

## Preliminary communication

## Intramolecular rearrangements in germyl(methyl)cyclopentadiene

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Metal-substituted derivatives of cyclopentadiene are currently the subject of much interest<sup>1-3</sup> as examples of fluxional organometallic molecules. Stereochemical non-rigidity as revealed by the incidence of temperature dependent NMR spectra has been observed in such compounds of both the transition<sup>2,4</sup> and the main group metals<sup>3,5</sup>. A confused situation remains however regarding systems where this type of metallotropic rearrangement must occur through exchange between isomeric forms. The work of Davison and Rakita<sup>5,6</sup> has indicated that methyl-substituted cyclopentadienyl derivatives of the Group IVB metals are fluxional molecules, in contrast to the earlier conclusion of Fritz and others<sup>7,8</sup> that the presence of a methyl group in the cyclopentadiene ring resulted in a static configuration for compounds like  $\text{Sn}(\text{C}_5\text{H}_4\text{Me})_4$ . However, more recently it has been reported that bis(trimethylstannyl)cyclopentadiene adopts a static 1,1-disubstituted structure<sup>9</sup>.

Preliminary studies on the <sup>1</sup>H NMR spectra of cyclopentadienyl derivatives of monogermene have demonstrated that the observation of coupling between metal and ring protons is useful in studying fluxional behaviour<sup>10</sup>. Further exploitation of this possibility has allowed significant elucidation of the properties of ring-substituted systems through a variable-temperature <sup>1</sup>H NMR study of germyl(methyl)cyclopentadiene. Of the eleven possible isomers for this molecule, only three (I, II and III) are expected to exhibit temperature-dependent NMR spectra since those with the metallo-group other than at the 1-position (vinylic isomers) should be stereochemically rigid<sup>3,6</sup>. Pertinent NMR data, given in Table 1, show that at 35°  $\text{H}_3\text{GeC}_5\text{H}_4\text{Me}$  is undergoing rapid metallotropic

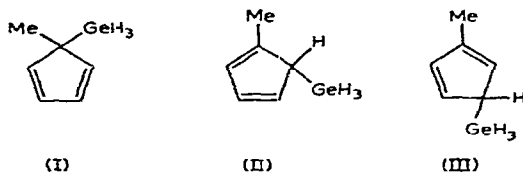


TABLE 1  
VARIABLE TEMPERATURE  $^1\text{H}$  NMR DATA <sup>a</sup> FOR GERMYL(METHYL)CYCLOPENTADIENE

Temperature	$\delta(\text{H}_{3,4,5})^b$	$\delta(\text{GeH}_3)$	$\delta(\text{H}_1)^c$	$\delta(\text{CH}_3)$
$-60^\circ$	6.08–5.63(6)	3.30(3) <sup>d</sup> , 3.27(3) <sup>e</sup>	2.95(1), 2.71(1)	1.61(6)
$35^\circ$	5.70 v br (4)	3.32(3)		1.63(3)
$100^\circ$ <sup>f</sup>	5.20(4), 5.08(3)	3.32(6) <sup>g</sup>		1.63(6)

<sup>a</sup> Neat liquid sample, chemical shifts ppm downfield from external TMS, relative intensities in parentheses (Varian A60D NMR spectrometer).

<sup>b</sup> Olefinic proton signal.

<sup>c</sup> 1-proton signal.

<sup>d</sup> Doublet,  $J = 1.0$  Hz.

<sup>e</sup> Doublet,  $J = 1.1$  Hz.

<sup>f</sup> Integration approximate only.

<sup>g</sup> Quintet,  $J = 0.55$  Hz.

rearrangement so that all four ring protons appear as a broad (ca. 80 Hz width) low-field signal and both  $\text{GeH}_3$  and  $\text{CH}_3$  protons give rise to singlets. The absence of any other resonances shows that the concentration of isomers other than I, II or III is very low. On cooling, splitting of the  $\text{GeH}_3$  resonance into two components is accompanied by the appearance of two signals separated by 0.24 ppm attributable to the tertiary hydrogens in II and III, and of coupling in the olefinic proton region. A low-temperature limiting spectrum is reached at ca.  $-50^\circ$  and is consistent with that of a roughly 50/50 mixture of isomers II and III with little evidence for I. The values for  $J(\text{HGeCH})$  of ca. 1 Hz are comparable to that observed<sup>10</sup> at low temperature for  $\text{H}_3\text{GeC}_5\text{H}_5$ . The evidence for two isomers of  $\text{H}_3\text{GeC}_5\text{H}_4\text{Me}$  (II and III) at  $-60^\circ$  contrasts with the suggestion<sup>11</sup> that for the silyl analogue only the 1,1-silyl(methyl) form is present at  $-50^\circ$ . Further studies on related compounds are in progress.

Above  $35^\circ$ , the  $\text{GeH}_3$  resonance splits into a quintet,  $J = 0.55$  Hz (Table 1). This observation is interpreted as coupling between the  $\text{GeH}_3$  protons and the four ring protons, the latter being equivalent through rapid exchange between I, II and III, and constitutes novel<sup>\*</sup> and unequivocal evidence for an intramolecular shift of the  $\text{GeH}_3$  group as the mechanism for the fluxional rearrangement. The other change on increasing the temperature is the partial resolution at  $100^\circ$  of the low-field resonance as would be expected<sup>1,3,5,6</sup> on approaching the fast exchange limiting spectrum.

\*Note added in proof. The observation of  $J(\text{HCPF})$  in the  $^{19}\text{F}$  NMR spectrum of  $\text{C}_5\text{H}_2\text{PF}_2$  above  $25^\circ$  has been reported in a very recent note<sup>12</sup>.

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