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NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF METAL CYCLOPENTADIENYLS
IV*. ^{13}C NMR SPECTRA OF σ-CYCLOPENTADIENYL COMPOUNDS OF SILICON, GERMANIUM AND TIN

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SUMMARY

^{13}C NMR spectra of silicon, germanium and tin cyclopentadienyl compounds have been studied. ^{13}C chemical shifts and $J(^{13}C\text{–}H)$ constants verify the σ-structure of the compounds. The variation of the ^{13}C NMR spectrum of $C_5H_5Ge(CH_3)_3$ with temperature shows that a fast metallotropic rearrangement occurs in this compound at as low a temperature as 20° ^{13}C NMR data are discussed with reference to the structure of metal cyclopentadienyls.

^{13}C NMR spectroscopy is very promising in the study of the structures of metal cyclopentadienyls or the dynamic processes occurring in these compounds[1-3]. This is due principally to the fact that chemical shifts of carbon ^{13}C correlate with electron densities of atoms or bonds[4]. Another promising application of the spectra is the investigation of dynamic processes. The ^{13}C spectra (especially, when used together with the $^{13}C\text{–}^{1}H$ double resonance) enable the difficulties inherent in the analysis of multiplet structures to be avoided. The range of chemical shifts given by carbon nuclei is much wider than that of protons, therefore ^{13}C NMR spectroscopy is more sensitive in (on the average, by two orders) faster processes. All such measurements are, however, somewhat complicated by a low signal-to-noise ratio obtained with samples containing ^{13}C in natural abundance. This paper reports certain parameters of the ^{13}C spectra obtained with the cyclopentadienyl compounds of silicon, germanium and tin.

Compounds $C_5H_5M(CH_3)_3$, where M = Si, Ge, Sn, and compound $C_5H_5SiCH_3Cl_2$ were obtained and purified according to known procedures[5,6]. With $C_5H_5SiCH_3Cl_2$, we used a sample enriched with a 5-methyldichlorosilylcyclopentadiene isomer up to 80% by the technique reported earlier: the sample of C_5H_6 was measured immediately after distillation to purify it from dimerization products. The synthesis, properties, and PMR spectra of 5,5'-bis(trimethylstannyl)cyclopentadiene will be reported in a later communication.

^{13}C NMR spectra were measured on a JNM 4H-100 spectrometer (JEOL)

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* For Part III see ref. 9.

using the NSS-method. The resonance frequency was 25.14 Mc for carbon ^{13}C. Carbon disulphide was used as external reference. The shifts were measured accurately to ±1.0 ppm. All compounds were studied as neat liquids in rotating ampoules (10 mm o.d.). The temperature was set by a JES-VT-3 bridge controller. Double heteronuclear resonance was accomplished by a JNM-SD-HC unit. Field sweep was used throughout in this study.

The results obtained with ^{13}C NMR spectra of compounds (I)–(VI) are shown in Table 1. The spectrum of cyclopentadiene reported earlier [7,8] coincides with that obtained by us. The shifts of the α- and β-carbons of C_5H_6 are equal, therefore the downfield region contains a doublet characterized by a 165 cps coupling which results from ^{13}C–^{1}H interaction. The operating resolution (about 5 cps) of the apparatus does not show any significant ^{13}C–C–^{1}H interaction.

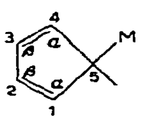
TABLE 1

PARAMETERS OF ^{13}C NMR SPECTRA OF VARIOUS CYCLOPENTADIENYL COMPOUNDS[a]

No.	Compound	C_1–C_4 atoms		C_5 atom		CH_3	Note
		Chemical shifts δC	Coupling constants $J(^{13}C–H)$	Chemical shifts δC	Coupling constants $J(^{13}C–H)$	Chemical shifts δC	
(I)	C_5H_6	60.8	165±2	151.2	125±5	—	r.t.
(II)	$C_5H_5Si(CH_3)_3$	59.7 62.3	167±5	140.7	[b]	194.8	r.t.
(III)	$C_5H_5Ge(CH_3)_3$	59.0 63.0	167±5	141.5	[b]	195.2	at −10°
(IV)	$C_5H_5SiCH_3Cl_2$	58.7 61.1	—	138.5	[b]	191.5	r.t.
(V)	$C_5H_4[Sn(CH_3)_3]_2$	58.3 65.5		140.3		194.3	r.t.
(VI)	$C_5H_5Sn(CH_3)_3$[c]	δ=79.5 $J(^{13}C–H)$=163±2				200.0	r.t.

[a] The shifts are in ppm from a CS_2 external reference, the coupling constants are in cps. [b] Too weak to be measured. [c] Fast exchange.

The spectra of compounds $C_5H_5Si(CH_3)_3$ and $C_5H_5SiCH_3Cl_2$ taken at room temperature, as well as the spectrum of $C_5H_5Ge(CH_3)_3$ taken at −10°, are all similar and correspond to the 5-isomer structure.



The downfield region (about 60 ppm from a CS_2 external reference) contains the signals of the α- and β-carbons, two doublets superimposed on account of the $J(^{13}C$–H) constant. The C_5 signal of carbon ^{13}C is shifted significantly upfield (about 140 ppm) and is difficult to measure because it interacts not only with the nearest proton (H_5) but also with neighbouring ones (1,4). The C_5 signal of carbon ^{13}C is measured reliably by using a ^{13}C–^{1}H spin decoupling which leads to collapse of the multiplet structure and the Overhauser effect (Fig. 1).

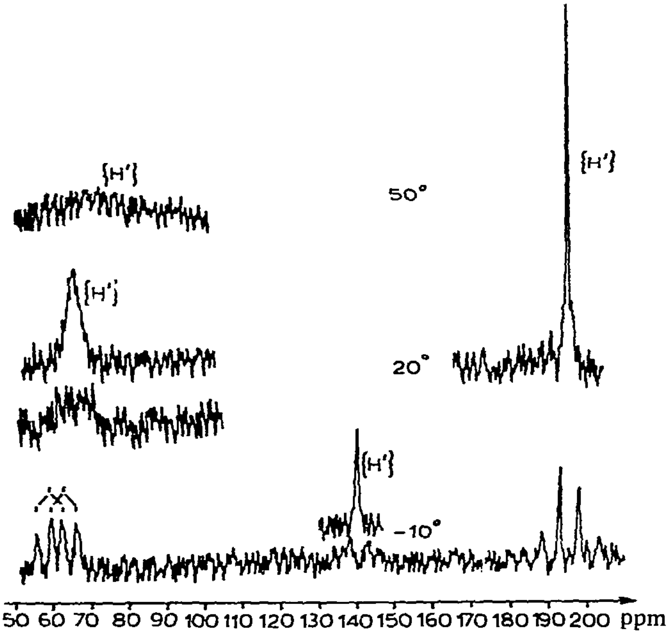


Fig. 1. ^{13}C NMR spectra of compound $C_5H_5Ge(CH_3)_3$ at various temperatures. {H'}, decoupling of protons.

If we assume that variation of the metal type produces a greater variation in chemical shift of the carbons (1,4), then Table 1 demonstrates that the downfield signal (58–59 ppm) relates to β-carbons. Note that the assignment requires a stricter criterion, similar to that used with PMR spectra [3,9].

The shifts of olefinic atoms, C_1–C_4, when compared with the shifts reported earlier[7,8] (*cf.* also cyclopentadiene), suggest that the compounds are σ-bonded containing localised double bonds.

Similar results were obtained with the PMR spectra.

Note that under the above conditions, the PMR spectra of compounds (II), (III) and (IV) actually contain no signals given by the 1,4- or 2,3-protons alone because exchange broadening occurs and the difference between the shifts of these protons is low (about 0.1 ppm) compared with that (about 3 ppm) in the ^{13}C spectra.

The temperature behaviour of the spectrum has been studied with compound $C_5H_5Ge(CH_3)_3$ (Fig. 1). When the temperature increases, the resonance lines of C_1–C_5 carbons are broadened through metallotropic rearrangement[1–3]. At room temperature, the signal width of olefinic C_1–C_4 atoms is about 80 cps and can be measured exclusively with the double ^{13}C–^1H resonance at 50°C.

The fact that the shifts given by ^{13}C nuclei are characteristic may be of use in finding the type of a cyclopentadienyl compound[9], *e.g.*, the spectrum of compound $C_5H_5Sn(CH_3)_3$ recorded at room temperature is a doublet, the shift being 79.5 ppm and the coupling 163 ± 2 cps, produced by spin–spin coupling ^{13}C–H. This is a consequence of all protons of the cyclopentadienyl ring being actually equivalent. Similar signals were observed by Lauterbur and King[10] with certain metal cyclopentadienyls. For the most part, these compounds (assumed to be π-complexes) displayed ^{13}C resonance in much farther upfield (90–125 ppm) than does compound (VI).

Thus, compound (VI) may be assumed to be σ-bonded and to undergo a fast metallotropic rearrangement, while the observed chemical shift is an average value of the shifts possible with the three positions: (1,4), (2,3), and (5). Since the rearrangement is degenerated we have:

$$\delta_C = \tfrac{1}{5}(2\delta_{C_{1,4}} + 2\delta_{C_{2,3}} + \delta_{C_5}) \qquad (1)$$

If the shifts are taken as the average values (Table 1, compounds (I), (II), (III), (IV),—in other words if $\delta_{C_{1,4}} = \delta_{C_{2,3}} = 61$ ppm while $\delta_{C_5} = 142$ ppm—then the re-averaged quantity, δ_C, will be equal to 77.2 ppm which is close to the experimental value, 79.5 ppm.

Constants $J(^{13}C\text{–}H)$ should be averaged in the same manner as chemical shifts during the metal migration in metal cyclopentadienyls, see eqn. (1). If we use the three readings of $J(^{13}C\text{–}H)$, equal to 167, 167 and 125 cps, respectively, then the averaged quantity will be equal to 159 cps which is close to the value observed with $C_5H_5Sn(CH_3)_3$. Since the constant $J(^{13}C\text{–}H)$ is about 175 cps (ref. 10) in most π-bonded cyclopentadienyl compounds, it is clear that this constant can also show whether a compound is σ- or π-bonded.

The structure of 5,5-bis(trimethylstannyl)cyclopentadiene ((V), Table 1) may be resolved in the same manner. The fact that the signals observed are given by C_α, C_β, and C_5 carbons itself suggests that compound (V) is σ-structured while both groups containing the metal are 5-positioned in the ring. Also, chemical shifts are not observed to be averaged, therefore compound (V) may be assumed to be stereochemically rigid. The PMR spectra of the molecule are not affected by temperature within as wide an interval as −100 to +100°. Thus, compound (V) does not undergo any fast metallotropic rearrangement under these conditions.

Our data show that ^{13}C NMR spectroscopy allows a better insight into exchange processes, and the data obtained with both ^{13}C and ^1H NMR spectroscopy (types of ^{13}C or ^1H spectra, ^{13}C or ^1H chemical shifts, $J(^{13}C\text{–}H)$ constants) used in conjunction may give a reliable classification of metal cyclopentadienyls.

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