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Preliminary communication

The fluxional behaviour of cyclopentadienyl derivatives of monogermane

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Stereochemical non-rigidity in cyclopentadienyl complexes of transition metals has been the subject of a number of recent investigations[1,2] but analogous main-group organometallic compounds have been less well studied[3,4]. Davison and Rakita have shown that trimethyl–Group IVB cyclopentadienyls exhibit fluxional behaviour[4]; the necessary rearrangement mechanism has been the subject of some speculation[4-7] but on presently available evidence a 1,2 metallo-shift is favoured[4,7]. To investigate the effect of the requirement of a simultaneous 1,2 shift around two rings, the temperature-dependent NMR spectrum of dicyclopentadienylgermane, $(C_5H_5)_2GeH_2$ has been examined and compared with that of its monocyclopentadienyl analogue $C_5H_5GeH_3$; a preliminary account of the results is given herein. Polymetallated cyclopentadienyls of Si, Ge and Sn have also been reported[8], but no NMR data were given.

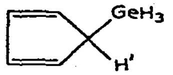
TABLE I

NMR DATA[a] FOR CYCLOPENTADIENYLGERMANES[b]

	T(°C)[c]	δ(C_5H_5)	δ(GeH)
$C_5H_5GeH_3$	40	5.56 (br)	3.33
	–20	5.56 m, 3.02 (br)	3.33 d
	–60	5.50 m, 3.02 m	3.33 d(m)
$(C_5H_5)_2GeH_2$	40	5.61	3.61
	–20	5.70 (br)	3.61
	–50	5.90 v (br)	3.60 (br)

[a] ppm to low field of external TMS. [b] Neat liquid samples. [c] Selected from data obtained at ca. 10° intervals.

Relevant NMR data are summarised in Table 1, and show that in both $C_5H_5GeH_3$ and $(C_5H_5)_2GeH_2$ fluxional behaviour is occurring, but evidently at markedly different rates. For $C_5H_5GeH_3$, a fixed configuration corresponding to:



is adopted at temperatures below -17° (± 4°) as indicated by the appearance of an upfield resonance due to δ(CH') and of J(H-H') = 1.7 Hz, in the GeH_3 resonance.

In the case of $(C_5H_5)_2GeH_2$, conversely, no change other than progressive broadening of the single C_5H_5 resonance (and ultimately that due to GeH_2) occurs on cooling to temperatures below−50°. This is characteristic[2,4] of a molecule undergoing fluxional exchange at a rate well above that at which individual proton environments are distinguishable. This is confirmed by the observation that the C_5H_5 resonance sharpens on increasing the temperature.

It is concluded that the dicyclopentadienyl compound undergoes intramolecular rearrangement much more readily than the monosubstituted germane. It is surprising that the requirement of simultaneous metallotropic rearrangement around two cyclopentadienyl rings should have such a marked effect. To attempt to elucidate this observation, investigation of further substituted germanes is being initiated.

In both $C_5H_5GeH_3$ and $(C_5H_5)_2GeH_2$ the (GeH) chemical shifts are close to those of corresponding alkylgermanes[9,10]. Vibrational spectra contain complex contours due to ν(C–H), consistent[4] with σ-bonded cyclopentadienyl groups. Strong bands at ca. 370 cm^{-1} in the Raman spectra are assigned to ν(Ge–C).

EXPERIMENTAL

The compounds were prepared by the interaction of halogenogermanes with KC_5H_5, and characterised by IR, Raman, NMR and mass spectroscopy.

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