Vinyl Derivatives of Silicon, Germanium, and Tin

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Reaction of MCl_4 (M = Si, Ge, or Sn) with vinylmagnesium bromide yields $M(CH{:}CH_2)_4$ as the major product for M = Si or Sn, but $Ge(CH{:}CH_2)_4$ and $Ge_2(CH{:}CH_2)_6$ are formed in comparable yield. Isolation of metal–metal bonded derivatives has allowed characterization by i.r., Raman, ^1H n.m.r., and mass spectroscopy of the compounds $M_2(CH{:}CH_2)_6$ (M = Si, Ge, or Sn). The mass spectra of tetravinyl-silane, -germane, and -stannane are reported and discussed in terms of the effect on fragmentation patterns of M–C bond strength. Tetravinylgermane is chemically very unreactive, but with dibromine in an equimolar ratio one Ge–C bond is cleaved to give $GeBr(CH{:}CH_2)_3$ while with dichlorine addition occurs forming $Ge(CHCl{\cdot}CH_2Cl)_4$.

VINYL derivatives of metals have been extensively studied[1] and the tetrasubstituted species thoroughly characterized for all the Group 4B elements.[2,3] Seyferth reported[2] that Grignard alkylation of germanium tetrachloride using vinylmagnesium bromide in tetrahydrofuran (thf) solution affords hexavinyldigermane as well as tetravinylgermane, the two compounds being formed in comparable yield. By contrast, similar treatment of silicon and tin tetrachlorides is said to produce only the tetravinyl derivatives.[3] The identification of metal–metal bonded compounds M_2R_6 as products of reactions of MCl_4 ($M = Si$ or Ge) with alkyl Grignard reagents in mixtures containing excess of magnesium metal however has led to the conclusion that insertion of Mg into the Ge–X bond of an organogermanium halide can occur[4] to give an organogermanium Grignard analogue [equation (1)]. Specific experiments designed to test this hypothesis have

$$MCl_4 \xrightarrow{RMgX} M(X)R_3 \xrightarrow{Mg} (R_3M\text{-}Mg\text{-}X) \xrightarrow{M(X)R_3} M_2R_6 \quad (1)$$

shown that in fact no reaction takes place between $Ge(Cl)R_3$ ($R = Me$ or Et) and magnesium metal under Grignard conditions, but have tended to substantiate the intermediacy of a germanium–magnesium complex originating from a Grignard-exchange reaction.[5] The alkylation of $GeCl_2$, formed through a reductive effect of the organomagnesium reagent on $GeCl_4$, has been proposed[2] as a possible alternative mechanism for the formation of $Ge_2(CH{:}CH_2)_6$ in substantial yield and could also account for the appearance of higher polygermanes in other reactions.

We now report a more detailed investigation of the reaction between the Group 4B tetrachlorides and vinylmagnesium bromide. This fully confirms the experimental observations of Seyferth[2] and has further resulted in the characterization of the hexavinyldimetal derivatives of silicon and tin together with octavinyltrisilane and -germane. Spectroscopic properties of some of the polymetallic compounds have been recorded. Analysis of the mass spectra of the pervinylmetal derivatives has established close similarities with those of the Group 4B tetra-allyls, which have been the subject of a detailed paper by Fishwick and Wallbridge.[6] Some reactions of tetravinylgermane have also been examined.

RESULTS AND DISCUSSION

Using thf as solvent, vinylmagnesium bromide reacted rapidly and exothermically with each of the tetrachlorides studied (those of Si, Ge, and Sn) and with hexachlorodisilane. In each case, yields of different vinylmetal derivatives were reasonably consistent for replicate experiments, and typical data are given in Table 1. Products were separated by fractional distillation or vapour-phase chromatography as shown in Table 2 for the germanes.

TABLE 1

Products from reactions with vinylmagnesium bromide

	Product yield [a]/%			
Reactant	$M(CH{:}CH_2)_4$	$M_2(CH{:}CH_2)_6$	$M_3(CH{:}CH_2)_8$	Polymeric [b]
$SiCl_4$	77·0	5·1	2·4	medium
$GeCl_4$	50·4	36·1	8·9	low [c]
$SnCl_4$	88·1	1·1	*d*	low [d]
Si_2Cl_6	*d*	53·0	trace?	high

[a] Based on quantity of halide used. [b] Qualitative estimate of yield of non-volatile material. [c] A further component isolated in very low yield (*ca.* 0·05 g) by g.l.c. was identified (mass spectrum) as $Ge_2(CH{:}CH_2)_3Cl_3$. [d] Not observed. [e] In some experiments crystalline material was obtained, possibly consisting of mixtures of pervinylcyclopolystannanes.

TABLE 2

Vinylgermanes

	Analyses/%					
	Calc.		Found			
Compound	C	H	C	H	B.p.(θ_c/°C), *P*/mmHg	Retention time/min [a]
$Ge(CH{:}CH_2)_4$	53·2	6·65	53·4	6·80	52—54, 27 [b]	4·9
$Ge_2(CH{:}CH_2)_6$	46·9	5·85	47·0	5·75	68—72, 0·1	15·0
$Ge_3(CH{:}CH_2)_8$	44·25	5·55	44·5	5·65	85—95, 0·005	59·0

[a] At 180 °C using g.l.c.; conditions as given in Experimental section. [b] Lit. value.[2] Isolated by condensing at −45 °C *in vacuo* using trap-to-trap distillation.

The high proportion of pervinylpolygermanes formed from $GeCl_4$ is of considerable interest and is not paralleled either by silicon or by tin, for each of which the tetravinylmetal derivative is the major product. Assumptions based on a 'reductive-coupling' mechanism for the formation of polymetallic species predict their isolation in increasing yield in the order $Si < Ge < Sn$, consistent with the increase in stability of the bivalent

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[1] D. Seyferth, *Progr. Inorg. Chem.*, 1962, **3**, 129.

[2] D. Seyferth, *J. Amer. Chem. Soc.*, 1957, **79**, 2738.

[3] S. D. Rosenberg, A. J. Gibbons, and H. E. Ramsden, *J. Amer. Chem. Soc.*, 1957, **79**, 515; D. Seyferth and F. G. A. Stone, *ibid.*, p. 2137.

[4] F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 1962, 3509.

[5] D. Quane and G. W. Hunt, *J. Organometallic Chem.*, 1968, **13**, P16; D. Quane, D. Garner, and P. Sheard, *Abs. 6th Internat. Conf. Organometallic Chem.*, Amherst, 1973, paper no. 168.

[6] M. Fishwick and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1971, 57.

state (for Sn^{II}, stable organic[7] and many inorganic derivatives have been obtained). However, organotin compounds with metal–metal bonds would be cleaved more easily than their germanium analogues; in particular, tin–tin bonds are known[8] to be broken by reaction with alkyl halides and by metal halides such as $AlCl_3$. Reactions of polytin species with free vinyl bromide, magnesium halide, or vinylmagnesium bromide would diminish the extent of their recovery as final products and contribute to the yield of tetravinylstannane or of highly polymeric material. Resistance of vinylpolygermanes to similar decomposition is consistent with the low reactivity of vinylgermanes indicated in this work and elsewhere.[2] An alternative rationalization of the observed distribution of products is that tin–magnesium compounds are formed very much less readily than their germanium counterparts, but this is not supported by the known chemistry of such species. For example, hexaphenyldistannane is cleaved by magnesium in thf giving $Mg(SnPh_3)_2$ whereas the corresponding digermane is unreactive.[9] The reaction between vinylmagnesium bromide and hexachlorodisilane led to isolation of hexavinyldisilane in 53% yield. A relatively large amount of greasy, non-volatile, material was also formed and no higher vinylpolysilanes were obtained.

Following some preliminary studies, Seyferth commented on the apparently low reactivity of tetravinylgermane compared to its tin analogue and attributed this to a significant difference in mean metal–carbon bond energy.[2] Our observations confirm a sometimes surprisingly inert character, even in relation to the behaviour of alkyl(vinyl)germanes. Like the latter, $Ge(CH{:}CH_2)_4$ and $Ge_2(CH{:}CH_2)_6$ are resistant to thermal polymerization and were recovered virtually quantitatively after long periods (>20 d) at 100—120 °C. Like the tetravinyl compound,[2] $Ge_2(CH{:}CH_2)_6$ was unaffected by prolonged heating with $GeCl_4$, and neither of the two reacted when heated under reflux in anhydrous acetic acid. Mercaptoglycolic acid reacts exothermically with trialkyl(vinyl)germanes to saturate the double bond[10] but was without effect on $Ge(CH{:}CH_2)_4$. No redistribution of the latter occurred with tetramethyltin, but with $SnCl_4$ at room temperature a slow reaction took place to give traces of chlorotrivinylgermane and a mixture of acetylene and ethylene. Under identical conditions, ethylene (only) was also evolved in substantial yield from mixtures of $Ge(CH{:}CH_2)_4$ and either chlorodiphenylphosphine or disodium tetrachloropalladate(II) in ethanol, but no volatile germanium-containing products could be isolated. With dry HCl at 100 °C for 21 d in a break-seal tube, tetravinylgermane was partially chlorinated to give chlorotrivinylgermane in 10% yield, but bubbling HCl gas through a hexane solution for 30 min gave only unreacted material.

Reaction of $Ge(CH{:}CH_2)_4$ with halogens provided evidence for a gradation in behaviour similar to that indicated by Seyferth's work for $Ge_2(CH{:}CH_2)_6$: the latter was brominated smoothly at ambient temperature with cleavage of the Ge–Ge bond forming $GeBr(CH{:}CH_2)_3$, whereas iodination was slow even under reflux conditions.[2] Tetravinylgermane did not react with di-iodine when heated under reflux in chloroform, but with dibromine immediate decolorization was observed, one Ge–C bond being cleaved with the formation of bromotrivinylgermane. By contrast, bubbling dichlorine through a solution of $Ge(CH{:}CH_2)_4$ in CCl_4 for 20 min led to isolation of a rather viscous colourless liquid shown by analysis to be $Ge(CHCl{\cdot}CH_2Cl)_4$, although mass spectroscopy suggested the presence of traces of chlorotrivinylgermane. For alkenyltriethylgermane, dibromine has been reported to cleave short side-chains (*e.g.* allyl) but saturate double bonds more remote from the metal atom.[11]

The vibrational spectra of the tetravinyl derivatives $M(CH{:}CH_2)_4$ (M = Si, Ge, Sn, or Pb) have been exhaustively discussed by Masetti and Zerbi.[12] Observation of extensive coincidence between i.r. and Raman bands attributable to M–C=C skeletal fundamentals led these authors to conclude that in the liquid and solid states low symmetry (C_2 or C_s) configurations predominate for each compound. Conversely, in an independent study of $Si(CH{:}CH_2)_4$, Davidson[13] proposed an almost complete assignment of gas-phase i.r. and liquid-phase Raman data in terms of idealized D_{2d} symmetry; however, a much more complex i.r. spectrum was observed for the solid. In the latter work, only very tentative evidence for interaction between vinyl π-electrons and silicon $3d$ orbitals could be found in the form of a shift of *ca.* 50 cm^{-1} to lower wavenumber of $\nu(C{=}C)$ relative to the terminal alkenes $RCH{:}CH_2$. However, more recently it has been suggested[14] that interpretation of the photoelectron spectra of mono-, di-, and tetra-vinylsilanes together with associated calculations necessitates the inclusion of d-orbital involvement in the Si–C bond, implying a significant $(p\rightarrow d)\pi$ interaction.

The i.r. and Raman spectra of the metal–metal bonded species $M_2(CH{:}CH_2)_6$ closely resembled those of the corresponding $M(CH{:}CH_2)_4$ compounds, and were assigned (Table 3) by analogy with published data for the latter. Characteristic differences between vibrational spectra for the two groups of compounds could not be found, unlike $GePh_4$ and Ge_2Ph_6 which can be distinguished by i.r. spectroscopy.[4] Each of the $M_2(CH{:}CH_2)_6$ derivatives (M = Si, Ge, or Sn) showed three very strong, polarized, Raman shifts near 1 590, 1 400, and 1 260 cm^{-1}, respectively assigned to a totally

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[7] L. D. Dave, D. F. Evans, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3684; P. G. Harrison and S. R. Stobart, *J.C.S. Dalton*, 1973, 940.

[8] W. P. Neumann, 'The organic chemistry of tin,' Interscience, 1970.

[9] T. McBride, unpublished work.

[10] P. Mazerolles and M. Lesbre, *Compt. rend.*, 1959, **248**, 2018.

[11] P. Mazerolles, M. Lesbre, and S. Marre, *Compt. rend.*, 1965, **261**, 4134.

[12] G. Masetti and G. Zerbi, *Spectrochim. Acta*, 1970, **A26**, 1891.

[13] G. Davidson, *Spectrochim. Acta*, 1971, **A27**, 1161.

[14] U. Weidner and A. Schweig, *J. Organometallic Chem.*, 1972, **37**, C29; **39**, 261.

symmetric C=C stretch, a CH_2 scissors, and a CH deformation mode. For the disilane, weak depolarized components present at higher wavenumber in each case are attributable to corresponding asymmetric vibrations. As suggested above, the observation of $\nu(C{=}C)_{sym}$ below 1 600 cm^{-1} may reflect some degree of donation of π-electron density towards the metal atom involving occupation of vacant metal *d* orbitals.

wavenumbers measured for hexavinyldi-germane and -stannane (230 and 169 cm^{-1}) are of considerable interest. This corresponds to a frequency decrease of *ca.* 15% in each case, which seems excessive for a simple substituent mass effect, and in contrast to M_2Ph_6 there are no strongly active symmetric vibrations of similar energy with which extensive mixing might be anticipated.[16] It is tempting therefore to seek a mechanism to account for weakening of the metal–metal bond through population of metal *d* orbitals. However, we feel that the association of any such percept with the lowering in $\nu(C{=}C)_{sym}$ as tenuous evidence for vinyl–metal $(p\rightarrow d)\pi$ bonding is contradicted by the evident lack of variation in ν(M–C) frequencies between MR_4 and M_2R_6 (M = Si, Ge, or Sn; R = Me or $CH{:}CH_2$). We thus concur with Davidson[13] that no convincing support for the existence of $(p\rightarrow d)\pi$ effects can be adduced for vinyl–Group 4B derivatives through vibrational spectroscopy.

TABLE 3

Vibrational spectra (cm^{-1})

$Si_2(CH{:}CH_2)_6$		$Ge_2(CH{:}CH_2)_6$		$Sn_2(CH{:}CH_2)_6$		
I.r.	Raman	I.r.	Raman	I.r.	Raman	Tentative assignment
3 060s	3 050w, dp	3 060vs	3 050w, dp	3 040s	3 040w, dp	$\nu_{sym}CH_2$
3 010m		3 005s (sh)	3 000vw, dp			$\nu_{asym}CH$
2 978s (sh)	2 975vs, p	2 985vs	2 980vs, p	2 980vs	2 978vs, p	$\nu_{sym}CH$
2 940vs		2 950vs	2 942w, dp	2 940vs	2 938w, dp	$\nu_{asym}CH_2$
2 880s (sh)	2 880s, p			2 870s (sh)		
2 120w		2 250w				
1 918w		1 896m		1 900w		2 × (954; 940; 945)?
1 640w (sh)	1 640m, p				1 650w, dp	$\nu_{asym}C{=}C$
1 595m	1 592vs, p	1 595w	1 590vs, p		1 582vs, p	$\nu_{sym}C{=}C$
1 515w						
	1 440w, dp					
1 408vs	1 407vs, p	1 396vs	1 398vs, p	1 390vs	1 396vs, p	CH_2 scissors
	1 295w, dp					
	1 272vs, p	1 260vs	1 265vs, p	1 245vs	1 256vs, p	CH def.
1 232w						
	1 165w, dp					CH_2 rock, wag; $C{=}CH_2$ twist
1 006vs	1 005w, dp	1 000vs	1 000w, dp	998vs	1 000w, dp	
954vs	960vw, dp	940vs		945vs		
782m						
710vs, br						ν(M–C) plus ν(Si–Si)
		670m			600w, p	
	585s, p	590vs, br	580w, dp	520vs, br	522w, dp	
550m, br	550m (sh)	550vs, vbr	5360s, p	480vs, br	511vs, p	
		335s	325w, dp			M–C=C def.
	305m, p					
			310m, p			
				290m, br	280m, dp	
			230vs, p			ν(Ge–Ge)
					169s, p	ν(Sn–Sn)

I.r., liquid film; Raman, neat-liquid samples.

Although identification of all the fundamentals of the $M_2(CH{:}CH_2)_6$ molecules is not possible from the data of Table 3, it is clear that the idealized centrosymmetric D_{3d} (staggered) configuration is inapplicable; indeed the large number of i.r.–Raman coincidences suggests much lower symmetry, at any rate in the condensed phase. Whatever model is chosen, however, the metal–metal stretching vibration will be totally symmetric and is expected to give rise to a strong polarized Raman shift in the low-wavenumber region. Appropriate bands are found at 230 cm^{-1} for the digermane and at 169 cm^{-1} for the distannane, but for $Si_2(CH{:}CH_2)_6$ no corresponding feature could be located. This parallels recent observations made by Hoffler *et al.*[15] for a number of disilane derivatives, where force-constant calculations showed distribution of ν(Si–Si) over several fundamentals in the range 350—600 cm^{-1}, and conflicts with the assignment[16] of the same mode in Si_2Me_6 as a relatively uncoupled vibration at 404 cm^{-1}. For related Group 4 hexamethyl derivatives, ν(M–M) was found[16] at 273 (M = Ge), 192 (Sn), and 116 cm^{-1} (Pb), so that the much lower

An analysis of the ^1H n.m.r. spectrum of hexavinyldigermane has been reported previously by Cawley and Danyluk.[17] A partially collapsed ABC pattern observed for the vinyl protons was used as the basis for an iterative computation of structural parameters, yielding $\delta_A = -335{\cdot}6$, $\delta_B = -357{\cdot}5$, and $\delta_C = -371{\cdot}6$ Hz from internal $SiMe_4$ with $J_{AB} = 2{\cdot}93$, $J_{AC} = 20{\cdot}07$, and $J_{BC} = 13{\cdot}32$ Hz. The most-intense spectral line was found at $-358{\cdot}6$ Hz, nearly coincident with the calculated δ_B; in the present work, a neat-liquid sample of $Ge_2(CH{:}CH_2)_6$ showed this line at -334 Hz and a

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[15] F. Hoffler and E. Hengge, *Monatsh.*, 1972, **103**, 1506, 1513.

[16] B. Fontal and T. G. Spiro, *Inorg. Chem.*, 1971, **10**, 9.

[17] S. Cawley and S. S. Danyluk, *Canad. J. Chem.*, 1968, **46**, 2373.

spectrum identical with that reported except for an additional splitting of line (10) (−361·5 Hz) and in the detection of line (1) (calculated at −310·9 Hz but not observed).

While we have not attempted fully to interpret the ^1H n.m.r. spectra of hexavinyldi-silane and -stannane, their overall appearance closely resembles that for the digermane, again consistent with the expected ABC character. The strongest components were at −334 and −357 Hz for the disilane and distannane respectively (from $SiMe_4$, neat-liquid samples), and for the disilane a narrower spread of spectral lines implied lower J values than for $M = Ge$ or Sn. Due to the complex nature of the spectra, proton-(^{117}Sn, ^{119}Sn) coupling constants could not be measured for the distannane.

Mass Spectra.—While the range of organometallic and metal–metal bonded derivatives of the Group 4B elements for which mass-spectroscopic data have been reported is considerable and general fragmentation properties following electron impact have been reviewed,[18] molecules containing only unsaturated organic groups have remained neglected in this context. Indeed, only two types of symmetrical species have been investigated, the tetraethynyls $M(C{:}CH)_4$ and the tetra-allyls $M(CH_2CH{:}CH_2)_4$. The first series showed very simple fragmentation behaviour with stepwise loss of ethynyl groups,[19] but a more complex situation was encountered for the allyls which decompose by elimination of various neutral hydrocarbons and organic radicals.[6] The tetravinyls $M(CH{:}CH_2)_4$ occupy a key position linking these two groups of compounds, so that their fragmentation patterns are of significant interest.

The mass spectrum of tetravinylsilane consisted of numerous low-intensity peaks in the form of several series with consecutive m/e values. This complicated behaviour results from the similarity of Si–C, C–C, and C–H bond energies so that essentially non-selective fragmentation occurs. By contrast for tetravinylgermane and -stannane the weaker M–C bonds result in the much simpler spectra shown in Table 4, which also contains abundances for the $M_2(CH{:}CH_2)_6$ compounds (M = Ge or Sn). The discontinuity in behaviour between the silicon compound and its germanium and tin analogues exactly parallels that found[6] for the tetra-allyls. Metastable ions observed in the spectra of the tetravinyl compounds are listed in Table 5.

The fragmentation routes established for MR_4 molecules have been usefully summarized by Fishwick and Wallbridge,[6] who in their work on allyl derivatives also reinvestigated the mass spectrum of tetramethylstannane. In general, the parent MR_4^+ ion is of low abundance and either loses a radical to give MR_3^+ or a neutral entity R–R to give $MR_2^{\dot{+}}$; the first of these is favoured resulting in characteristically high MR_3^+ fragment-ion abundances and further decomposition is also dominated by the formation of even-electron ions.

TABLE 4

Mass-spectral data (70 eV) for vinyl-germanes and -stannanes

	A *			
Ion family	$Ge(CH{:}CH_2)_4$	$Sn(CH{:}CH_2)_4$	$Ge_2(CH{:}CH_2)_6$	$Sn_2(CH{:}CH_2)_6$
$M_2(CH{:}CH_2)_6^{\dot{+}}$			1·3	1·1
$M_2(CH{:}CH_2)_5(CH_2)^+$				0·3
$M_2(CH{:}CH_2)_5^+$			0·5	0·5
$M_2(CH{:}CH_2)_4^{\dot{+}}$			6·2	4·6
$M(C_{16}H_{19})^+$				tr.
$M_2(CH{:}CH_2)_3^+$			1·3	0·3
$M_2(CH{:}CH_2)_2(CH_3)^+$				0·2
$M_2(CH{:}CH_2)_2H^+$				0·3
$M_2(CH{:}CH_2)_2^{\dot{+}}$			20·7	
$M_2(CH{:}CH_2)(CH_4)^{\dot{+}}$				4·3
$M_2(CH{:}CH_2)^+$			4·6	4·9
$M_2CH_5^+$				4·6
$M(C_{10}H_7)^+$				4·3
$M(CH{:}CH_2)_4^{\dot{+}}$	2·9			
$M(CH{:}CH_2)_3C_2H_2^+$	23·7			2·5
$M(C_7H_9)^+$	0·5			
$M(CH{:}CH_2)_3H^{\dot{+}}$	1·2			
$M(CH{:}CH_2)_3^+$	15·1	23·9	28·5	22·3
$M(C_5H_7)^+$	0·9			
$M(CH{:}CH_2)_2H^+$	10·8	14·1		6·4
$M(CH{:}CH_2)_2^{\dot{+}}$	21·5	8·8	1·8	4·6
$M(CH{:}CH_2)C^+$	3·7		7·3	
$M(CH{:}CH_2)^+$	25·6	24·9	10·4	13·7
$M(CH_3)^+$	6·9			
MH^+	4·8	7·8		3·7
$M^{\dot{+}}$	2·6	19·1	tr.	7·1
Hydrocarbons	5·7	1·4	17·3	15·2

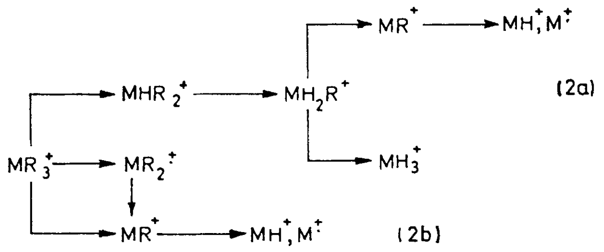
* % Ion abundance, summed over metal isotopes.

TABLE 5

Observed metastable transitions

Transition	m* (obs.)
$(CH_2{:}CH)_3Si^+ \longrightarrow (CH_2{:}CH)_2SiH^+ + C_2H_2$	63·2
$(CH_2{:}CH)_3Si^+ \longrightarrow (CH_2{:}CH)Si(C_2H_2)^+ + C_2H_4$	60·2
$(CH_2{:}CH)_2Si^{\dot{+}} \longrightarrow Si(C_3H_3)^+ + CH_3{\cdot}$	54·8
$(CH_2{:}CH)_2SiH^+ \longrightarrow (CH_2{:}CH)Si^+ + C_2H_4$	36·4
$(CH_2{:}CH)_3{}^AGe^+ \longrightarrow (CH_2{:}CH)_2{}^AGeH^+ + C_2H_2$	107·4 (*A* = 74), 105·4 (72), 103·5 (70)
$(CH_2{:}CH)_3{}^ASn^+ \longrightarrow (CH_2{:}CH)_2{}^ASnH^+ + C_2H_2$	152·4 (*A* = 120), 150·4 (118), 148·4 (116)
$(CH_2{:}CH)_3{}^ASn^+ \longrightarrow (CH_2{:}CH){}^ASn^+ + C_4H_6$	107·5 (*A* = 120), 105·7 (118), 103·8 (116)
$(CH_2{:}CH)_2{}^ASn^+ \longrightarrow {}^ASn^+ + C_4H_6$	82·8 (*A* = 120), 81·0 (118), 79·2 (116)

Fragmentation of the MR_3^+ ion follows two competing reactions (2a) and (2b); the second of these, (2b), becomes increasingly predominant with decreasing M–C and M–H bond strengths.



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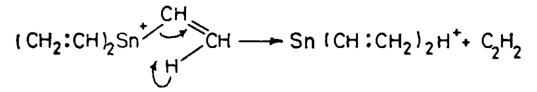
[18] D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev.*, 1968, **22**, 317.

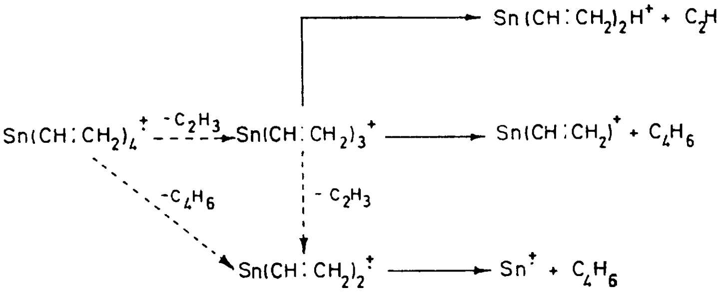
[19] W. Davidsohn and M. C. Henry, *J. Organometallic Chem.*, 1966, **5**, 29.

Molecular-ion abundances were low for tetravinylsilane and -germane, and the parent ion could not be detected for tetravinylstannane. For the latter the only abundant odd-electron ions were due to $\mathrm{Sn}^{+\cdot}$ formed by butadiene elimination from the less abundant $\mathrm{Sn(CH{:}CH_2)_2}^{+\cdot}$ fragments. Decomposition of $\mathrm{Sn(CH{:}CH_2)_3}^{+}$ ions occurred through loss of either acetylene or butadiene, the former corresponding to transfer of a β-hydrogen atom to the metal [equation (3)] and accounting for the strongest metastable observed


$$(\mathrm{CH_2{:}CH})_2\overset{+}{\mathrm{Sn}}\mathrm{CH{:}CH(H)} \longrightarrow \mathrm{Sn(CH{:}CH_2)_2H^{+}} + \mathrm{C_2H_2} \quad (3)$$

in any of the spectra. These three processes provide routes to all ion families of high abundance in the spectrum of the tin compound and metastable transitions confirm the fragmentation pattern shown in the Scheme. The only metastable-supported step in the decomposition of the germane was analogous to equation (3), but butadiene loss from $\mathrm{Ge(CH{:}CH_2)_3}^{+}$ was also confirmed in the spectrum of hexavinyldigermane, suggesting a similar fragmentation pattern to that outlined in the Scheme. Hydrogen-radical loss from the molecular ion to give an intense $\mathrm{Ge(CH{:}CH_2)_3}$-$\mathrm{C_2H_2}^{+}$ ion emphasizes the tendency towards formation of even-electron fragments and reflects the increase in metal–carbon bond strength between the tin and germanium compounds. The latter when coupled with the more electropositive character of tin also accounts for the increased importance of $\mathrm{M(CH{:}CH_2)_2}^{+\cdot}$ fragments in the spectrum of the germane at the expense of a marked decrease in intensity of $\mathrm{M}^{+\cdot}$ ions.

The greatly increased importance of C–C and C–H bond scission in the fragmentation of tetravinylsilane has already been commented on, and is substantiated by the data of Table 5. Thus elimination of acetylene, ethylene, and methyl radicals but not of butadiene was observed, together with hydrogen-radical and -molecule loss for which metastable ions were also detected. This corresponds to a transference from (2b) to (2a) as the predominating fragmentation route as a result of increased M–C and M–H bond energies as noted earlier.



SCHEME

The mass spectra of the polymetal species exhibited similar trends. Thus for hexavinyldisilane a very complex fragmentation pattern is suggested by the wide variety of ions detected, whereas for the germanium and tin compounds the measured ion abundances (Table 4) corresponded to identifiable ion families. Total ion current carried by fragments containing two metal atoms appears to closely follow established metal–metal bond energies: M = Si, *ca.* 60; Ge, 35; and Sn, 21% respectively. Observation of the molecular ion for hexavinyldistannane contrasts with the situation found for tetravinylstannane and may result from a delocalization of the positive charge over two metal atoms. Likewise, successive loss of vinyl groups (probably *via* acetylene and/or butadiene elimination, *cf.* the Scheme) is evident down to $\mathrm{Sn_2(CH{:}CH_2)}^{+}$. An interesting feature of the spectrum of the digermane when compared with that of its tetravinyl counterpart is the enhanced importance of odd-electron ions, most notably $\mathrm{Ge_2(CH{:}CH_2)_2}^{+\cdot}$. However, the latter appears to take the place of $\mathrm{Ge(CH{:}CH_2)}^{+\cdot}$, the abundance of which for the monogermane has already been commented on; its formation corresponds to elimination of two molecules of butadiene from the molecular ion, *via* $\mathrm{Ge_2(CH{:}CH_2)_4}^{+\cdot}$, which is also of reasonable abundance and its intensity emphasizes the increase in stability of dimetal fragments between tin and germanium.

A close relation between fragmentation patterns for Group 4B vinyl and allyl derivatives is clearly established by the present work. In particular, the important steps for the germanium and tin species are: (i) β-elimination [*cf.* equation (3)] leading respectively to acetylene or allene loss; (ii) simultaneous elimination of two organic groups *via* formation of the appropriate diene, either butadiene or hexadiene; and (possibly less significantly); (iii) radical loss of vinyl or allyl. It therefore seems likely that similar processes will dominate the fragmentation of other more complicated alkenyl species.

EXPERIMENTAL

Physicochemical measurements were made using the following instrumentation: Perkin-Elmer 457 (i.r. spectra); Cary 83 with 488·0 nm sample illumination (Raman spectra); Varian A60-D (^{1}H n.m.r. spectra); and AEI MS902 (mass spectra). Vinylmagnesium bromide was synthesized from vinyl bromide in tetrahydrofuran (thf).

Reactions of Tetrachlorides of Silicon, Germanium, and Tin, and of Hexachlorodisilane with Vinylmagnesium Bromide.—Slow addition of the halide to a solution of vinylmagnesium bromide in thf containing excess of 'active' magnesium metal was followed by heating under reflux for 3 h. Hydrolysis (NH_4Cl solution) and subsequent extraction into diethyl ether yielded the tetravinyl compound *via* fractional distillation; further distillation at reduced pressure followed by preparative-scale v.p.c. (Autoprep, 15% APL column, 180 °C) afforded pure fractions of the hexa- and octa-vinyl derivatives. Typical yields and physical data are contained in Tables 1 and 2. The tetravinyls were finally purified using fractional-condensation techniques on a high-vacuum system.

Reaction of Tetravinylgermane.—*With di-iodine.* Di-iodine (1·44 g, 5·68 mmol) in $CHCl_3$ (15 cm^3) was added slowly in a dinitrogen atmosphere to tetravinylgermane (1·03 g, 5·68 mmol) in the same solvent. After heating under reflux for 1 h, removal of volatiles resulted in recovery of 65% of $Ge(CH{:}CH_2)_4$. The residue was mainly di-iodine and no other vinylgermanium product could be isolated.

With dibromine. Slow addition of dibromine (0·91 g, 5·68 mmol) to tetravinylgermane (1·03 g, 5·68 mmol) using $CHCl_3$ as solvent was accompanied by immediate decolorization. Heating under reflux as above followed by microdistillation afforded a pale yellow liquid (*ca.* 80% yield) shown by i.r. and mass spectroscopy to be trivinylgermanium bromide.

With dichlorine. Dichlorine was bubbled through a solution of tetravinylgermane (0·50 g, 2·88 mmol) in CCl_4 (4 cm^3) for 20 min. Subsequent distillation gave a rather viscous colourless liquid [0·5 g, b.p. 80 °C (0·05 mmHg)] shown by i.r. and mass spectroscopy to be $Ge(CHCl{\cdot}CH_2Cl)_4$ (Found: C, 20·05; H, 2·45. Calc. for $C_8H_{12}Cl_8Ge$: C, 20·65; H, 2·60%) containing a trace of $Ge(CH{:}CH_2)_3Cl$.

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