Stereochemical Non-rigidity in Germylcyclopentadiene and Related Derivatives of Germane

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The compounds germylcyclopentadiene (I), germyl(methyl)cyclopentadiene (II), methylgermylcyclopentadiene (III), bis(cyclopentadienyl)germane (IV), and germylindene (V) have been synthesised through reaction of halogenogermanes with appropriate hydrocarbon anions. Using variable-temperature ^1H n.m.r. spectroscopy, it has been found that while compounds (I)—(IV) are fluxional at 35 °C, the onset of similar behaviour for (V) occurs only at 175 °C. For compounds (I) and (II), spin coupling between protons at Ge and on the C_5 ring could be resolved (*a*) below −20 °C, establishing the identity of the species present at the slow-exchange limit in each case, and (*b*) above 50 °C, providing novel evidence for an intramolecular, metallotropic shift as the mechanism for rearrangement. I.r. and Raman spectra for compounds (I)—(V) have been partly assigned, with ν[Ge–C(ring)] near 370 cm^{-1}; mass spectra show fragmentation patterns indicating extensive transfer of H from Ge to the organo-group. Heating compound (I) results in partial prototropic rearrangement to 2- and 3-germyl isomers; several reactions of (I), including those with HCl and Me_3SnH, have been investigated.

A PRONOUNCED contrast between the properties of methylcyclopentadiene and those of trimethyl Group IVB derivatives of cyclopentadiene has begun to emerge as a result of recent investigations. While the former exists as a mixture of 1-, 2-, and 3-isomers in equilibrium and rapidly dimerizes at ambient temperature,[1] the trimethyl-silyl, -germyl, and -stannyl compounds are dynamic systems which provide a particularly lucid demonstration of the occurrence of fluxional behaviour, and possess considerable thermal stability as monomers.[2,3] A further interesting feature of the tin–cyclopentadienyl linkage in $Me_3Sn(C_5H_5)$ is its unusual reactivity, giving a useful synthetic route to a variety of trimethyl-tin and metal–tin bonded derivatives, and this is to some extent paralleled by the silicon and germanium analogues.[4]

The nature of the molecular processes which confer stereochemical non-rigidity on $Me_3M(C_5H_5)$ (M = Si, Ge, or Sn) compounds and related metallo-substituted cyclopolyenes has been closely examined, both by specific ^1H n.m.r. experiments [2,5] and also theoretically.[6,7] Presently available evidence favours a rearrangement of the 1-metallo-derivative by an intramolecular, metallotropic, and probably 1,2-, shift,[2,5,8] although a 1,3-shift has also been considered, particularly for indenyls.[9] A much slower prototropic shift to give vinylic isomers which are non-fluxional has been demonstrated for several species, notably $Me_3Si(C_5H_5)$ where formation of 2- and 3-isomers during gas-phase pyrolysis experiments has been studied and shown to be reversible.[10]

Attracted by the possibility of observing spin coupling between protons situated respectively within a metallotropic group and on the supporting ring system, which might be expected to provide a new and sensitive probe for elucidating fluxional characteristics, we have investigated the behaviour of several related derivatives of germane. For the simplest of these, germylcyclopentadiene (I) we have also conducted a preliminary exploration of chemical activity.

RESULTS AND DISCUSSION

Reaction of bromogermane, dibromogermane, or chloromethylgermane with appropriate cyclopentadienyl anions at 20 °C in the absence of solvent readily afforded germylcyclopentadiene (I), germyl(methyl)cyclopentadiene (II), methylgermylcyclopentadiene (III), bis(cyclopentadienyl)germane (IV), and germylindene (V). All these compounds are colourless volatile liquids with low m.p.s [*ca.* −100 °C for (II)]; unlike the parent hydrocarbons,[1] (I)—(IV) showed no tendency to dimerize over long periods at ambient temperature. The isomeric species (II) and (III) are very similar in volatility and also in u.v. absorption spectrum (gas-phase $\lambda_{max.}$ respectively at 260, 264 nm, shifted from 240 nm for cyclopentadiene), but can readily be distinguished by other spectroscopic methods. ^1H N.m.r. spectra of compounds (I)—(IV) were very simple at 35 °C, as illustrated in Figure 1 for (I), suggesting fluxional character; for (V), a spectrum attributable to the 1-isomer, showing extensive proton non-equivalence and spin coupling, was observed at the same temperature. These conclusions were confirmed by the results of variable-temperature ^1H n.m.r. studies, described in full below; certain of these data have already been reported in preliminary form.[11,12]

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[1] S. M. Csicsery, *J. Org. Chem.*, 1960, **25**, 518; V. A. Korenevsky and N. M. Sergeyev, *J. Amer. Chem. Soc.*, 1972, **94**, 8586.

[2] A. Davison and P. E. Rakita, *J. Amer. Chem. Soc.*, 1968, **90**, 4479; *Inorg. Chem.*, 1970, **9**, 289.

[3] N. M. Sergeyev, G. I. Avramenko, A. V. Kisin, V. A. Korenevsky, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1971, **32**, 55 and references therein.

[4] E. W. Abel, S. A. Keppie, M. F. Lappert, and S. Moorhouse, *J. Organometallic Chem.*, 1970, **22**, C31; E. W. Abel and S. Moorhouse, *ibid.*, 1971, **28**, 211; **29**, 227.

[5] F. A. Cotton and T. J. Marks, *Inorg. Chem.*, 1970, **9**, 2802.

[6] Chan-Cheng Su, *J. Amer. Chem. Soc.*, 1971, **93**, 5653.

[7] J. Dalton, *Inorg. Chem.*, 1972, **11**, 915; *J. Organometallic Chem.*, 1972, **39**, 251 and references therein.

[8] J. E. Bentham and D. W. H. Rankin, *J. Organometallic Chem.*, 1971, **30**, C54.

[9] A. Davison and P. E. Rakita, *J. Organometallic Chem.*, 1970, **23**, 407 and references therein.

[10] E. W. Abel and M. O. Dunster, *J. Organometallic Chem.*, 1971, **33**, 161.

[11] S. R. Stobart, *J. Organometallic Chem.*, 1971, **33**, C11.

[12] S. R. Stobart, *J. Organometallic Chem.*, 1972, **43**, C26.

^1H *N.m.r. Spectra.*—Equivalence among the five ring protons, resulting in a single characteristically broadened resonance at τ 4·44, was found at 35 °C for compound (I), establishing the occurrence at this temperature of rearrangement similar to that encountered for related σ-bonded metal cyclopentadienyl compounds.[2,3,5] The only other feature, a sharp uncoupled peak at τ 6·67, was in the expected region for protons of the GeH_3 group (Figure 1). Cooling to below −20 °C allowed the spectrum of the 'static' configuration (VI) to be observed; the ring protons became distinguishable as olefinic (a,a′, b,b′) or tertiary (x), and coupling with the latter split the Ge*H* resonance into a doublet [Figure 1(*a*), (*b*)]. Surprisingly, no chemical-shift difference or coupling between a,a′ and b,b′ protons could be resolved above −70 °C [Figure 1(*a*)]. Values for ^1H n.m.r. parameters are recorded in Table 1, along with those for compounds (II)—(V).

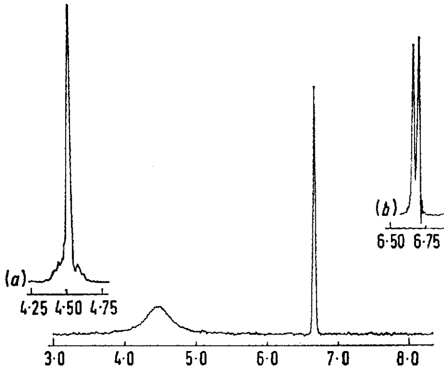


FIGURE 1 ^1H N.m.r. spectrum of germylcyclopentadiene at 35 °C [inset at − 60 °C: (*a*) τ 4·50 region; (*b*) τ 6·50—7·00 region]

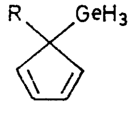
While structure (VI) can be assigned to all ground-state configurations involved in a fluxional rearrangement of compound (I), for (II) the related process necessarily requires exchange between non-equivalent (isomeric) forms. As discussed earlier,[12] those taking part in a metallotropic rearrangement will be restricted to (VII)—(IX) since all other isomers are expected to be non-fluxional. These considerations are supported by the data observed for compound (II). At 35 °C, a spectrum closely resembling that shown in Figure 1 was obtained, with an additional sharp singlet at τ 8·37 due to the methyl protons. Cooling resulted in a slow-exchange limit in which two different Ge*H* resonances were present, each coupling to a tertiary (x) proton; two peaks attributable to the latter showed a chemical-shift difference of 0·24 p.p.m. We assign these features to the two non-*gem*-isomers (VIII) and (IX) (although these two cannot be distinguished from one another without recourse to decoupling experiments) in approximately equal concentrations from peak intensities. From the absence of other signals in this region, the concentration of (VII) or of any vinylic isomer must be very low. Splitting of the methyl resonance centred at

TABLE 1

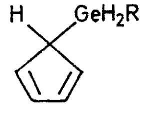
^1H N.m.r. data [a]

t/°C	Compound	Chemical shifts (τ [b])				Coupling constants/Hz	
35		$H_{aa'bb'x}$	H_y	H_z		J_{yz}	
	(I)	4·44 (br)	6·67				
	(II)	4·30 (v.br)	6·68	8·37			
	(III)	4·38 (br)	6·28	10·20		3·5	
	(IV)	4·39	6·39				
−60		$H_{aa'bb}$	H_x	H_y	H_z	J_{xy}	J_{yz}
	(I)	4·50	6·98	6·67		1·7	
	(II) [c]	3·94—4·37 [d]	7·05 7·29	6·70 6·73	9·39 [d]	1·0 1·1	
	(III)	3·71, 3·74	6·75	6·31	10·30	2·0	3·5
	(IV)		4·10 (v.br)	6·40 (br)			
100		$H_{aa'bb'x}$	H_y	H_z		$J_{(aa'bb'x)y}$	J_{yz}
	(I)	4·50—4·59 (br)	6·67			0·45	
	(II)	4·80—4·92 (br)	6·68	8·37		0·55	
	(III)	4·51	6·28 [d]	10·05 [d]		n.r.	n.r.
35		H_{phenyl}	H_{ab}	H_x	H_y	J_{xy}	
	(V)	3·02—3·44 [d]	3·72, 4·10 [d]	6·78	7·00	2·2	

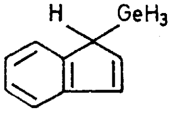
[a] Measured at 60 MHz on neat liquid samples in sealed capillaries as described in Experimental section. Data taken from measurements at *ca.* 10 °C intervals. All changes with temperature of τ and *J* reversible. [b] Proton environments distinguished as follows: a,a′,b,b′ olefinic C_5-ring hydrogen atoms; x, tertiary C_5-ring hydrogen; y, substituent Ge*H* hydrogens; z, substituent methyl hydrogens. Integration gave relative intensities consistent with proposed assignments throughout. [c] Two isomers distinguishable (see text). [d] Multiplet pattern, *J* values not determined.



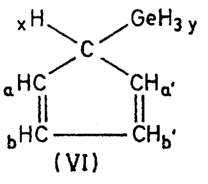
(I; R = H)
(II; R = Me)



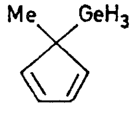
(III; R = Me)
(IV; R = C5H5)



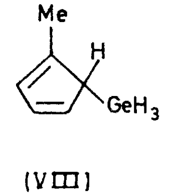
(V)



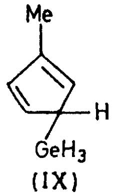
(VI)



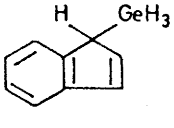
(VII)



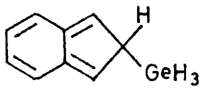
(VIII)



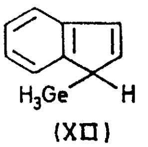
(IX)



(X)



(XI)



(XII)

τ 8·39 was also evident, but coupling constants could not be separated from a possible chemical-shift difference between (VIII) and (IX). The low-field signal consisted of a complex pattern approximating to that expected for the a,a′, b protons.

Observation of coupling between the tertiary ring protons and those of the GeH_3 group thus facilitates identification of species present at the slow-exchange limit, but this provides no new information concerning the nature of the fluxional process. However, on heating compound (I) or (II) towards a fast-exchange limit, coupling between ring- and germyl-protons was again observed, to give respectively a sextet [Figure 2(*a*)] and a quintet [Figure 2(*b*)] at 100 °C. It is clear therefore that the observed coupling involves all ring protons in each case; this constitutes unequivocal evidence for an intramolecular shift of the GeH_3 group as the mechanism giving rise to stereochemical non-rigidity.

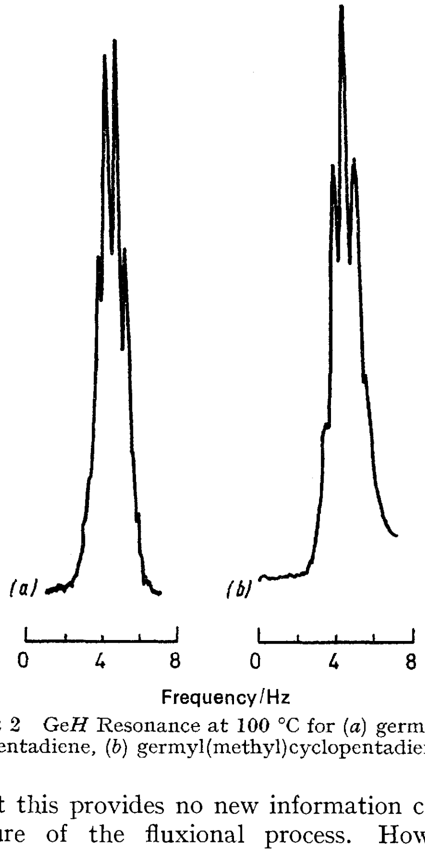


FIGURE 2 Ge*H* Resonance at 100 °C for (*a*) germylcyclopentadiene, (*b*) germyl(methyl)cyclopentadiene

At ambient temperature, compound (III) showed equivalence among the cyclopentadienyl protons, together with the expected coupling between germylene and methyl protons with *J* 3·5 Hz, comparable with that in methylgermane.[13] The methyl resonance was centred at τ 10·20, this unusually high-field shift possibly resulting from the proximity of the C_5H_5 ring. Cooling to −60 °C split each component of the Ge*H* quartet into a doublet, *J* 2·0 Hz, through coupling with H_x, and, unlike compound (I), a chemical-shift difference between $H_{a,a'}$ and $H_{b,b'}$, was resolved although very small (0·03 p.p.m.); the triplet structure of the methyl signal remained unchanged. Heating to 100 °C resulted in collapse of the Ge*H* quartet into a multiplet, not fully resolved but consistent with the quartet of sextets anticipated by analogy with the behaviour of compounds (I) and (II). Unexpectedly, however, concomitant similar collapse of the methyl triplet at τ 10·20 appeared to take place, giving an unresolved pattern. This puzzling observation is being further investigated through examination of related germylene and silylene derivatives but we are unable to account for it at the present time.

Compounds (IV) and (V) provide a contrast to the essentially similar ^1H n.m.r. properties found for (I)—(III). The first of these showed a ‘ dynamic ’ spectrum throughout the temperature range −60 to 100 °C, but coupling of the GeH_2 hydrogen atoms with those of the cyclopentadienyl rings was not observed. Progressive broadening of the C_5H_5 resonance towards −60 °C indicates that the slow-exchange limit may be well below this temperature, showing[2,3,14] qualitatively that fluxional exchange in compound (IV) is much more rapid than for (I)—(III).

Although the substituent-ring proton coupling observed at elevated temperature for compounds (I) and (II) (Figure 2) establishes that fluxional character results through an intramolecular metallotropic shift, it offers no distinction between a 1,2- and a 1,3-rearrangement. For related Group IVB derivatives, the 1,3-mechanism has been considered to be more probable for σ-indenyl compounds than for the analogous cyclopentadienyls.[9] It might be hoped that for compound (V), coupling between the GeH_3 group and the C_5-ring hydrogen atoms would allow a distinction between 1,2- and 1,3-shifts: the first, involving (X)—(XII), might be expected to show a quartet Ge*H* resonance near the fast-exchange limit through coupling with H_{1-3}, whereas for the 1,3-shift coupling with $H_{1,3}$ ($J_{H\mathrm{GeC_1C_2}H}$ very small by analogy with germylcyclopentadiene) only would give rise to a triplet. This hope was not realised in practice, since at 35 °C the spectrum observed was that of the ‘ static ’ configuration (X), assigned in the way shown in Table 1. Between 175 and 195 °C a partial coalescence of the C_5-ring a,b,x pattern could be seen, together with collapse of J_{xy} in the Ge*H* resonance, corresponding to the onset of fluxional exchange on the ^1H n.m.r. time-scale, but further measurements at higher temperature were not possible due to instrumental limitations. Similar differences in rate between the fluxional behaviour of Group IVB indenyls and their cyclopentadienyl analogues have been emphasised elsewhere,[9] a possible contributing factor being involvement in a 1,2-metallotropic shift of the energetically unfavoured iso-indenyl structure (XI).

Vibrational Spectra.—Data for compound (I) are

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[13] J. E. Drake, R. T. Hemmings, and C. Riddle, *J. Chem. Soc.* (*A*), 1970, 3359.

[14] J. L. Calderon, F. A. Cotton, and J. Takats, *J. Amer. Chem. Soc.*, 1971, **93**, 3587; F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257.

collected in Table 2, and confirm by their complexity, particularly in the C–H stretching region, the incidence of a low-symmetry, σ-bonded structure.[2] Considerations based on the point group C_s predict that of the $20a' + 16a''$ fundamentals those associated with the germyl group will account for $5a' + 3a''$; these latter were observed in the i.r. spectrum near 2 100 (Ge–H stretching, $2a' + a''$), at 800—900 (GeH_3 deformations, $2a' + a''$), and more tentatively at 520 cm^{-1} (GeH_3 rocking, $a' + a''$) close in wavenumber to the corresponding a_1 and e modes in the spectrum of methylgermane.[15] Polarization properties of Raman counterparts further allowed separation into a' and a'' vibrations in each case.

TABLE 2

Vibrational spectrum (cm^{-1}) of germylcyclopentadiene

I.r. (gas)	Raman (liquid)	Approximate description [a]
3 105	3 120w, pol	
3 093 m	3 089m, pol	
3 082		
	2 965w	ν(CH)
2 932w	2 2928m, pol	
	2 835w	
2 120s, sh		ν_{asym}(GeH)
2 099 vs	2 053vs, pol	ν_{sym}(GeH)
2 088		
1 635w		
	1 600m, pol	ν(C=C)
	1 565w, pol	
1 492*R*		
1 486*Q* m	1 480w	
1 470*P*	1 460vs, pol	ν(C=C) + α(C=C–H)
	1 430w	
1 396m	1 380m, dp	
1 292vw		
1 230 w	1 200w, pol	
1 223		
1 130	1 120sh	ν(CC) + ν(C=C) + α(C=C–H)
1 118w, br	1 110s, pol	
1 100	1 090w, dp	
1 001 s	1 012m ,pol	
996	948vs, pol	ν(CC)
961*R*		
955*Q* m	950m, dp	γ(C–H) + α(C–C–H)
950*P*		
	910w, dp	
894*R*		
887*Q* s	877s, dp	$\delta_{asym}(GeH_3)$
881*P*		
871m, sh		
830*R*		
823*Q*	824s, pol	
820 vvs	820m, sh, dp	$\delta_{sym}(GeH_3)$
815*P*		
811		
788*R*		
781*Q* m		
774*P*	770m, pol	β(C–C–C)
680*R*		
675*Q* s	672s, pol	γ(C–H)
667*P*		
593 m	595vw	
589		
520m, br	530vw, br	$\rho(GeH_3)$
360m	369vs, pol	ν(Ge-ring)
	315vw	
	270vw	
	194w, dp	δ(Ge-ring)
	115m, dp	

[a] *Cf.* ref. 17 for classification of ring modes.

Vibrational analysis of the cyclopentadiene molecule has been the subject of two recent studies,[16,17] which emphasise the likelihood of extensive mixing of individual modes; nevertheless, comparison with these results allows an approximate assignment of remaining features observed above 500 cm^{-1} for compound (I) in the way suggested in Table 2. In a similar fashion, the i.r. and Raman wavenumbers listed for compounds (II)—(V) in the Experimental section can be divided first into those providing evidence for the presence of a GeH_3 or GeH_2 group, and secondly those characteristic of the appropriate cyclopentadienyl unit.

The spectrum of cyclopentadiene contains[16,17] no strongly Raman-active vibrations below 500 cm^{-1}. Consequently, the intense and polarised band at 369 cm^{-1} for compound (I) can be attributed to the a' Ge–C(ring) stretching fundamental. This conclusion is supported by the appearance of similar shifts at 377—392 cm^{-1} for compounds (II), (IV), and (V). For (III), both types of Ge–C stretch could be distinguished in the Raman effect: again, a band due to ν[Ge–C(ring)] at 371 cm^{-1}; and also ν[Ge–C(methyl)], at 603 cm^{-1}. These observations establish a wavenumber region for germanium-to-cyclopentadienyl stretching which is substantially lower in energy than that for ν(Ge–C) in alkylgermanes,[15,18] and which may be compared with a value of 413 cm^{-1} for ν[(Si–C(ring)] in $Me_3Si(C_5H_5)$ given elsewhere.[19] Further Raman bands for compound (I) at 194 (dp) and 115 cm^{-1} (pol) can tentatively be assigned respectively to a'' and a' Ge–C(ring) bending modes.

Mass Spectra.—The polyisotopic character of germanium combined with the occurrence of stepwise hydrogen loss from hydride species gives rise to families of fragment ions in the mass spectra of germane derivatives, but while complete analysis can present difficulties as discussed elsewhere[18,20] predominant features are usually readily discernable.

Mass spectral data are summarised in Table 3. All five compounds clearly showed parent-ion families which included that involving ^{76}Ge (*i.e.* the molecular ion) and which, except for compound (IV), had strikingly high abundances. For the monosubstituted germanes (I), (II), and (V), all other metal-containing ions were present in only low abundance and the remaining intense fragment is that due to the organo-group in each case. Different behaviour was evident for compounds (III) and (IV), cleavage of a germanium–carbon bond corresponding to process (1) giving rise to strong

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[15] D. F. Van de Vondel and G. P. Van der Kelen, *Bull. Soc. chim. belges*, 1965, **74**, 453.

[16] E. Gallinella, B. Fortunato, and P. Mirone, *J. Mol. Spectroscopy*, 1967, **24**, 345.

[17] K. E. Blick, J. W. deHaan, and K. Niedenzu, *Spectrochim. Acta*, 1970, **26***A*, 2317.

[18] A. Carrick and F. Glockling, *J. Chem. Soc.* (*A*), 1966, 623; K. M. Mackay, R. D. George, P. Robinson, and R. Watt, *ibid.*, 1968, 1920.

[19] H. P. Fritz, *Adv. Organometallic Chem.*, 1964, **1**, 239.

[20] K. M. Mackay, S. T. Hosfield, and S. R. Stobart, *J. Chem. Soc.* (*A*), 1969, 2312; R. D. George, K. M. Mackay, and S. R. Stobart, *ibid.*, 1970, 3250.

$RGeH_x^+$ ion multiplets ($R = Me$ or C_5H_5, the latter in both cases; $x = 0$ or 1) of substantially higher abundance than the parent family. By contrast loss of a methyl group from compound (II) did not appear to be important, $C_5H_xGe^+$ ions here being very low in intensity.

TABLE 3

Ion abundances

	Compound				
	(I)	(II)	(III)	(IV)	(V)
Ion	*A* [a]	*A*	*A*	*A*	*A*
$GeC_{10}H_x^+$				5·9 [b]	
$GeC_9H_x^+$				1·4	23·1 [b]
$GeC_7H_x^+$				0·1	1·1
$GeC_6H_x^+$		17·0 [b]	9·3 [b]	0·1	0·5
$GeC_5H_x^+$	33·6 [b]	3·2	27·0	45·1	1·4
$C_{10}H_x^+$				1·9	
$GeC_4H_x^+$	1·8	2·5	2·4	0·1	0·8
$C_9H_x^+$					53·8 [c]
$GeC_3H_x^+$	11·2	4·1	6·7	8·0	
$GeC_2H_x^+$	5·3	6·8	3·0	4·0	1·6
$C_7H_5^+$					2·9
$GeCH_x^+$	1·6		20·4		2·0
$C_6H_x^+$		42·4 [d]	0·5	2·8	
GeH_x^+	5·0	4·7	3·5	3·5	1·9
$C_5H_x^+$	33·0 [f]		18·9 [g]	14·6 [h]	5·6
$C_4H_x^+$	0·6	9·5	0·9	3·1	1·2
$C_3H_x^+$	7·3	6·1	6·3	10·8	2·6
$C_2H_x^+$	0·7	3·6	0·9	1·9	1·5

[a] *A* = % ion abundance, summed over x and Ge isotopes where applicable. No entry: ion not present in spectrum, or $A \approx 0$. [b] Parent-ion family. [c] $x = 9$, 13·9; $x = 8$, 14·7; $x = 7$, 21·7%. [d] $x = 9$, 21·0; $x = 8$, 5·8; $x = 7$, 8·3%. [e] $x = 9$ only observed. [f] $x = 7$, 19·1; $x = 6$, 8·8; $x = 5$, 2·6%. [g] $x = 7$, 6·3; $x = 6$, 7·6; $x = 5$, 2·9%. [h] $x = 7$, 1·7; $x = 6$, 7·0; $x = 5$, 3·3%.

$$R^1R^2GeH_2^{+\bullet} \longrightarrow \begin{cases} R^1GeH^{+\bullet} + R^2H \\ R^2GeH^{+\bullet} + R^1H \end{cases} \qquad (1)$$

$$(R^1 = Me,\ R^2 = C_5H_5;\ \text{or}\ R^1 = R^2 = C_5H_5)$$

An intriguing feature of the fragmentation of these molecules is the transfer of hydrogen atoms presumably initially bonded to Ge to the unsaturated carbon skeleton of the organic grouping. Thus for compound (I) the most abundant C_5-containing ion was not that with *m/e* either 65 or 66 ($C_5H_5^+$ or $C_5H_6^{+\bullet}$) although both of these were present, but that at *m/e* = 67, $C_5H_7^+$ (Table 3). Analogously, for (II) and (V) ions due to $C_6H_9^+$ and $C_9H_9^+$ respectively were very intense, suggesting that process (2) may be occurring, involving elimination of Ge as a neutral species. This has been observed for certain other organogermanes[21] where the ionization potential of a hydrocarbon radical is lower than that of the metal. For the diorganogermanes (III) and (IV) strong $C_5H_6^{+\bullet}$ fragments occurred with $C_5H_7^+$ lowered in abundance. Only very limited loss of hydrogen within parent-ion families was evident and might be associated with these observations; for example, for compound (I) all $C_5H_xGe^+$ ions had $x = 5$—8, while for (III) $C_6H_xGe^+$ ions were almost entirely those with $x = 10$. Corresponding transfer of both organic groups and hydrogen across germanium–metal bonds is well established in the mass spectra of germanes and their organo-derivatives.[18,20,21]

$$RGeH_x^+ \longrightarrow RH_x^+ + Ge \qquad (2)$$

Fragmentation of the C_5 ring without loss of Ge was also observed for compound (I) as a metastable-supported process, (3). Weak rearrangement ions $C_{10}H_x^+$ ($x = 8$—12) and $C_6H_6^{+\bullet}$ were detected for compound (IV), and similarly $C_6H_9^+$ was observed for (III). Doubly charged ions arising from the highly abundant hydrocarbon fragments could be distinguished in each case, $C_9H_7^{2+}$ for (V) being the most prominent of these.

$$C_5H_8Ge^{+\bullet} \longrightarrow C_3H_4Ge^{+\bullet} + C_2H_4 \qquad (3)$$
$$m^* = 87{\cdot}8,\ 89{\cdot}5,\ \text{and}\ 91{\cdot}5$$

Reactivity of Germylcyclopentadiene.—The high thermal stability of the monomeric (I) molecule is emphasised by its recovery in 31% yield after 94 h at 64 °C. The ^1H n.m.r. spectrum of the involatile product formed as a result of heating under these conditions is consistent with Diels–Alder addition to give dimerized species, possibly present as more than one isomer. Examination of the recovered compound (I) using the same technique revealed that partial isomerization of the initially pure 1-germylcyclopentadiene to the 2- and 3-germyl forms had taken place. Ashe[22] and Abel[10] have noted similar behaviour for $Me_3Si(C_5H_5)$, and have discussed the prototropic rearrangement whereby vinylic isomers must be formed. By analogy with the assignment of their ^1H n.m.r. data, we suggest interpretation of resonances observed for the mixture of germyl isomers in the way shown in Table 4. Heating to 133 °C for a shorter period resulted in a smaller recovery (16%) of compound (I) but produced no marked change in the proportion of vinylic species, suggesting that, as in the case of the trimethylsilyl compound,[10] their formation is reversible.

TABLE 4

^1H N.m.r. parameters [a] for germylcyclopentadiene isomers

	$\tau\ H_{2-5}$	$\tau\ H_1$	$\tau\ GeH_3$	% Present in mixture [b]
$1\text{-}GeH_3(C_5H_5)$	3·95		6·25	78
$2\text{-}GeH_3(C_5H_5)$	3·37	6·92	6·17	15
$3\text{-}GeH_3(C_5H_5)$	3·11	6·66	5·96	7

[a] $CDCl_3$ Solution at 35 °C relative to internal Me_4Si. [b] After heating as described in the text.

With dry HCl, 32% completion of reaction occurred according to equation (4). Remaining material was involatile and presumably polymeric in nature. No analogous cleavage occurred with formic acid. Reaction of compound (I) with primary and secondary amines to give digermane and trigermane has already been

$$(C_5H_5)GeH_3 + HCl \longrightarrow GeH_3Cl + C_5H_6 \qquad (4)$$

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[21] D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev.*, 1968, **22**, 317.

[22] A. J. Ashe, *J. Amer. Chem. Soc.*, 1970, **92**, 1233.

communicated[23] and is being investigated further. Methanethiol, a reagent which very readily protolyses tin(II) cyclopentadienyl compounds to give a tin(II) dithiolate,[24] was without effect on compound (I). Likewise, attempted deprotonation of (I) in an effort to obtain $[(C_5H_4)GeH_3]^-$ proved to be unpromising both with potassium and butyl-lithium, although the latter readily forms salts with cyclopentadiene and methylcyclopentadiene.

A slow reaction at 60 °C with Me_3SnH produced, in addition to monogermane, a small amount of a liquid product with chemical shifts and proton–tin coupling constants identical with those reported[2] for $Me_3Sn(C_5H_5)$, indicating reaction (5a), though to only a small extent; an additional product, however, present in a ratio of about 0·3 : 1 with $Me_3Sn(C_5H_5)$, showed n.m.r. signals appropriate for the novel compound Me_3SnGeH_3, so that we tentatively suggest that reaction (5b) may also be occurring.

$$(C_5H_5)GeH_3 + Me_3SnH \begin{array}{l} \nearrow Me_3Sn(C_5H_5) + GeH_4 \qquad (5a) \\ \searrow Me_3SnGeH_3 + C_5H_6 \qquad (5b) \end{array}$$

EXPERIMENTAL

Manipulation of volatile compounds was carried out using a conventional vacuum system with taps and joints lubricated with Apiezon N grease. I.r. spectra were measured using a Perkin-Elmer 457 spectrometer, Raman spectra from 488·0 nm (argon-ion laser source) with a Cary 83 instrument, and mass spectra with an AEI MS902 mass spectrometer. For all ^1H n.m.r. measurements, a Varian A60-D instrument was used; chemical shifts at 35 °C were determined relative to Me_4Si in $CDCl_3$ contained in standard 5 mm n.m.r. tubes, in which samples of the compounds under investigation, sealed *in vacuo* in 2 mm o.d. micro-tubes, were immersed and centred. This technique facilitated variable-temperature measurements in the range −80 to 195 °C, the $CDCl_3$–Me_4Si being replaced by either CS_2 or hexachlorobutadiene where necessary.

Bromogermane and dibromogermane were prepared by direct bromination of germane at −78 °C followed by separation at −45 °C. Methylgermane, obtained by $LiAlH_4$ reduction of $MeGeCl_3$, was reacted with BCl_3 to give chloromethylgermane as described by Drake *et al.*[13] Cyclopentadiene and methylcyclopentadiene were obtained by thermal cracking of the dimers, and indene was purified by condensation in a trap at 0 °C; these materials were then converted to their potassium salts by reaction with the metal in dry diethyl ether at −78 °C, giving involatile, air-sensitive white ($C_5H_5^-$ and $MeC_5H_4^-$) or pale green ($C_9H_7^-$) products.

Preparations.—Germylcyclopentadiene, (I). Typically, bromogermane (1·446 g, 9·22 mmol) was condensed on to excess of solid $K(C_5H_5)$. Slow warming (20 min) to room temperature followed by fractionation through traps at −45, −63, and −196 °C afforded, in addition to small amounts of GeH_4 and C_5H_6 at −196 °C, *germylcyclopentadiene* (949 mg, 6·73 mmol, 73%) held as a colourless liquid at −63 °C (Found: C, 42·3; H, 5·55. Calc. for C_5H_8Ge: C, 42·65; H, 5·70%). Vapour pressure: at 0·1, 10·8; at 20·4 °C, 31·8 mmHg.

Germyl(methyl)cyclopentadiene, (II). Reaction between bromogermane and $K(C_5H_4Me)$ under identical conditions gave the liquid *product* (*ca.* 45%) which distilled very slowly out of a trap at −45 °C (Found: C, 46·65; H, 6·40. Calc. for $C_6H_{10}Ge$: C, 46·55; H, 6·45%). Vapour pressure: at 0·2, 3·3; at 19·1 °C, 10·3 mmHg. I.r. (gas phase): 3 080m; 2 975m,sh; 2 935m; 2 890m; 2 102s; 2 078vs; 1 600w,br; 1 450w,br; 1 380m,br; 1 300w; 995m; 950w; 880s; 820vs; 730w; 680s,sh; 670s; 590w; 560w; and 515w,br cm^{-1}. Raman (pure liquid): ν(GeH) 2 075vs, pol; $\delta(GeH_3)$ 831w, 810w, pol; ν[C(Me)–C(ring)] (?), 405s, pol; ν[Ge–C-(ring)] 377vs, pol; δ[C(Me)–C(ring)] (?), 262m, pol; and δ[Ge–C(ring)] 160m, dp,110m, pol cm^{-1}.

Methylgermylcyclopentadiene, (III). Similar reaction between pure $MeGeH_2Cl$ and $K(C_5H_5)$ yielded the colourless liquid *product* (25%), held at −45 °C and characterized by Raman, n.m.r., and mass spectroscopy. I.r. (gas phase): 3 095m; 3 000w; 2 934m; 2 084s,sh; 2 063, 2 054vs; 1 635vw,br; 1 472m; 1 390vw,br; 1 247m; 1 090vw; 983s; 950m; 881s; 867m,sh; 830vs; 773m; 694vs,sh; 675vs; 666vs,sh; and 600m cm^{-1}. Raman (pure liquid): ν(GeH) 2 065s, pol; $\delta(GeH_2)$ 831m, pol; ν(GeC) 603vs, pol; ν[Ge–C(ring)], 371vs, pol; δ[C–Ge–C(ring)] 228m, pol; and δ[Ge–C(ring)], 194m,dp cm^{-1}.

Germylindene, (V). On warming bromogermane to −30 °C with solid $K(C_9H_7)$ the mixture changed in colour from pale green to bright canary yellow. Warming further to room temperature over 30 min followed by fractionation gave in addition to indene, held in a trap at −25 °C, the liquid colourless *product* condensed at 0 °C (Found: C, 56·3; H, 5·25. Calc. for $C_9H_{10}Ge$: C, 56·65; H, 5·30%). I.r. (liquid film): 3 060s,br; 2 910m,br; 2 065vs; 1 450m; 1 220w; 1 195w; 1 030m; 980w; 930w,br; 865m; 810vs; 752vs; 732m; 685w; 605w; 586w; 556w; 510w,br; 430m; and 385w cm^{-1}. Raman (pure liquid): ν(GeH), 2078s, pol; $\delta(GeH_3)$, 815w, pol; and ν[Ge–C(ring)], 391vs, pol cm^{-1}.

Bis(cyclopentadienyl)germane, (IV). Pure GeH_2Br_2 and excess of $K(C_5H_5)$ were held together at −20 °C for 90 min, after which time slow warming to 20 °C followed by prolonged pumping through a trap held at 0 °C afforded the liquid *product*, characterized by exact mass determination for the ion $^{12}C_{10}{}^{1}H_{12}{}^{76}Ge^+$ (Found: m/e = 208·0155. Calc.: m/e = 208·0154). Raman (pure liquid): 3 115m; 3 080m; 2 935m,br; 2 040s, pol; 1 605vw; 1 550vw; 1 462vs, pol; 1 380m; 1 115s; 1 090w; 1 020m; 970vs, pol; 950s; 910m; 860w,br; 830m; 779m; 716w; 683m; 668m; 620m,br; 480m,sh; 359vs, pol; 300w; 230w,br; and 190w,br cm^{-1}.

Reactions of Germylcyclopentadiene.—Thermal stability. A sample of germylcyclopentadiene (70·4 mg, 0·51 mmol), previously shown by n.m.r. to consist entirely of the 1-isomer, was sealed in a glass break-seal tube and heated at 64 °C. After 94 h the tube was opened and products separated to give a fraction condensing at −63 °C and a liquid phase involatile at 20 °C. The ^1H n.m.r. spectrum of the latter was complex, showing resonances at τ 3·5—4·6, near τ 7·0 and 8·5, and with seven lines in the 6·0—6·8 region; the volatile component possessed a gas-phase i.r. spectrum showing it to be germylcyclopentadiene (22·7 mg,

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[23] P. C. Angus and S. R. Stobart, *J.C.S. Chem. Comm.*, 1973, 127.

[24] P. G. Harrison, *J.C.S. Chem. Comm.*, 1972, 544; P. G. Harrison and S. R. Stobart, *Inorg. Chim. Acta.*, 1973, **7**, 306.

0·16 mmol), but the ^1H n.m.r. spectrum included, in addition to expected resonances, new peaks, at τ 3·11, 3·34, 5·96, 6·17, 6·66, and 6·92 in $CDCl_3$ solution, attributable to vinylic isomers present in the ratios 0·10 and 0·20 : 1 with the 1-isomer. A further experiment with heating at 133 °C for 26 h yielded 16% recovery of germylcyclopentadiene showing identical ^1H n.m.r. features but with ratios of vinylic isomers increased slightly to 0·12 and 0·24 : 1.

With hydrogen chloride. Germylcyclopentadiene (65·9 mg, 0·47 mmol) and excess of dry HCl were allowed to react at 20 °C for 1 h, after which time the only volatile products were chlorogermane (16·1 mg, 0·15 mmol) and traces of C_5H_6.

With formic acid and methanethiol. Prolonged gas-phase contact (24 h) at 20 °C produced no reaction between germylcyclopentadiene and either of these reagents.

With trimethylstannane.—Germylcyclopentadiene (101·8 mg, 0·72 mmol) and Me_3SnH (184·2 mg, 1·11 mmol) were heated together at 60 °C for 12 h, when the liquid phase was pale yellow. Fractionation afforded GeH_4 (10·2 mg, 0·14 mmol), unchanged germylcyclopentadiene (44·1 mg, 0·31 mmol), traces of C_5H_6, unreacted Me_3SnH, and a small condensate (*ca.* 15 mg) held at −45 °C. Examination of the latter by ^1H n.m.r. spectroscopy revealed signals at τ 3·98 and 9·97, ratio *ca.* 5 : 9, showing satellites due to proton–tin coupling respectively with J 22·6 and 52·7, 54·9 Hz; weaker features at τ 5·73 and 9·47, ratio *ca.* 1 : 3, the second with satellite J *ca.* 55 Hz, were also observed. A yellow involatile gum remained in the reaction vessel.

With potassium metal. Germylcyclopentadiene (45·0 mg, 0·32 mmol) was condensed on to potassium (19·8 mg) in dry diethyl ether. Warming to room temperature resulted in a slow reaction to give hydrogen (2·23 ml at 0 °C and 760 mmHg) and an insoluble orange material. Removal of volatiles, including GeH_4 (8·9 mg, 0·11 mmol), was followed by treatment of the orange solid first with MeI and then with HCl, but neither reaction produced any volatile Ge-containing species.

With butyl-lithium. Successive treatment of germylcyclopentadiene with butyl-lithium in pentane (to give a white precipitate) and methyl iodide gave only GeH_4 and C_2H_6 as volatile products.

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