), 1385 (m), 1361 (m), 1292 (w), 1232 (w), 1185 (s), 1130 (w), 1108 (w), 1083 (s), 1029 (m), 989 (m), 971 (s), 913 (sh), 871 (vs, br), 824 (m), 768 (vvs), 714 (s), 665 (m), and 636 (s) cm^{-1}.

Preparation of Methylcyclopentadienyltrimethylstannane.—The compound $(CH_3)_3SnC_5H_4CH_3$ was prepared in a similar manner to cyclopentadienyltrimethylstannane, fractionating the methylcyclopentadiene monomer as in the analogous silane and germane synthesis. The product was obtained as a pale yellow liquid at 50° (2.3 mm); $n^{22}{}_D$ **1.5283**. The infrared spectrum showed 3081 (vs), 3060 (vs), 2922 (vvs), 2858 (vs), 2730 (m), 2354 (m), 1778 (m), 1717 (m), 1689 (m), 1603 (m), 1566 (s), 1558 (m, sh), 1480 (vs), 1375 (s), 1309 (s), 1285 (w), 1227 (m), 1210 (s), 1189 (vs), 1162 (s), 1099 (m), 1080 (m), 1033 (m), 1020 (m), 994 (m), 983 (s), 967 (s), 900 (vvs, br), 750 (vvs, br), 645 (s), 620 (m), and 597 (s) cm^{-1}.

Anal. Calcd for $C_9H_{16}Sn$: C, 44.50; H, 6.64. Found: C, 44.64; H, 6.71.

Preparation of Pentamethylcyclopentadienyltrimethylstannane.—The compound $(CH_3)_3SnC_5(CH_3)_5$ was prepared in a manner similar to that of the analogous germanium compound. The product was collected as a yellow liquid at 92° (2 mm). The infrared spectrum showed 3620 (w), 2958 (s), 2920 (vs), 2860 (s), 2730 (w), 2345 (w), 1680 (w), 1605 (w), 1445 (m), 1370 (m), 1258 (m), and 1240 (w) cm^{-1}.

Anal. Calcd for $C_{13}H_{24}Sn$: C, 52.55; H, 8.09. Found: C, 51.74, 52.74; H, 7.89, 8.18.

Results

Proton Magnetic Resonance Spectra.—The variable-temperature nmr spectrum of $(CH_3)_3SiC_5H_5$ at 100 MHz (Figure 1) exhibits the resolved AA′BB′ part of an AA′BB′X pattern for the four olefinic protons at temperatures below 20°. On warming, the upfield portion of the signal collapses more rapidly.

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[7] H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.* (Amsterdam), **1**, 313 (1964).

TABLE I
NUCLEAR MAGNETIC RESONANCE DATA[a]

	H_1	$H_{2,5}$	$H_{3,4}$	CH_3	$(CH_3)_3M$	Temp, °C	Solvent
$(CH_3)_3SiC_5H_5$	6.71	~3.4	~3.4	...	10.01	−10	Neat
	4.13	4.13	4.13	...	10.01	+130	Neat
$(CH_3)_3SiC_5H_4CH_3$	6.9, 7.0[b]	3.5–4.0	3.5–4.0	8.00	10.10	−42	Neat
	...	4.46[c]	5.10[c]	7.96	10.04	138	Neat
$(CH_3)_3GeC_5H_5$	6.53	~3.5	~3.5	...	9.95	−57	Neat
	4.13	4.13	4.13	...	9.90	93	Neat
$(CH_3)_3GeC_5H_4CH_3$	6.66, 6.82[b]	3.6–4.0	3.6–4.0	7.94	9.93	−40	Neat
	...	4.30[c]	4.68[c]	7.95	9.88	+105	Neat
$(CH_3)_3GeC_5(CH_3)_5$	...	...	...	8.23, 8.80[d]	10.03[d]	−54	CS_2
	...	...	...	8.31	10.01	+36	Neat
$(CH_3)_3SnC_5H_5$	4.06[e] (22.5)	4.06[e] (22.5)	4.06[e] (22.5)	...	9.94[e] (51.0, 53.5)	31, −80	CS_2
$(CH_3)_3SnC_5H_4CH_3$	...	4.34[c]	4.47[c]	7.96[e] (10.5)	10.01[e] (50.5, 53.0)	31, −85	CS_2
$(CH_3)_3SnC_5(CH_3)_5$	...	...	...	8.23[e] (19.9)	10.04[e] (48.1, 50.3)	30, −100	CS_2

[a] Chemical shifts in τ units. [b] Positions of methine (tertiary) proton signals at slow-exchange limits for $(CH_3)_3MC_5H_4CH_3$ compounds. [c] Assignment of these signals to adjacent (to ring methyl) or nonadjacent protons is not established. [d] Signals at τ 8.31, 8.80, and 10.16 in $CDCl_3$ (−60°). [e] Values of ^{117}Sn–H, ^{119}Sn–H coupling costants inhertz in parentheses.

In other respects the reversible spectral changes occur as described by Fritz.[8]

Samples of $(CH_3)_3SiC_5H_5$ gave rise to several additional resonances in the trimethylsilyl, olefin, and tertiary proton regions which did not show reversible temperature-dependent behavior. The intensity of these extra peaks depended on the age of the sample. Fresh, carefully distilled samples showed little or no evidence of these extraneous signals but they were present in samples kept at room temperature for more than a few hours. Heating the samples accelerated the formation of these peaks.

Cyclopentadienyltrimethylgermane showed the same variable-temperature behavior (Figure 2) as the corresponding silane. At +93° two peaks are observed at τ 4.13 and 9.95 in the ratio 5:9. At lower temperatures the low-field resonance first broadens and then changes to two signals at τ 6.53 and 3.5 in the ratio 1:4, the latter being the AA′BB′ part of an AA′BB′X pattern. The slow exchange limit is reached at −57°.

Cyclopentadienyltrimethyltin has a single sharp resonance at τ 4.06 for all five ring hydrogens at temperatures as low as −60°. Below this temperature some broadening of the signal is observed but resonances due to separate cyclopentadienyl proton environments could not be obtained. At all temperatures studied satellites arising from tin to proton coupling were observed (ring protons, $|J_{^{117}Sn}, J_{^{119}Sn}|$ = 22.5 Hz unresolved; trimethylstannyl protons, τ 9.94, $|J_{^{117}Sn-H}|$ = 51.5 Hz and $|J_{^{119}Sn-H}|$ = 53.4 Hz).

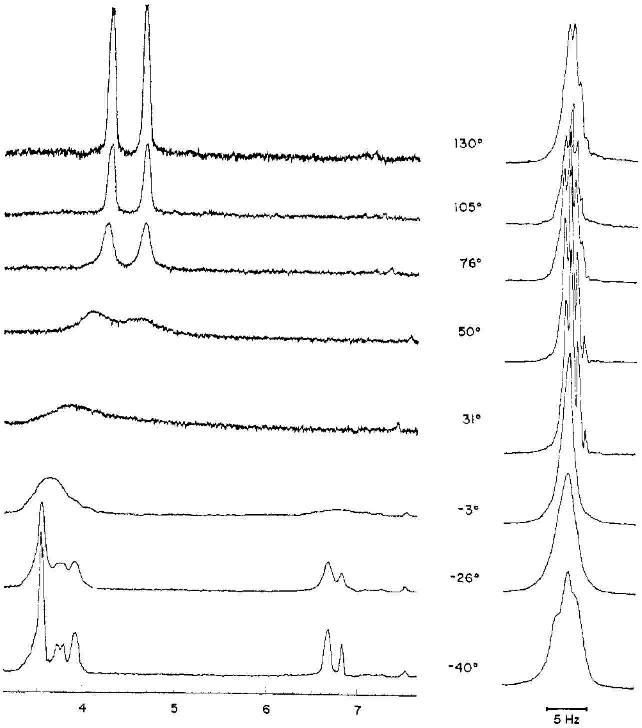

Figure 3.—The proton magnetic resonance spectra of methylcyclopentadienyltrimethylgermane, $(CH_3)_3GeC_5H_4CH_3$, at several temperatures. The ring methyl signal at τ 8 is given at the right with an expanded scale.

The variable-temperature nmr spectra of methylcyclopentadienyltrimethylsilane and -stannane have been published previously by us.[1] The pertinent data are presented in Table I. Spectra for the corresponding germanium compound are given in Figure 3. In the fast-exchange limit at temperatures above +105° there are four resonances at τ 4.30, 4.68, 7.95, and 9.88 in the area ratio 2:2:3:9. Decoupling studies at +130° indicate that the signal at τ 7.95, an unsymmetrical triplet, is coupled to the protons at τ 4.68 but not appreciably coupled to those at τ 4.30. The changes observed as the temperature is decreased closely parallel those in the analogous silane. For the compound $(CH_3)_3SnC_5H_4CH_3$ significant broadening of the fast-exchange spectrum occurs at temperatures below −60°.[1]

Pentamethylcyclopentadienyltrimethylgermane, $(CH_3)_3GeC_5(CH_3)_5$, displays two peaks above 0° at τ 8.31 and 10.03 in the area ratio 5:3 (Figure 4). At lower temperatures the resonance at τ 8.31 broadens and below −13° two peaks are seen in the ratio 4:1 at τ 8.23 and 8.80, respectively. The slow-exchange limit is reached at −54°. No marked solvent depen-

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(8) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.* (Amsterdam), **4**, 313 (1965).

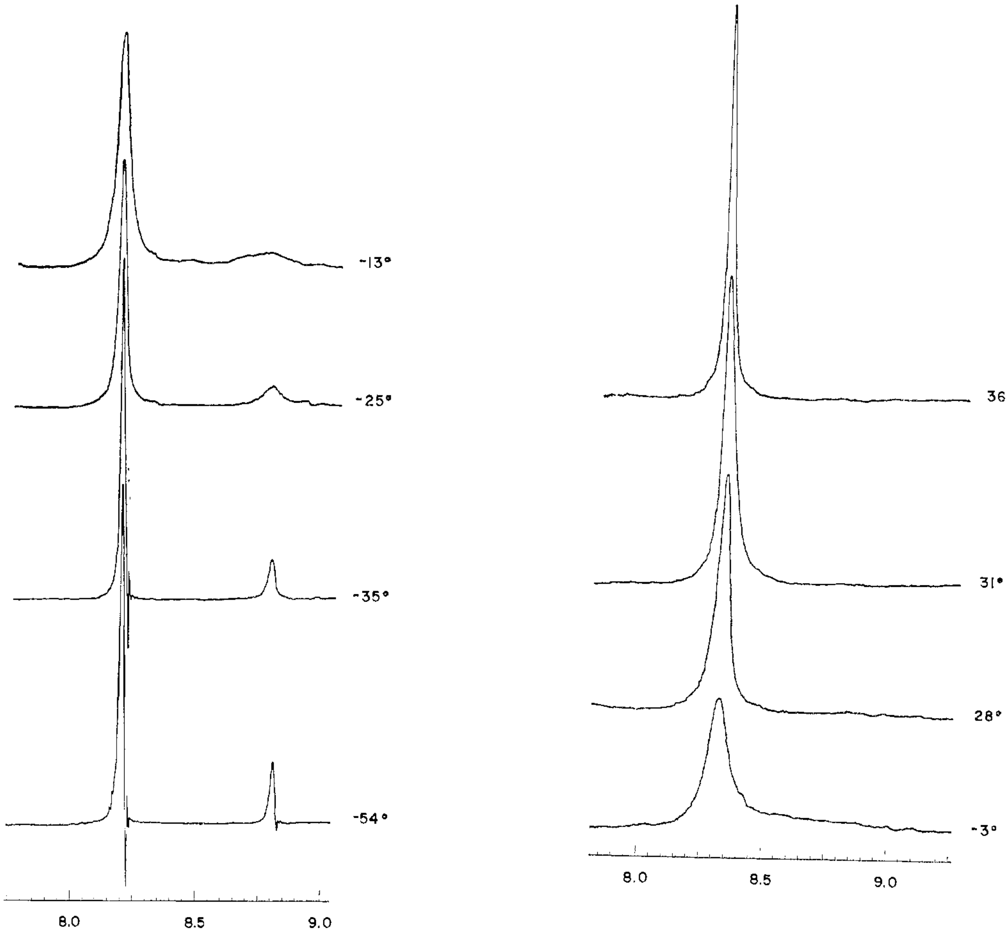

Figure 4.—The proton magnetic resonance spectra of pentamethylcyclopentadienyltrimethylgermane in the region τ 8–9 at several temperatures.

dence was noticed for spectra recorded in both CS_2 and $CDCl_3$ solution.

The tin compound $(CH_3)_3SnC_5(CH_3)_5$, as described previously,[1] shows only broadening of the two resonances at τ 8.19 and 10.03 even at −100°.

Infrared Spectra.—All three cyclopentadienyltrimethyl compounds show several absorptions in the infrared spectra above 3000 cm^{-1} (Figure 5) in the region characteristic of olefin–hydrogen stretching. Bands were observed for $(CH_3)_3SiC_5H_5$ at 3121, 3094, and 3075 cm^{-1}. The corresponding germanium and tin compounds had absorptions at 3110, 3090, and 3070 cm^{-1} and at 3065, 3054, 3042, and 3014 cm^{-1}, respectively.

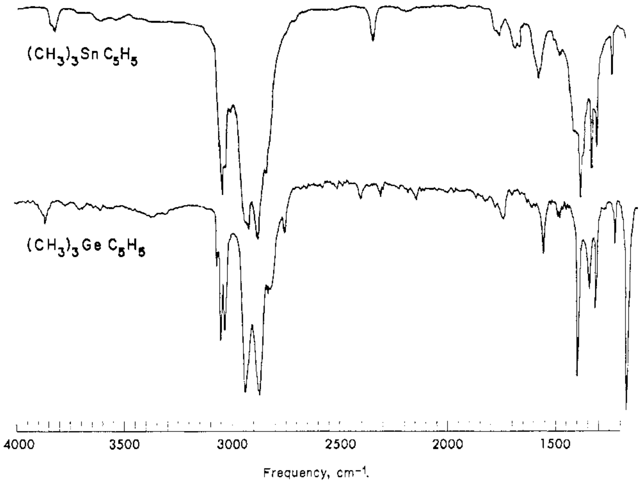

Figure 5.—The infrared spectra of cyclopentadienyltrimethylgermane and -stannane in the region 4000–1200 cm^{-1}.

Discussion

The variable-temperature proton nmr spectra of $(CH_3)_3SiC_5H_5$ at 100 MHz show that as the temperature is increased, the upfield portion of the AA′BB′ pattern for the four olefin protons collapses more rapidly. From these observations it can be concluded[9] that the rearrangement is nondissociative since a dissociation–recombination process would result in a symmetric collapse of all the proton signals.[10] For the same reason the process must be predominantly 1,2 or 1,3 shifts since a random process would also give rise to a symmetric collapse.[11] The choice between the two alternative mechanisms depends on the assignment of the two olefinic signals to the two types of olefin protons in the σ-cyclopentadienyl ring. If we use the ABX pattern in the spectrum of indenyltrimethylsilane[12] as a model system (for which the high-field portion of

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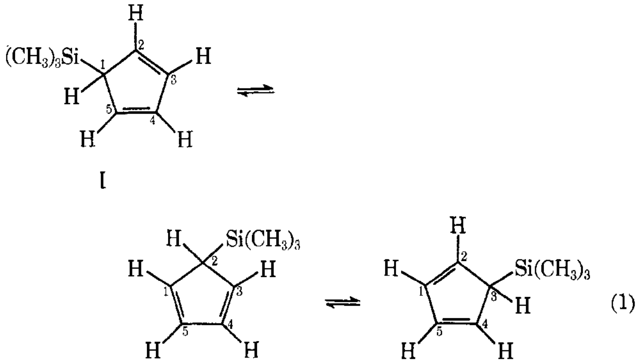
[9] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

[10] The presence of tin satellites in the fast-exchange spectrum offers convincing evidence for the *intramolecular* rearrangement of the stannanes.

[11] G. M. Whitesides and J. S. Fleming, *ibid.*, **89**, 2855 (1967).

[12] P. E. Rakita and A. Davison, *Inorg. Chem.*, **8**, 1164 (1969).

the olefinic resonances is unambiguously assigned to H(2)), then we must conclude that the rearrangement in cyclopentadienyltrimethylsilane occurs by 1,2 jumps (reaction 1). Our results on this and all other[12,13] fluxional molecules of group IVa metals can be explained by a 1,2-shift mechanism.

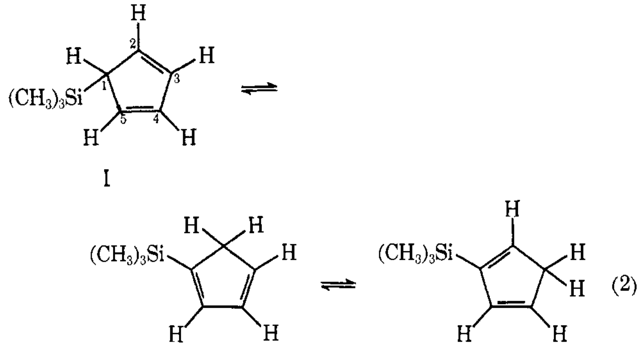


I

II III

(1)

An alternative temperature-dependent rearrangement process has been postulated[14] to account for the observed spectral changes. This process, illustrated in reaction 2, corresponds to a series of 1,2 (or 1,3) proton shifts around the C_5 ring. Evidence for this comes from the isolation of Diels–Alder adducts obtained from both structures I and V.[14]



I

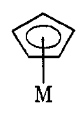
IV V

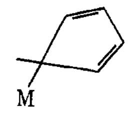
(2)

Such an explanation is not in agreement with our experimental results, however. The proton migration, which is undoubtedly responsible for the vinylsilane Diels–Alder product, cannot be sufficiently rapid[15] to account for the reversible-temperature nmr results. Moreover for $(CH_3)_3SiC_5H_4CH_3$ proton migration would give rise to only one ring hydrogen resonance at the fast-exchange limit whereas two peaks of equal intensity are obtained, as predicted from the $(CH_3)_3Si$ migration mechanism. In addition, lifetimes for proton migration in cyclopentadiene and methylcyclopentadiene vary from several minutes to a few hours[15] and a comparable value would be expected for the trimethylsilyl compound. It is likely then that these two processes occur simultaneously for $(CH_3)_3SiC_5H_5$ and $(CH_3)_3SiC_5H_4CH_3$, albeit at considerably different rates:[3,16] (1) the rapid intramolecular rearrangement which gives rise to the reversible nmr spectrum (reaction 1) and (2) the relatively slow formation of isomeric structures which do not have temperature-dependent nmr spectra (reaction 2). It is compounds like IV and V and the corresponding ones for $(CH_3)_3SiC_5H_4CH_3$ which are responsible for the additional resonances in the spectra of $(CH_3)_3SiC_5H_5$ and $(CH_3)_3SiC_5H_4CH_3$, first noted by Strohmeier[17] and postulated by Fritz and Kreiter[8] to be due to dimeric structures. Facile hydrogen migration does not appear to take place in the case of the germanium or tin compounds, although additional signals appear in the proton nmr spectra of samples stored for several months at room temperature.

The pentamethylcyclopentadiene compounds provide examples of fluxional molecules which cannot rearrange by proton migration. The trimethylstannyl[1] and trimethylgermyl derivatives were prepared and the latter was studied through the full range of fluxional nmr behavior. At the slow-exchange limit the two types of olefinic ring methyl groups exhibit no measurable difference in chemical shifts, appearing as a single peak of relative area 12 in both CS_2 and $CDCl_3$. This contrasts with the recently published result[18] that bis(pentamethylcyclopentadienyl)mercury displays two olefinic ring methyl signals separated by 0.08 ppm.

The infrared spectra in the C–H stretching region allow a clear choice to be made between σ- and π-bonded cyclopentadiene rings. Because of the short time scale for infrared spectroscopy (10^{-13} sec),[19] the ir spectra of any molecule which is fluxional on the proton nmr time scale ($\sim 10^{-3}$ sec) will be characteristic of the instantaneous (slow-exchange) structure. Group theoretical analysis of the two structures VI and VII, based on the symmetries of the metal–cyclopentadiene moiety, gives rise to the representations indicated.





Symmetry	C_{5v}	C_s
$\Gamma_{\nu(C-H)}$	$A_1 + E_1 + E_2$	$3A' + 2A''$
Ir active	$A_1 + E_1$	$3A' + 2A''$

For the symmetrically π bonded cyclopentadiene ring only two bands are allowed in the infrared spectrum in the C–H stretching region corresponding to the totally symmetric A_1 mode and the doubly degenerate E_1 mode. The A_1 stretch, furthermore, is polarized along the fivefold axis while the C–H bond is essentially perpendicular to this axis. In consequence, the A_1 mode would be expected to be weak, if observed at

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[13] The molecule 1,2-bis(trimethylsilyl)indene undergoes a rapid intramolecular rearrangement which does not occur by 1,3 jumps: A. Davison and P. E. Rakita, submitted for publication.

[14] C. S. Kraihanzel and M. L. Losee, *J. Am. Chem. Soc.*, **90**, 4701 (1968).

[15] The migratory aptitudes of protons or methyl groups in cyclopentadienes and indenes is well documented: J. W. DeHaan and H. Kloosterziel, *Rec. Trav. Chim.*, **87**, 298 (1968); S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965); W. R. Roth, *Tetrahedron Letters*, 1009 (1964); L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Am. Chem. Soc.*, **91**, 1578 (1969).

[16] G. A. Shchembelov amd Yu. H. Ustynyuk, *Dokl. Akad. Nauk SSSR*, **173**, 847 (1967).

[17] W. Strohmeier and R. M. Lemmon, *Z. Naturforsch.*, **14a**, 109 (1959).

[18] B. Floris, G. Illuminati, and G. Ortaggi, *Chem. Commun.*, 492 (1969).

[19] E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

all.[20] On the other hand all five C–H stretching modes for the σ-C_5H_5 group of C_s symmetry are infrared active and the four associated with the olefinic hydrogens would be expected to occur at frequencies greater than 3000 cm^{-1}. Thus the 3000-cm^{-1} region offers a clear and simple choice to be made regarding the mode of bonding of C_5H_5 rings in these compounds, a point overlooked by Fritz[21] in his review of infrared spectra of metal-C_nH_n systems.

The infrared spectra of $(CH_3)_3SiC_5H_5$, $(CH_3)_3GeC_5H_5$, and $(CH_3)_3SnC_5H_5$ (Figure 5) all show several absorptions above 3000 cm^{-1}, consistent *only* with the σ-cyclopentadienyl geometry. We feel justified in concluding that $(CH_3)_3SnC_5H_5$ has a fluxional σ-bonded C_5H_5 ring but that the barrier to migration of the $(CH_3)_3Sn$ group around the ring is so low that even at $-80°$ only one proton resonance can be observed. The suggestion by others[22,23] that the C_5H_5 rings in tin(IV)–cyclopentadiene compounds are π bonded has no basis in experimental fact.

Acknowledgments.—We thank the Alfred P. Sloan Foundation for a fellowship (A. D.), 1967–1969, and the National Science Foundation for a predoctoral fellowship (P. E. R.), 1966–1968, and Grant GP 6672. We also wish to thank Dr. Arthur J. Ashe, III, for informing us of his results in advance of publication.

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The Infrared Spectrum of the 3,5-Dimethyl-1,2-dithiolylium(I) Cation

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Received June 23, 1969

The infrared spectrum of bis(3,5-dimethyl-1,2-dithiolylium) tetrachloroferrate(II) has been recorded from 1700 to 300 cm^{-1}. Assignments for the in-plane vibrations of the cation were obtained by a normal coordinate analysis. A planar and cyclic structure adopted for the 3,5-dimethyl-1,2-diselenolylium(I) cation permitted vibrational assignments by the same normal-coordinate treatment. The nature of bonding in cyclic disulfides and diselenides is discussed.

Introduction

Under conditions which have favored the formation of dithioacetylacetone chelates[1] from ordinary metal salts, the reaction of iron(III) produced a compound[2] whose properties and structure were completely different. This compound was identified as bis(3,5-dimethyl-1,2-dithiolylium) tetrachloroferrate(II) by X-ray diffraction[3] and consists of planar, five-membered, cyclic disulfide cations and an anionic iron chloride species. In aqueous solution the cation has been reduced to a dithioacetylacetone species whose brief existence could only be recognized by the *in situ* formation of dithioacetylacetone chelates.[4] The disulfide cation may, therefore, be considered as a potential source of the unstable ligand and dithioacetylacetonates which have eluded previous synthetic attempts.

Although infrared spectra have been reported for various salts containing the disulfide cation, assignment of the frequencies was considered only tentative.[5,6] A normal-coordinate analysis of the cation has now been completed with good agreement between calculated and observed frequencies. Assignments for in-plane vibrations were accordingly made. The results of these calculations are reported here.

Experimental Section

Preparation of $(C_5H_7S_2)_2FeCl_4$.—Hydrogen chloride gas was bubbled through a solution of 18 g of anhydrous ferric chloride and 20 ml of acetylacetone in 300 ml of ethanol cooled to $-10°$. After 1 hr the hydrogen chloride was replaced by hydrogen sulfide and the bubbling was continued 1 hr. Dark red-violet crystals precipitated after dilution with 300 ml of anhydrous ether. The product was washed with ether and dried *in vacuo*. *Anal.* Calcd for $C_{10}H_{14}Cl_4S_4Fe$: Fe, 12.14. Found: Fe, 11.85.

Spectral Measurements

The spectrum was recorded with a Perkin-Elmer 521 infrared spectrophotometer over the range 1700–300 cm^{-1}. Potassium bromide and cesium bromide pellets and a Nujol mull were prepared. Calibration of frequency readings was performed with polystyrene film and water vapor.

Method of Calculation

The point symmetry of the planar 1,2-dithiolylium cation is C_{2v} if the methyl groups are considered as point masses as shown in Figure 1. This simplification

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