

have been formulated as $\text{Co}^{\text{III}}\text{O}_2^-$ species.⁶⁸ Similarly, an $\text{Fe}^{\text{III}}\text{O}_2^-$ formulation has been invoked to describe the bonding of O_2 to divalent iron.⁶⁹ The bonding of O_2 is proposed to involve transfer of an electron from the O_2 moiety, formally oxidizing the iron to the trivalent state and reducing the O_2 to coordinated superoxide. The interaction has been characterized as (1) donation to a lone pair of electrons from the sp^2 rehybridized superoxide orbital into the empty d_{z^2} iron orbital and (2) coupling of the superoxide unpaired electron with the unpaired iron electron by overlap of a π^* orbital of O_2^- with the half-filled d_{xz} iron orbital.⁶⁰ This electron coupling has been viewed as an antiferromagnetic exchange coupling, as in the Weiss proposal,⁶⁹ and also as a "significant bonding" interaction.⁶⁰ Recently it has been proposed⁷⁰ that a spin polarization mechanism is operative resulting in the relatively large cobalt hyperfine interaction. In this view of the interaction there is no necessity to transfer an electron from the $\text{Co}(\text{II})$ to the O_2 .

In this work, we have observed complete electron transfer from $\text{Fe}(\text{II})$, $\text{Mn}(\text{II})$, and $\text{Co}(\text{II})$ to *o*-quinones upon coordination, yielding $\text{M}^{\text{III}}\text{SQ}^-$ complexes. The EPR results for $\text{Co}(\text{salen})(3,5\text{-DBSQ})$ indicate the complete oxidation of $\text{Co}(\text{II})$ to $\text{Co}(\text{III})$ with the concomitant reduction of the dibutylated quinone to the semiquinone. This electron transfer

is found to be essential for the *o*-quinone coordination. In the case of the iron and manganese systems, complete coupling of the semiquinone electron to the metal center occurs via a strong antiferromagnetic exchange interaction.

No molecular structural similarity between the semiquinone complexes and the O_2 adducts of analogous iron and cobalt complexes may be drawn, however. Dioxygen is known to bond in Fe and Co complexes in an end-on manner. Semiquinone coordination occurs through both oxygen atoms, analogous to the Griffith model of O_2 binding. This type of oxygen bonding has been indicated for porphyrin complexes of manganese, in which the O_2 appears to be coordinated as a peroxide, i.e., $\text{Mn}^{\text{IV}}\text{O}_2^{2-}$.⁷¹

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Registry No. $\text{Fe}(\text{salen})(9,10\text{-phenSQ})$, 72796-12-4; $\text{Fe}(\text{salen})(1,2\text{-NSQ})$, 72796-13-5; $\text{Fe}(\text{salen})(3,5\text{-DBSQ})$, 72796-14-6; $[\text{Fe}(\text{salen})]_2(\text{Cl}_4\text{cat})$, 72796-15-7; $[\text{Fe}(\text{salen})\text{Cl}]_2$, 15308-73-3; 1,4,6,7,8,9-hexachlorodibenzo-1,4-dioxin-2,3-quinone, 65005-72-3; $\text{Mn}(\text{salen})(3,5\text{-DBSQ})$, 72796-16-8; $\text{Co}(\text{salen})(3,5\text{-DBSQ})$, 72796-17-9; $[\text{Co}(\text{salen})]_2(\text{Cl}_4\text{cat})$, 72796-18-0; $\text{Mn}(\text{salen})\text{Cl}$, 53177-12-1; $\text{Fe}^{\text{II}}(\text{salen})$, 14167-12-5; $\text{Mn}^{\text{II}}(\text{salen})$, 36026-26-3; $\text{Co}^{\text{II}}(\text{salen})$, 36870-54-9.

Supplementary Material Available: Tables IV-VIII of experimental magnetic susceptibility data (5 pages). Ordering information is given on any current masthead page.

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Stereochemically Nonrigid Silanes, Germanes, and Stannanes. 8.¹ Tetracyclopentadienyl and Tetrakis(methylcyclopentadienyl) Derivatives of Germanium(IV) and Tin(IV)

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The compounds GeR_4 ($\text{R} = \text{C}_5\text{H}_5$ or $\text{C}_5\text{H}_4\text{CH}_3$) have been synthesized, making possible a comparison with the already known tin analogues by IR, NMR, and mass spectroscopy. Attempts to prepare corresponding silicon or lead derivatives were unsuccessful; however, the species $\text{M}(\text{C}_5\text{H}_5)_3\text{Cl}$ ($\text{M} = \text{Ge}$ or Sn) have also been characterized, and the influence of chloro substitution at the tin center on $^{117,119}\text{Sn}$ -H coupling constants and on $^{119\text{m}}\text{Sn}$ Mössbauer parameters is commented on. The temperature dependence of ^{13}C as well as ^1H NMR spectra for the MR_4 derivatives has been investigated, and the intramolecular rearrangement behavior in the methylcyclopentadienyl compounds has been rationalized. The spectral changes observed for $\text{Ge}(\text{C}_5\text{H}_4\text{CH}_3)_4$ are consistent with degenerate exchange between identical configurations resulting from equilibrium preponderance of a preferred nongeminal arrangement.

Introduction

Homoleptic compounds formed between quadrivalent tin and cyclopentadiene or methylcyclopentadiene were isolated in 1965 by Fritz and Kreiter.² These authors deduced from variable-temperature NMR spectroscopy that while in $\text{Sn}(\text{C}_5\text{H}_5)_4$ (**1**) a rapid rearrangement process led to equivalence among all ^1H nuclei in the molecule, the methylcyclopentadienyl analogue (**2**) showed no corresponding dynamic behavior. This conclusion^{2,3} was subsequently argued to be

incorrect by Davison and Rakita,⁴ and as a result of a further study by Campbell and Green,⁵ it is now clear that $\text{Sn}(\text{C}_5\text{H}_4\text{CH}_3)_4$ (**2**) exhibits the kind of behavior we^{6,7} have termed *quasi-fluxional*, i.e., undergoes nondegenerate intramolecular rearrangement. The original controversy^{2,4} can be attributed to the rapidity of metallotropic shifts in both compounds **1** and **2** as a result of which no conspicuous spectral changes occur within an accessible temperature range. The molecular and crystal structure of compound **1** has been determined by

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Table I. Comparison of Spectroscopic Data for Compounds 1 and 6

compd	NMR data ^a		^{119m} Sn Mössbauer data ^b		IR ^c
	² J(¹¹⁷ Sn-H)	² J(¹¹⁹ Sn-H)	IS	QS	
Sn(C ₅ H ₅) ₄	25.4	26.6	1.56	0	755 vs, br, 639 s, br, 575 mw, 350 vs, 330 s
Sn(C ₅ H ₅) ₃ Cl	29.9	31.1	1.56	1.45	750 s, br, 647 s, 562 mw, 352 s, 333 s, 317 m

^a Coupling constants (averaged in fast limit), Hz. ^b Measured at 77 K by using a Harwell constant-acceleration spectrometer; isomer shift (IS) in mm s⁻¹ relative to 0 for SnO₂ and quadrupole splitting (QS) in mm s⁻¹. ^c In cm⁻¹; in range 300–800 cm⁻¹.

diffraction methods and confirms⁸ a tetrahedral arrangement of η¹ rings about the metal atom. We have synthesized the hitherto unknown germanium analogues of compounds 1 and 2 with the expectation^{4,6,9} that rearrangement rates would be slower and would result in significant temperature dependence of NMR data. That this has proved to be the case is reported in the present paper, leading to a comparison by ¹³C as well as ¹H NMR spectroscopy between Ge(C₅H₅)₄ (3) and Ge(C₅H₄CH₃)₄ (4) and their tin(IV) counterparts.

During the progress of this research the related M(C₅H₅)₃Cl derivatives [(5) M = Ge; (6) M = Sn] have also been characterized. Attempts to prepare the silicon analogues of 1 and 3 or 2 and 4 were unsuccessful, and reaction of lead(IV) acetate with Na(C₅H₅) gave Pb(C₅H₅)₂.

Experimental Section

Reactions were conducted in an atmosphere of dry dinitrogen gas. Solvents were dried and purified by using standard procedures. Cyclopentadiene and methylcyclopentadiene were obtained by thermal "cracking" of the dimers immediately prior to use. Instrumentation used to measure the spectroscopic data has been detailed in earlier papers.^{1,6,7}

Syntheses. Tetracyclopentadienylgermanium(IV). To dry potassium cyclopentadienide (0.085 mol) prepared by reaction of the metal with cyclopentadiene monomer in diethyl ether was added benzene (50 cm³) and then over 1/2 h was added GeCl₄ (3.56 g, 0.017 mol) in benzene (30 cm³). Stirring at ambient temperature for 6 h afforded a yellow, gelatinous mixture to which dry hexane (25 cm³) was added; after the solution was stirred for a further 1/2 h, a white solid (KCl) settled to leave a clear yellow solution. Filtration and removal of solvent yielded the product (4.75 g, 86%) obtained as a pale yellow solid, mp 116 °C dec. (Anal. Calcd for C₂₀H₂₀Ge: C, 72.16; H, 6.01. Found: C, 71.9; H, 5.83.)

Tetrakis(methylcyclopentadienyl)germanium(IV). Benzene (100 cm³) was added to dry potassium methylcyclopentadienide (0.105 mol). After addition over 1 h of GeCl₄ (5.4 g, 0.025 mol), the mixture was stirred for 48 h and then filtered and benzene was removed to leave a dark yellow oil. This was dissolved in dry hexane, and the mixture was filtered and pumped to remove the solvent. Repetition of this procedure followed by prolonged pumping (48 h, 10⁻² mmHg) finally yielded the product (7.25 g, 74%), a viscous, air-sensitive amber oil. (Anal. Calcd for C₂₄H₂₈Ge: C, 74.09; H, 7.26. Found: C, 73.7; H, 6.98.)

Tetracyclopentadienyltin(IV) and Tetrakis(methylcyclopentadienyl)tin(IV). These compounds were prepared as described previously,^{2,5} as bright yellow crystals, mp 73 °C, and a yellow-orange, viscous oil, respectively.

Chlorotricyclopentadienylgermanium(IV) and -tin(IV). The products were obtained as pale yellow solids after recrystallization from benzene from reactions similar to those described above but utilizing 3 (rather than 4) molar equiv of cyclopentadienide anion/1 mol of metal halide. (Anal. Calcd for C₁₅H₁₅ClGe: C, 59.39; H, 4.99. Found: C, 59.09; H, 4.99. Anal. Calcd for C₁₅H₁₅ClSn: C, 51.55; H, 4.30. Found: C, 51.31; H, 4.13.)

Results and Discussion

The isolation of tetracyclopentadienylgermanium(IV) (3) and its methylcyclopentadienyl analogue (4) was readily accomplished by a very similar procedure to that used^{2,5} to obtain

Table II. Abundances^a for Major Fragment Ions

ion family ^c	ion abund ^b			
	Ge-(C ₅ H ₅) ₄	Sn-(C ₅ H ₅) ₄	Ge-(C ₅ H ₄ CH ₃) ₄	Sn-(C ₅ H ₄ CH ₃) ₄
MR ₄ ⁺	0.5		1.1	
MR ₃ ⁺	6.9	4.8	1.2	7.1
MR ₂ ⁺	1.9	0.7	0.2	1.4
MR ⁺	77.0	74.6	97.5	66.8
MC ₃ H _n ⁺	8.0	3.0		
MC ₂ H _n ⁺	3.4	2.1		
M ⁺	1.0	14.7		13.2

^a 70-eV ionizing voltage. ^b % of metal-containing ions, summed within each family resulting from metal isotope distribution and hydrogen loss. ^c M = Ge or Sn; R = C₅H₅ or C₅H₄CH₃.

the corresponding tin derivatives. Physically there is a strong resemblance between each pair of compounds, M(C₅H₅)₄ (M = Ge or Sn) being air-stable, yellow crystalline solids while M(C₅H₄CH₃)₄ are orange-yellow oils which are somewhat air sensitive. In a number of different experiments, SiCl₄ with KC₅H₅ or KC₅H₄CH₃ gave only brown, gummy oils which set to glassy material over 12 h. We have noted similar though slower polymerization of other poly(cyclopentadienyl)silanes.¹⁰ With lead(IV) acetate, NaC₅H₅ appeared to yield mainly Pb(C₅H₅)₂, identified by comparison with an authentic sample.

Recovery of products from reactions using ca. 3:1 ratio of C₅H₅:MCl₄ afforded compounds 5 and 6, M(C₅H₅)₃Cl (M = Ge or Sn), pale yellow solids which were superficially difficult to distinguish from the tetrasubstituted cyclopentadienyls and were characterized by microanalysis and mass spectrometry. Other measurements also provided contrasting results for Sn(C₅H₅)₄ and Sn(C₅H₅)₃Cl. (Table I). Thus while ¹H chemical shifts for the single resonance resulting from rapid metalotropism were identical (τ 4.19 in C₆D₆), the coupling constants ²J(¹¹⁷Sn-H) and ²J(¹¹⁹Sn-H) between metal nucleus and proton (averaged environment) increased on introduction of the electron-withdrawing chlorine substituent. The latter also resulted in observation of a quadrupole-split Mössbauer resonance: the regular geometry⁸ of compound 1 led to an unsplit line with IS = 1.56 mm s⁻¹, but a doublet was observed for 6, separation 1.45 mm s⁻¹. These values are of some interest in that the IS are somewhat higher than those reported for related organotin compounds, and the QS is anomalously small.¹⁰ Additionally compound 6 showed three strong IR absorptions in the 300–400 cm⁻¹ range [ν(Sn-Cl) with ν(Sn-C_{ring})] while 1 showed only two. IR spectra for compounds 1–6 consist of a very large number of absorptions attributable to substituent vibrations, but since they provide little information other than to indicate that compound 3 is isostructural with 1,⁸ wavenumbers have not been listed here.

An extensive compilation of mass spectral data for η¹-cyclopentadienyl derivatives of silicon, germanium, and tin has recently been published.¹¹ This included ion-abundance data and a fragmentation scheme for compound 1 and supported the view that while η⁵-cyclopentadienyls characteristically

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Table III. NMR Data^a for Cyclopentadienyls 1, 3, 5 and 6

¹ H ^b compd	temp, K	δ(H _{a,a'})	δ(H _{b,b'})	δ(H _x)
Ge(C ₅ H ₅) ₄ (3)	203	6.63	6.28	3.26
	300		5.86 ^c	
Ge(C ₅ H ₅) ₃ Cl (5)	193	6.62	6.29	3.24
	300		5.83 ^c	
Sn(C ₅ H ₅) ₂ (1)	300		5.92 ^{c-e}	
Sn(C ₅ H ₅) ₃ Cl (6)	300		5.81 ^{c,d,f}	

^a Chemical shifts, ppm, measured positive downfield from SiMe₄ in 5% CDCl₃ solution. ^b Measured at 60.0 and 90.0 MHz. ^c Exchange-broadened averaged chemical shift. ^d For coupling constants see Table I. ^e See also ref 2; δ(¹³C) = 114.5, ¹J(Sn-C) = 17.7 Hz (¹¹⁷Sn, ¹¹⁹Sn components not resolved) at 300 K. ^f In C₆D₆ solution.

fragment via C-C bond fission, the η¹ analogues decompose by elimination at the M-C linkage. This is further illustrated in Table II for compounds 1-4. While the molecular ion abundance for 1 is extremely low (0.016%¹²), those for the germanes 3 and 4 are clearly discernible, reflecting the increase in M-C bond energy. As has been found for other group 4 organometallics, subsequent fragmentation is dominated by formation of even-electron ions by radical elimination,¹² giving principally MR⁺ whence fission of the C₅ unit ultimately occurs via acetylene ejection¹¹ to give MC₃ and MC₂ fragments. Compound 2 also gave a parent ion (4.8%) and together with 6 showed M(C₅H₅)₂Cl⁺ much more prominently than M(C₅H₅)₃⁺ with conversely M(C₅H₅)⁺ about 3 times as intense as MCl⁺.

NMR Spectra: Fluxional Characteristics. Data for the cyclopentadienyl compounds 1, 3, 5, and 6 are listed in Table III. As reported earlier,² the ¹H spectrum for 1 consists of a sharp, single resonance exhibiting satellite lines (due to ¹¹⁷Sn, 7.67, and ¹¹⁹Sn, 8.68%; *I* = 1/2; for coupling constants see Table I) which is essentially invariant with temperature down to -80 °C. That this is the result of averaging of proton environments due to rapid intramolecular rearrangement has recently been confirmed¹³ by using a ¹H{¹¹⁹Sn} INDOR experiment: splitting of the observed resonance was assigned to the central portion of a 21-line multiplet structure due to coupling of the ¹¹⁹Sn nuclear spin with 20 equivalent protons in the fast-limiting situation. Accordingly the ¹³C spectrum consists of a sharp singlet [with ¹J(¹³C-^{117,119}Sn) = 17.7 Hz] at all accessible temperatures. Essentially the same behavior was encountered for compound 6, the increase in ²J(H-^{117,119}Sn) having already been commented on. By contrast, ¹H spectra at ambient temperature for the germanium analogues 3 and 5 contained much broader singlets, the line width of which increased with decreasing temperature and then split below -30 °C into components assigned to incompletely resolved aa'bb'x multiplets. This is consistent with (a) equivalence resulting from identical behavior of all cyclopentadienyl groups in each compound (cf. ref 14) and (b) metallotropic migration having Δ*G*[‡] in the expected^{9,14} range (around 50 kJ mol⁻¹). For the tin compounds Δ*G*[‡] is lower and only fast-limiting characteristics^{2,9,13} can be discerned, the persistence of coupling between metal and ¹H or ¹³C nuclei establishing intramolecularity.

Rationalization of the nonrigid behavior of the methylcyclopentadienyl derivatives 2 and 4 is more problematical. Data are given in Table IV; the ¹H spectrum for Ge(C₅H₄CH₃)₄ at 27 °C is shown in Figure 1, and the temperature-dependence of the ¹³C spectrum for the same compound is illustrated in Figure 2.

Table IV. NMR Data^a for Tetrakis(methylcyclopentadienyl)germanium and -tin

compd	temp, K	¹ H ^b			
		δ(H _{2,4})	δ(H ₅)	δ(H ₁)	δ(H _{CCH₃})
Ge(C ₅ H ₄ CH ₃) ₄	223	6.25, 5.90	6.40	3.12	2.08
	300 ^c	6.10		4.75	2.06
Sn(C ₅ H ₄ CH ₃) ₄ ^d	300	5.97		4.95	2.05

compd	temp, K	¹³ C				
		δ(C ₃)	δ(C _{2,4})	δ(C ₅)	δ(C ₁)	δ(C _{CCH₃})
Ge(C ₅ H ₄ CH ₃) ₄	223 ^e	141.2	134.0, 128.0	134.0	49.0	15.5
	300 ^e	141.0	131.2		n.o.	15.3
Sn(C ₅ H ₄ CH ₃) ₄	300	139.5	123.6		96.5	15.4

^a Chemical shifts, ppm, measured positive downfield from SiMe₄ in 10% (¹H) or 50% (¹³C) CDCl₃ solution. Ring numbering refers to a 1-metallo-3-methyl system, i.e., configuration A; see text. No differentiation between resonances due to 2- or 4-nuclei is implied (see text). ^b Measured at 90 MHz. ^c See also Figure 1. ^d For ^{117,119}Sn-¹H coupling constants see ref 5. ^e See also Figure 2.

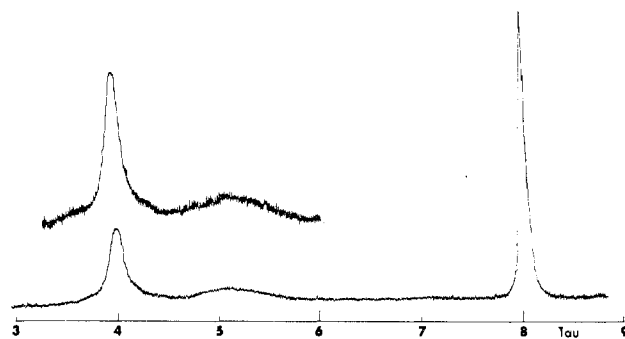
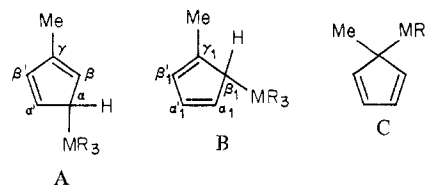


Figure 1. Hydrogen-1 NMR spectrum of tetrakis(methylcyclopentadienyl)germane at 27 °C.

Like the cyclopentadienyl 1 the tin compound exhibits a fast-limiting ¹H NMR spectrum down to -60 °C; this has been discussed⁵ in terms of rapid nondegenerate rearrangement involving predominance of a nongeminal ring configuration represented by A over the isomeric arrangement B [MR₃ =



Sn(C₅H₄CH₃)₃]. In a recent paper we have formalized⁶ the dynamic behavior of corresponding methylcyclopentadienyl derivatives (MR₃ = SiH₃, GeH₃, GeMe₃, or SnMe₃) as isomerization between A and B, neglecting the participation of the geminal species C; the fast-limiting ¹³C resonant frequencies ν₁, ν₂, and ν₃ can then be expressed by using (α, α', β, β', and γ) and (α₁, α'₁, β₁, β'₁, and γ₁), the frequencies assigned to isomers A and B in the slow limit. This leads to identification of the ratio of equilibrium concentrations [A]:[B] with the frequency separation ν₂ - ν₁ and to the conclusion that while for SnMe₃(C₅H₄CH₃) [B] is comparable with [A], for compound 2 [A] ≫ [B], as suggested by Campbell and Green.⁵ These facts also support our proposal⁶ that steric requirements of the substituents R in (C₅H₄CH₃)MR₃ together with the size of M will control the equilibrium [A]:[B] ratio.

It is now possible to account for the appearance of Figures 1 and 2. The latter differs from comparable data for GeMe₃(C₅H₄CH₃) (Figure 1 of ref 6) in that (i) only one resonance attributable to the methyl carbon atom is present,

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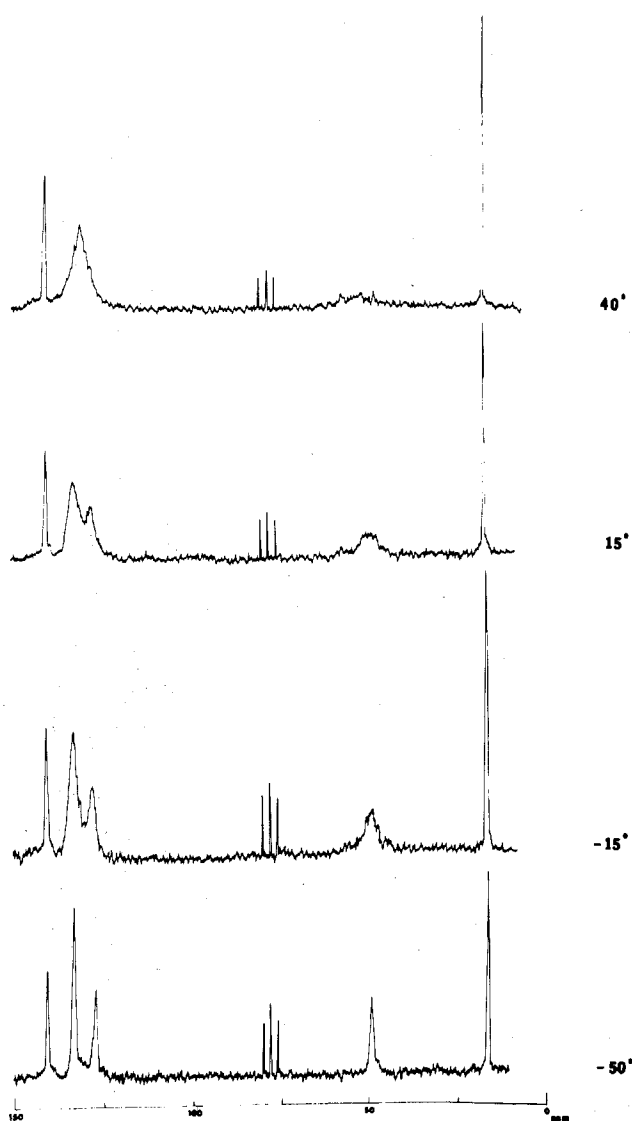
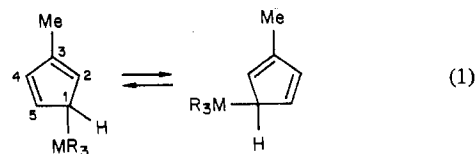


Figure 2. Carbon-13 NMR spectrum of tetrakis(methylcyclopentadienyl)germane at various temperatures. The triplet centered at 77.2 ppm is due to CDCl_3 .

at 15.3 ppm, and (ii) there is only one signal due to a ring carbon bearing the methyl group (that at highest frequency, 141.0 ppm). Moreover neither of these features exhibits any variation in frequency or line width during coalescence of the remaining portion of the spectrum. We conclude that on decreasing the size of the metal atom by substituting germanium for tin in $\text{M}(\text{C}_5\text{H}_4\text{CH}_3)_4$, only one ring configuration is

detectable because steric restrictions have increased the $[\text{A}]:[\text{B}]$ ratio to a point at which $[\text{B}]$ can be neglected. The changes shown in Figure 2 will therefore closely approximate to the degenerate (i.e., fluxional) rearrangement eq 1, and the



numbering system used in Table IV can be adopted. The result of this process is to average C_1, C_5 (to give ν_1) and C_2, C_4 (ν_2) at different rates (because of the much larger frequency separation between the first pair) and to produce no change in C_3 and C_{Me} as observed. Thus at 35°C ν_2 is obvious (131.2 ppm) while ν_1 is establishing itself much more slowly (at the mean of $\text{C}_1, 49.0$ ppm, and $\text{C}_5, 134.0$ ppm) and will be extremely broad and cannot be distinguished.

Similarly, although the shape of the ^1H spectrum shown in Figure 1 is rather surprising on first inspection, it again results from differential collapse of resonances for two pairs of nuclei: H_2 and H_4 , averaging to 6.10 ppm at 27°C over a chemical shift difference of 0.35 ppm; and H_1 and H_5 (assigned to lines at 3.12 and 6.40 ppm, respectively, at -50°C), coalescing much more slowly to give the very broad feature centered at 4.75 ppm. This parallels exactly the situation for the tin analogue where, although line widths of both the corresponding fast-limit resonances are similar, manipulation of coupling constants led to the conclusion⁵ that the low-field component is due to the $\text{H}_{\beta,\beta'}$ protons of configurations A and B. It is also worth commenting that the resonances listed in Table IV at 223 K retained residual broadening (ca. 20 Hz) due to unresolved proton-proton coupling together with viscosity effects of mixtures of liquid 4 with suitable solvents.

In confirming proposals we put forward earlier⁶ these observations provide an interesting example of the kinetic influence of steric and size effects on equilibrium isomer distribution (a thermodynamic property). More generally, they also constitute a model for analysis of dynamic behavior of any (η^1 -methylcyclopentadienyl)metal derivative or indeed of related classes of compounds which undergo nondegenerate rearrangement.

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Registry No. 1, 3559-76-0; 2, 34703-11-2; 3, 28314-32-1; 4, 72582-07-1; 5, 72582-08-2; 6, 53323-79-8; potassium cyclopentadienide, 30994-24-2; potassium methylcyclopentadienide, 41066-45-9; GeCl_4 , 10038-98-9.