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MASS SPECTRA OF *monohapto*-CYCLOPENTADIENYL DERIVATIVES OF GROUP IVB ELEMENTS

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Summary

Dissociative ionisation of organometallic cyclopentadiene derivatives containing one, two or three $M(CH_3)_3$ groups (M = Si, Ge, Sn) has been studied.

Among the monometallated compounds, $C_5H_5Si(CH_3)_2Cl$, $C_5H_5Si(CH_3)_2OCH_3$ and $(C_5H_5)_4Sn$ have also been investigated. To verify fragmentation patterns, the spectra of deuterated compounds such as $C_5D_5Si(CH_3)_3$, $C_5D_5Sn(CH_3)_3$, $C_5D_4Si_2(CH_3)_6$ and $C_5D_3Si_3(CH_3)_9$ have been measured. Dissociative ionisation of h^1-cyclopentadienyl derivatives has been shown to differ essentially from that of h^5-compounds.

Introduction

h^1-Cyclopentadienyl compounds of transition or non-transition elements, representative of fluxional molecules, are at present under intense physical and chemical study (NMR, IR, X-ray, electron diffraction [1]). These studies aim mainly at clarifying those peculiarities of electron molecular structure which govern intramolecular metallo- and proto-tropic rearrangements in the compounds. Mass spectrometric data are very informative of these features. Rakita and coworkers [2] studied a series of indanyl and indenyl compounds of Group IVB elements and demonstrated that the ionization potentials found from mass spectra can be used to show convincingly whether or not the π-electron system is σ—π hyperconjugable with the metal—carbon bond. Egger was the first to point out that mass spectrometry may be used to differentiate between h^1- and h^5-cyclopentadienyl compounds [3]. His qualitative approach led to the conclusion that the h^1-C_5H_5—M bond should be about 30 kcal/mol weaker than the alkyl—M bond, while the h^5-C_5H_5—M bond should be much stronger.

Egger's assumption was that mass spectral molecular ion fragmentation depends on bond strengths and he predicted the prevailing degradation routes, and a difference between mass-spectral patterns, of the h^1 and h^5 types. The spectrum of $C_5H_5Pt(CH_3)_3$ proved its h^5 structure.

Lorberth studied fragmentation of h^1-$C_5H_5HgCH_3$ and h^1-$C_5H_5HgC_2H_5$ under the action of electron impact [4]. Alber and Schröer [5] in their short communication report only the main fragments for $(C_5H_5)_2Sn(CH_3)Cl$ and $(C_5H_5)_2Sn(CH_3)I$.

We wanted to solve the following two problems.

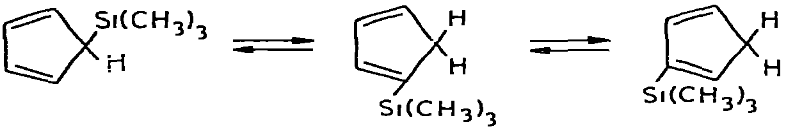
(1) To find criteria for assigning a structure to a Group IVB cyclopentadienyl on the basis of its mass spectral molecular ion fragmentation.

(2) To clarify electronic structural features that relate to anomalous physical and chemical properties of the compounds.

The present paper deals with mass spectra of sixteen organometallic cyclopentadiene derivatives containing one, two or three identical or different $M(CH_3)_3$ groups (M = Si, Ge, Sn) in the same cyclopentadienyl,

Experimental

Trimethylsilylcyclopentadiene (I) was synthesized according to ref. 6. It is an equilibrium mixture of three isomers, Ia, Ib and Ic, due to prototropic rearrangement.



(Ia) (Ib) (Ic)

Ashe's method [7] of recrystallisation at low temperature gave us 98% pure Ia. The same method yielded a mixture containing 26% of Ib + Ic*. Ia deuterated in the ring was obtained by the same preparative technique [6] but using cyclopentadiene-d_6 [8]. The Ashe recrystallisation resulted in a 98% pure deuterated Ia (referred to as d_5-Ia) whose isotope composition** was d_5, 58.5%; d_4, 30.2%; d_3, 9.5%; d_2, 1.8%, and in a mixture containing 18.6% of Ib + Ic (d_5, 53.5%; d_4, 33.4%; d_3, 8.9%; d_2, 4.8%). Pure 5-isomers of $C_5H_5Ge(CH_3)_3$ (IV), $C_5H_5Sn(CH_3)_3$ (V) and $C_5D_5Sn(CH_3)_3$ (d_5-V) were obtained according to refs. 9 and 10***.

The dimetallated cyclopentadienes were synthesized as descibed by us earlier [12]. Bis(trimethylsilyl)cyclopentadiene deuterated in the ring, (d_4-VII; d_4, 74%; d_3, 17%; d_2, 9%), was obtained from d_5-I similarly [12].

Trimetallated cyclopentadienes were synthesized as in ref. 12 except for 2,5,5-tris(trimethylsilyl)cyclopentadiene (XII) synthesized by us [13] through

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* The isomer ratio was found by integrating the PMR $Si(CH_3)_3$ signals in the diluted solution in benzene [7].

** Found from mass spectra.

*** The organotin derivatives were obtained by modifying the Jones and Lappert [10] procedure and applying this to metallation of C_5H_6 and $C_5H_5M(CH_3)_3$ with $(C_2H_5)_2NSn(CH_3)_3$ [11].

a procedure similar to that described by Jutzi [14].

2,5,5-Tris(trimethylsilyl)cyclopentadiene was obtained by metallating bis(trimethylsilyl)cyclopentadiene (VII) with butyllithium and treating the resulting organolithium compound with trimethylchlorosilane*. A deuterated 2,5,5-tris(trimethylsilyl)cyclopentadiene, (d_3-XII; d_3, 77.5%; d_2, 18.6%; d_1, 1.8%), was obtained from d_4-VII.

Mass spectra were measured on a standard MKh-1303 intrument; the direct inlet of samples into the ion source was used. The inlet temperature was 25°, the ionisation chamber temperature 180°. Ionising voltage was 50 V for monometallated compounds (70 V for VI recorded at 30°) and 70 V for the di- and tri-metallated compounds.

Ionisation potentials for I, III, V, VII and XII were recorded on an MKh-1311 photoionisation machine fitted with an all-glass direct inlet accessory.

To facilitate interpretation, all mass spectra (except for some silicon-containing compounds) were recalculated for the monoisotopic form using ^{28}Si, ^{74}Ge and ^{120}Sn.

Results and discussion

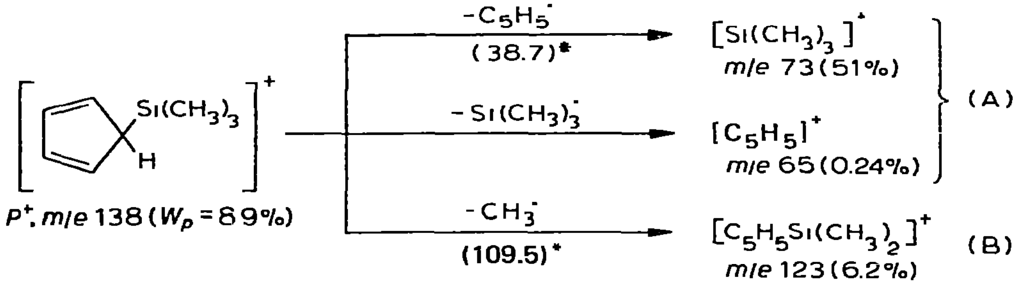
*Monometallated cyclopentadienes $C_5H_5MR_3$ (M = Si, Ge, Sn)***

(a) M = Si

5-Trimethylsilylcyclopentadiene (I). The main fragmentation route for I acted upon by electron impact or photoionisation pulse is the C_5H_5—Si bond fission, in the course of which positive charge is localised on the silicon-containing fragment and the $[Si(CH_3)_3]^+$ peak occurs at m/e of 73. Photoionisation at 10.2 eV leads only to peaks of P^+ (m/e 138) and $[Si(CH_3)_3]^+$ (m/e 73), the intensities ratio being 1.54/1. Electron impact at 50 eV (Fig. 1 and Scheme 1) leads to peaks of P^+ (its stability against decomposition, W_P, is 8.9%, ref. 15), $[Si(CH_3)_3]^+$ (the most intense peak), $[C_5H_5]^+$ (m/e 65), $[C_5H_5Si(CH_3)_2]^+$ (m/e 123); the latter ion is formed by methyl abstraction from P^+ (route B). Consequent-

SCHEME 1

FRAGMENTATION OF P^+ OF Ia. ELECTRON IMPACT, 50 eV.



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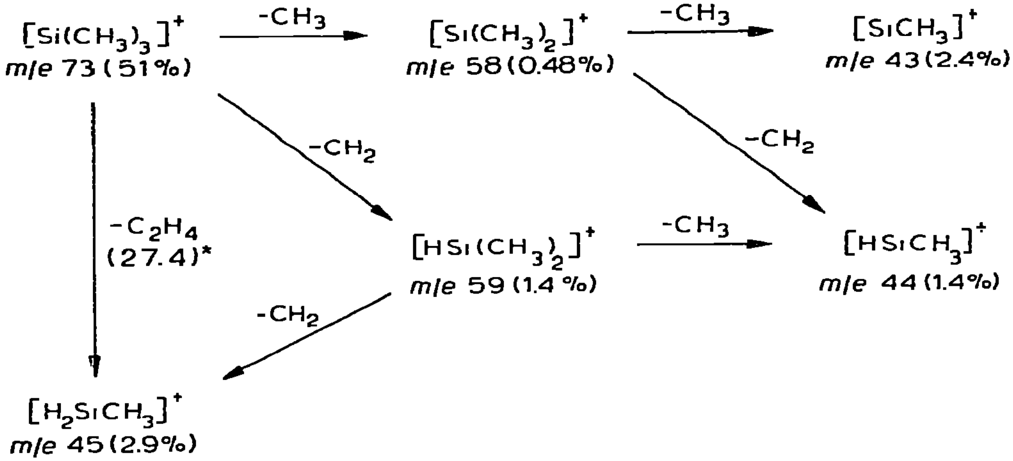
[*] Details of the synthesis, structure assignments, and metallotropic rearrangements will be published soon.

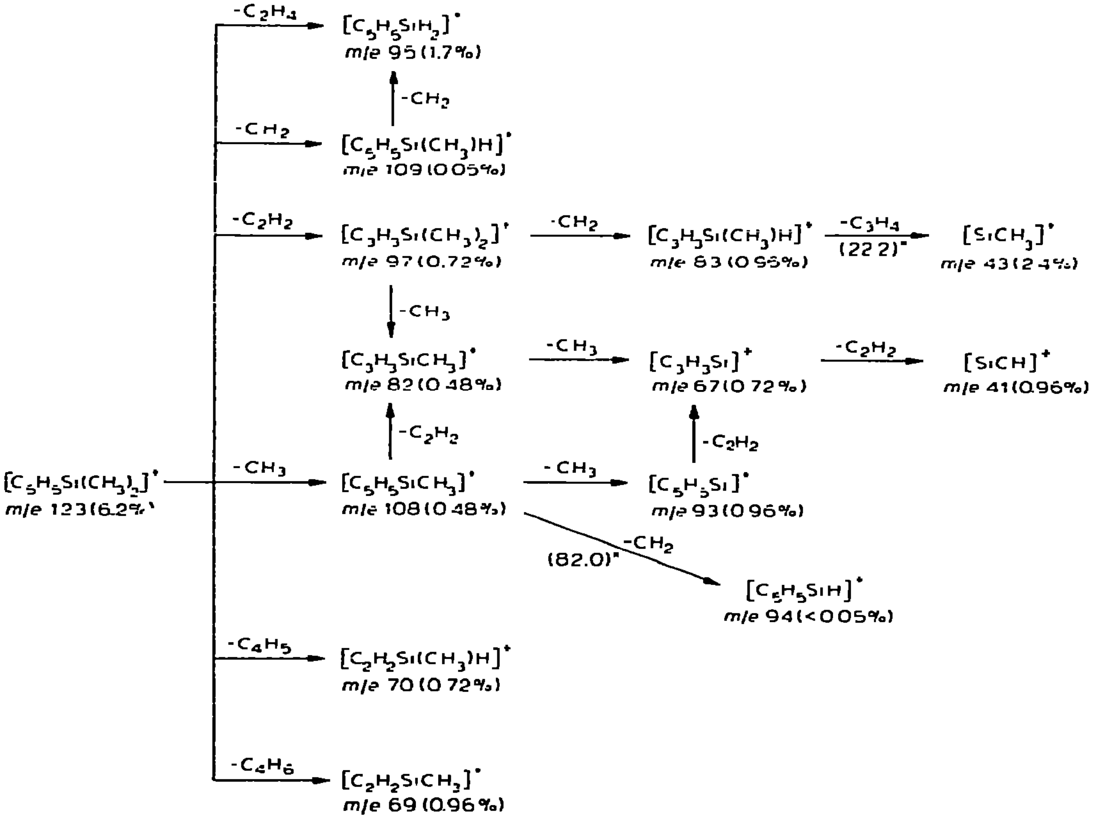
[**] See also ref. 36. *Note:* For all monometallated cyclopentadienes a rearrangement of the molecular ion is observed. It is accompanied by elimination of a cyclopentadiene molecule. The rearrangement agrees with the metastable peaks found for I and IV.

ly, the C_5H_5—Si bond fission (route A) predominates markedly, and the positive charge is localised mainly on the silicon-containing fragment.

SCHEME 2. FRAGMENTATION OF $[Si(CH_3)_3]^+$ (*m/e* 73).



SCHEME 3*. FRAGMENTATION OF $[C_5H_5Si(CH_3)_2]^+$ (*m/e* 123) IN THE SPECTRUM OF Ia.



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* The degradation of $[C_5H_5Si(CH_3)H]^+$ (*m/e* 109) may be accompanied by a rearrangement and elimination of $[C_5H_6]^+$. Indeed, a metastable ion at m^* 17.0 may be indicative of this process.

The $[Si(CH_3)_3]^+$ (*m/e* 73, Scheme 2) fragmentation is similar to fragmentations of all $(CH_3)_3Si$-containing compounds [16-18]; CH_3, CH_2 and C_2H_4 neutral species are abstracted. Consequently, the silicon-containing fragments between *m/e* 73 and 43 may be assumed to form from $[Si(CH_3)_3]^+$ rather than $[C_5H_5Si(CH_3)_2]^+$ (*m/e* 123). An exception is $[SiCH_3]^+$ (*m/e* 43) formed from $[C_5H_5Si(CH_3)_2]^+$, as verified by a metastable peak at m^* 22.2.

The fragmentation of $[C_5H_5Si(CH_3)_2]^+$ (*m/e* 123, Scheme 3) consists of abstraction of ethylene, methylene and methyl species from the silicon, and acetylene elimination from the ring. Also, some rearrangements are observed accompanied by ring opening and the loss of C_4H_6 and C_4H_5 neutral fragments (C_3H_3 from the ring, CH_3 and CH_2 from the silicon).

All these paths may be substantiated by collating the spectrum of Ia with

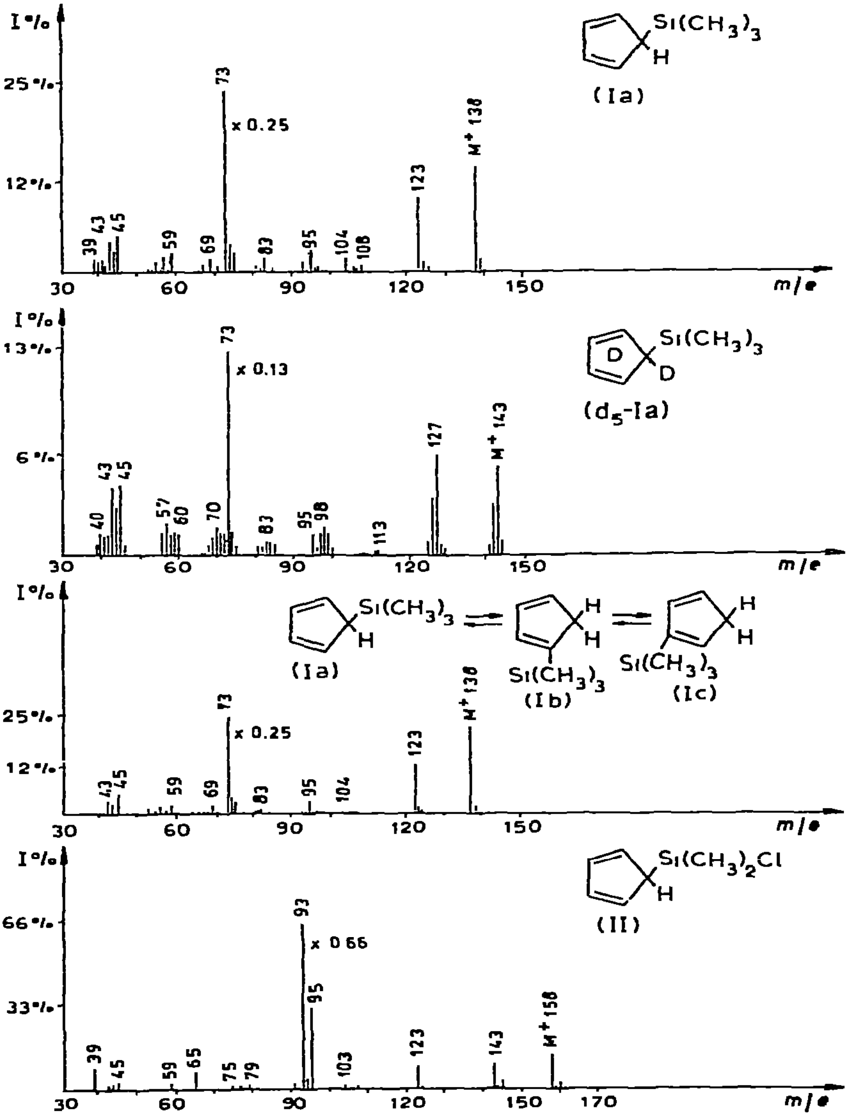


Fig. 1. Mass spectra of Ia, d_5-Ia, the I isomers mixture enriched in Ia + Ib, and of II.

the spectrum of its deuterated derivative. The shifts of the filial ions towards higher masses are quite demonstrative.

The probabilities of the dissociation by routes A and B are 71 and 19.7% respectively. Inevitable inaccuracies in constructing the fragmentation pattern may lead to errors of about ± 10% in the values of N_A and N_B, but the accuracy is satisfactory for discussing qualitative patterns.

The spectra of d_5-Ia, Fig. 1, show that no randomisation of deuterium between the ring and the silicon-methyls is caused by electron impact. The stability of P^+ is somewhat decreased ($W_P = 6.7\%$).

A mixture of isomers of I enriched in vinyl isomers (26% of Ib + Ic), Fig. 1, gives a spectrum identical with that of the pure Ia as to positions of all fundamental peaks, but differing in relative intensities. The most significant fact is an increase of W_P to 14%; N_A and N_B are 64.4 and 16.6% respectively and, within the accuracy discussed, close to those for Ia.

Chlorodimethylsilylcyclopentadiene (II) and methoxydimethylsilylcyclopentadiene (III). The behaviour of II and III is similar to that of Ia. The spectrum of II recorded at 50 eV is shown in Fig. 1. Again, the main fragmentation route is the C_5H_5—Si bond fission ($N_A = 74.4\%$), the methyl radical abstraction probability is 6.6%, the probability for chlorine is 4.5%, and the molecular ion stability W_P is 8.9%. The transitions P^+—CH_3 (*m/e* 158 → 143) and P^+—C_5H_5 (*m/e* 158 → *m/e* 93) agree with metastable peaks at m^* 129.6 and 54.6.

The spectrum of III obtained under the same conditions is shown in Fig. 2. As before, the prevailing route is the C_5H_5—Si bond dissociation ($N_A = 67\%$), the probability of abstraction CH_3 from P^+ is 8.4%, whereas the probability is as low as 1.4% for the Si—OCH_3 bond rupture. The molecular ion stability at 50 eV ($W_P = 9.1\%$) falls to 3% at 80 eV. A characteristic of fragmentation of P^+—CH_3 and $[Si(CH_3)_2OCH_3]^+$ is elimination of a formaldehyde molecule, CH_2O. The metastable peaks at m^* 85.6, 51.5, and 39 respectively indicate the following transitions:

$$\begin{array}{lcl}
[C_5H_5Si(CH_3)OCH_3]^+ & \longrightarrow & [C_5H_5SiHCH_3]^+ \\
m/e\ 139 & & m/e\ 109 \\
P^+ & \longrightarrow & \overset{+}{Si}(CH_3)_2OCH_3 \\
m/e\ 154 & & m/e\ 89 \\
[Si(CH_3)_2OCH_3]^+ & \longrightarrow & H\overset{+}{Si}(CH_3)_2 \\
m/e\ 89 & & m/e\ 59
\end{array}$$

A doubly-charged ion, $[P—CH_3]^{2+}$, is observed at 80 eV (*m/e* 69.5, intensity 0.35%).

(b) M = Ge

Trimethylgermylcyclopentadiene (IV). A mass spectrum of IV recorded at 50 eV is shown in Fig. 2, and the main fragmentation routes in Scheme 4. Similar to silyl cyclopentadienes I-III, the prevailing route is the C_5H_5—Ge bond decomposition (N_A 66%) in P^+ (*m/e* 184), leading to $[Ge(CH_3)_3]^+$ (*m/e* 119), the most

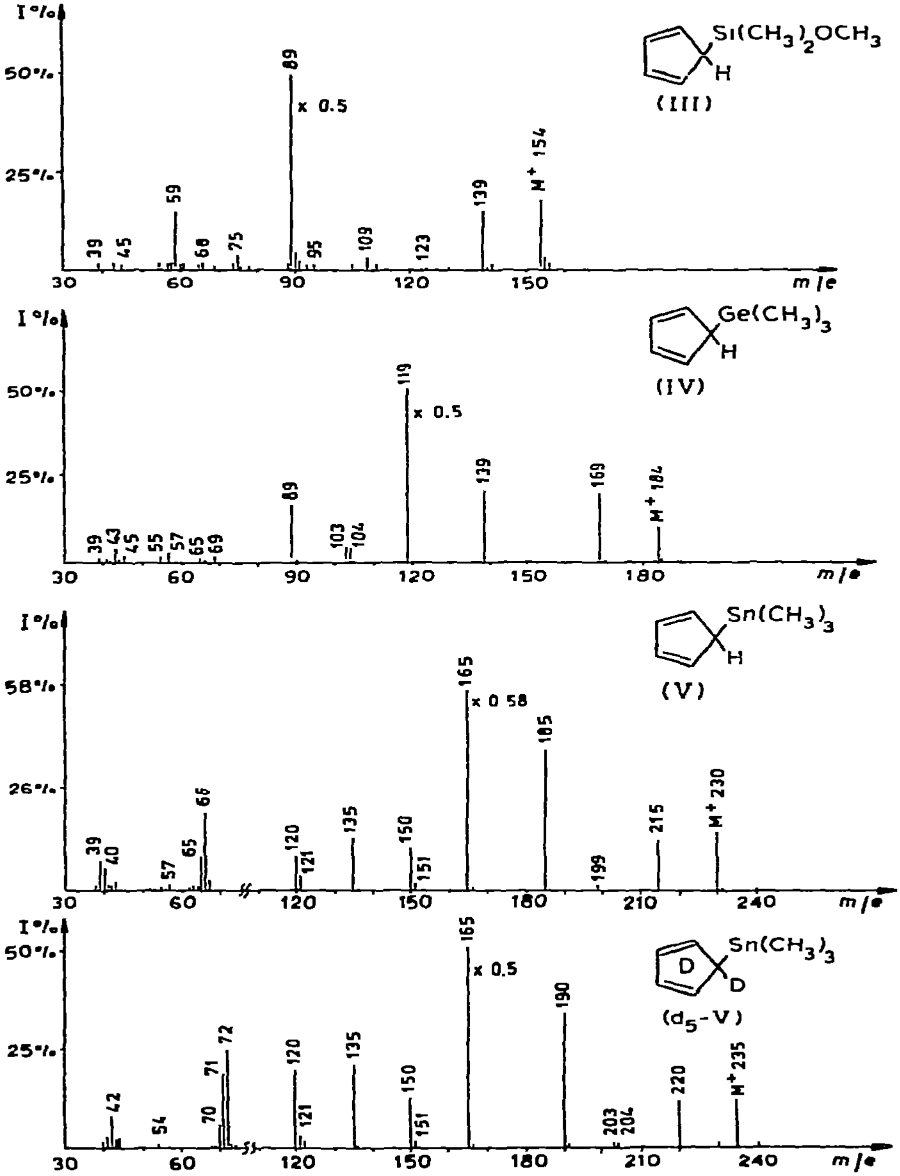


Fig. 2. Mass spectra of III, IV, V and d_5-V.

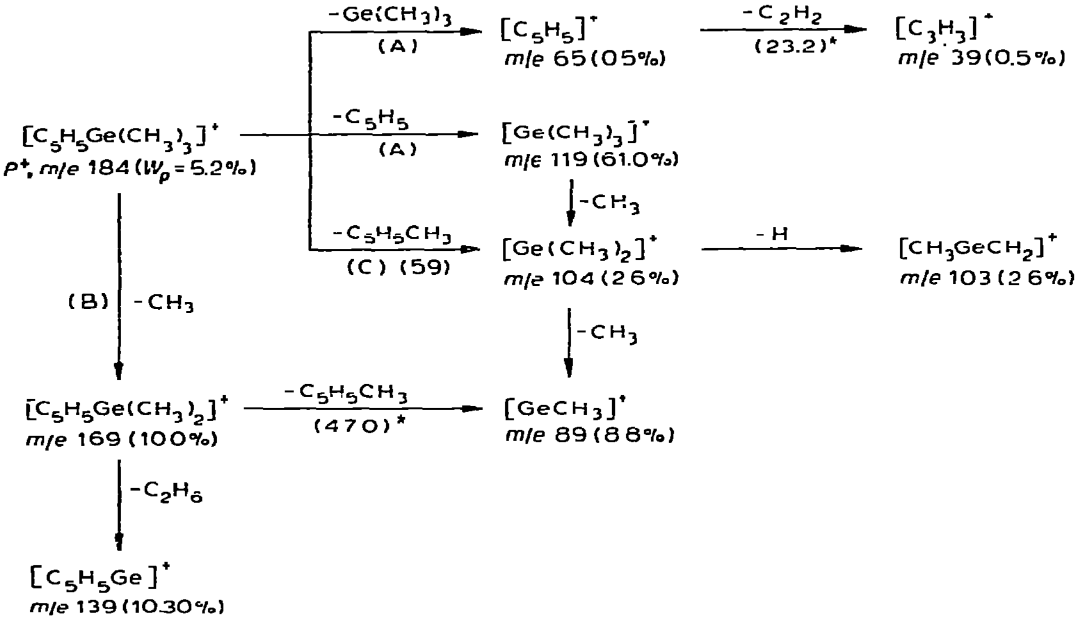
intense peak in the spectrum. The abstraction of CH_3 from P^+ is probable at a level of $N_B = 28\%$. The molecular ion stability W_P is 5.6%, that is, by a factor of 1.5 lower than with I.

IV differs from I in that it expels a methylcyclopentadiene molecule from its P^+ (route C) while a similar rearrangment occurs in P^+—CH_3 (*m/e* 169) and agrees with metastable peaks at m^* 59 and 47.

Although P^+ and P^+—CH_3 decompose to give $C_5H_5CH_3$, N_B and N_A may be calculated easily since the $[Ge(CH_3)_2]^+$ (*m/e* 104) and $[GeCH_3]^+$ (*m/e* 89) peaks are small. The respective filial intensities are also negligible.

SCHEME 4*

FRAGMENTATION OF IV. ELECTRON IMPACT, 50 eV.



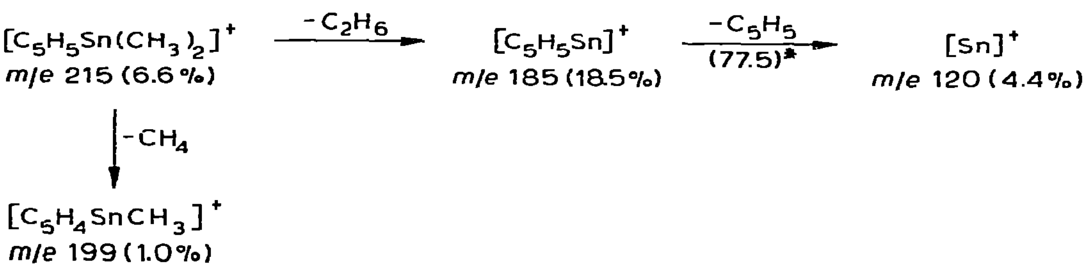
(c) M = Sn

Trimethylstannylcyclopentadiene (V). The spectrum of V measured at 12 eV displays peaks of P^+ (*m/e* 230, W_P = 32.6%), $[Sn(CH_3)_3]^+$ (*m/e* 165, 54.4%). $[C_5H_5Sn(CH_3)_2]^+$ (*m/e* 215, 8.6%), $[C_5H_5Sn]^+$ (*m/e* 185, 2.4%), and also $[Sn(CH_3)_2]^+$ (*m/e* 150, low intensity) and $[C_5H_5]^+$ (*m/e* 65, low intensity). The C_5H_5—Sn bond rupture probability is N_A = 54%, the CH_3 abstraction probability is N_B = 13%.

The spectrum of V at 30 eV is shown in Fig. 2. The molecular ion stability falls to 7.5%. The spectrum readily reveals the further fragmentation of

SCHEME 5

FRAGMENTATION OF P^+ OF V. ELECTRON IMPACT, 30 eV.



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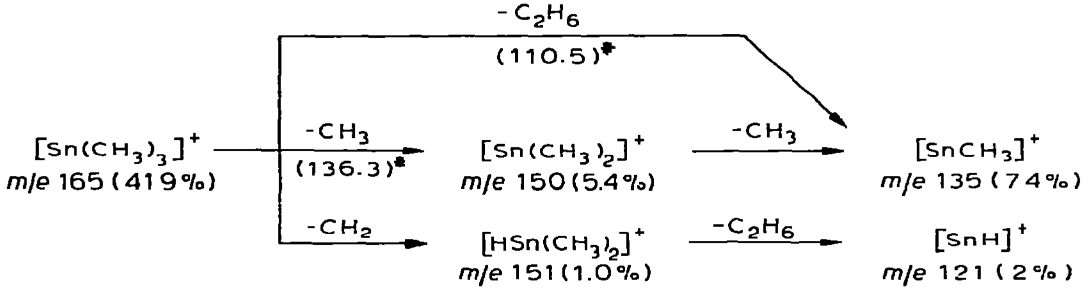
* This scheme omits the degradation of $[Ge(CH_3)_3]^+$ (*m/e* 119) by elimination of C_2H_4, verified by a metastable peak m^* at 69.9. Decomposition of this type is characteristic of molecules containing a $Ge(CH_3)_3$ group [37, 38].

SCHEME 6

FRAGMENTATION OF $[Sn(CH_3)_3]^+$ (*m/e* 165).



$[C_5H_5Sn(CH_3)_2]^+$ (*m/e* 215) and $[Sn(CH_3)_3]^+$ (*m/e* 165) [34] shown in Schemes 5 and 6. The prevailing fragmentation probabilities are N_A = 61% and N_B = 31%.

A specific feature of V compared to Ia and IV is the absence of any C—C ring bond decomposition in the filial ions, and the decomposition of $[C_5H_5Sn]^+$ (*m/e* 185) leading to the C_5H_5 abstraction (cf. the metastable peaks in the spectra of V and d_5-V).

The ion $[C_5H_5Sn]^+$ (*m/e* 185) is also observed as the most intense ion in the spectrum of $(h^5\text{-}C_5H_5)_2Sn$. Unlike V in the spectrum of $(C_5H_5)_2Sn$, this ion undergoes not only C_5H_5—Sn bond fission but also acetylene elimination. It is very probable, therefore, that these two ions of the same composition are of different structure [19].

Finally, we have observed that $[C_5H_5Sn(CH_3)_2]^+$ decomposes to lose a CH_4 molecule, with CH_3 being removed from the metal and hydrogen from the ring. This is readily seen from the shift of four mass units of the resulting $[C_5H_4SnCH_3]^+$ (*m/e* 199) in the spectrum of d_5-V.

In conclusion, in I-IV as well as in V the predominant route is the C_5H_5—Sn bond fission accompanied by the positive charge localisation on the metal-containing fragment. The fragmentation of $[C_5D_5Sn(CH_3)_3]^+$ (d_5-V) was studied at 12, 30, and 50 eV. As with d_5-I, the deuterium is not randomised between the ring and the methyls. The spectrum of d_5-V at 50 eV is shown in Fig. 2, from which it can be seen that there is no significant difference between the behaviour of V and d_5-V, the observed shifts towards higher masses agreeing with the fragmentation pattern assumed. The fragmentation parameters found at 12 eV are N_A = 64, N_B = 10, W_P = 26.1%; at 30 eV N_A = 65.6, N_B = 27.8, W_P = 6.6%; and at 50 eV N_A = 66.5, N_B = 28.3, W_P = 5.4%.

Tetracyclopentadienyltin (VI). The spectrum of VI at 70 eV is shown in Fig. 3, and its fragmentation pattern in Scheme 7.

The molecular ion stability is the lowest among the compounds studied. As with V, the predominant fragmentation route is the C_5H_5—Sn bond fission leading to $[(C_5H_5)_3Sn]^+$ (*m/e* 315). Further decomposition of $[(C_5H_5)_3Sn]^+$ (*m/e* 315) proceeds via loss of C_5H_5, dicyclopentadiene, or C_9H_8. The latter rearrangement is supported by the metastable peak at m^* 112.6. The ion $[C_6H_7Sn]^+$ (*m/e* 199) formed via this route may have a cyclohexadiene ring in its structure: this is suggested by its further decomposition which consists of a rearrangement and elimination of butadiene verified by the metastable peak at m^* 105.6.

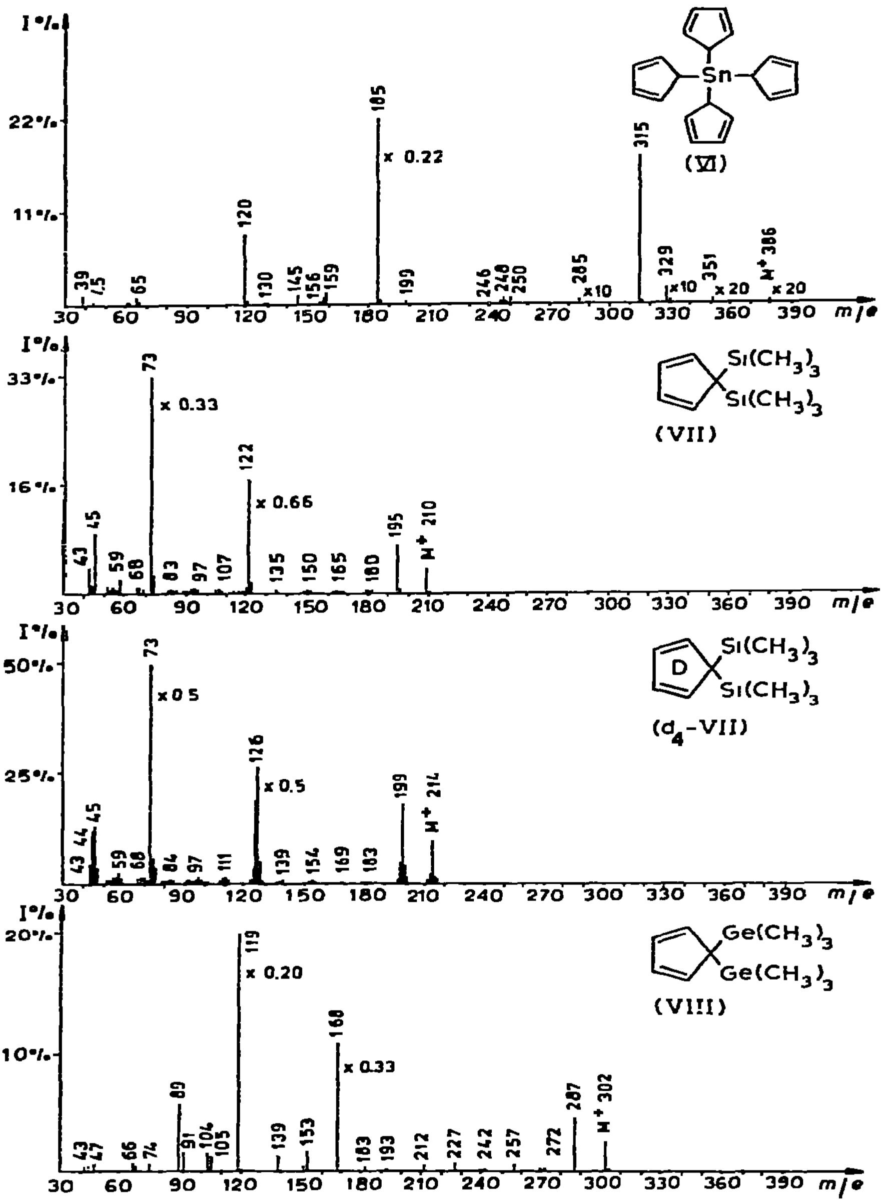


Fig. 3. Mass spectra of VI, VII, d_4-VII and VIII.

Table 1 lists stabilities of molecular ions of the compounds I-VI, and degradation probabilities for C_5H_5—M and R—M bonds. For comparison, the Table includes data for CH_2=$CHSi(CH_3)_3$ [20, 21] and the data obtained by Egger for h^5-$C_5H_5Pt(CH_3)_3$ [3].

These data demonstrate that, unlike h^5-compounds, h^1-C_5H_5 compounds decompose principally via the C_5H_5—M bond fission, in accordance with the qualitative predictions by Egger. The fact that $N_A/N_B \gtrsim 1$ suggests that the structure is of the h^1-type, and this ratio may be used as a criterion for discerning between the structures: for h^5-species, e.g. $C_5H_5Pt(CH_3)_3$, $N_A/N_B \leqslant 1$ [3].

SCHEME 7

FRAGMENTATION OF VI. ELECTRON IMPACT, 70 eV.

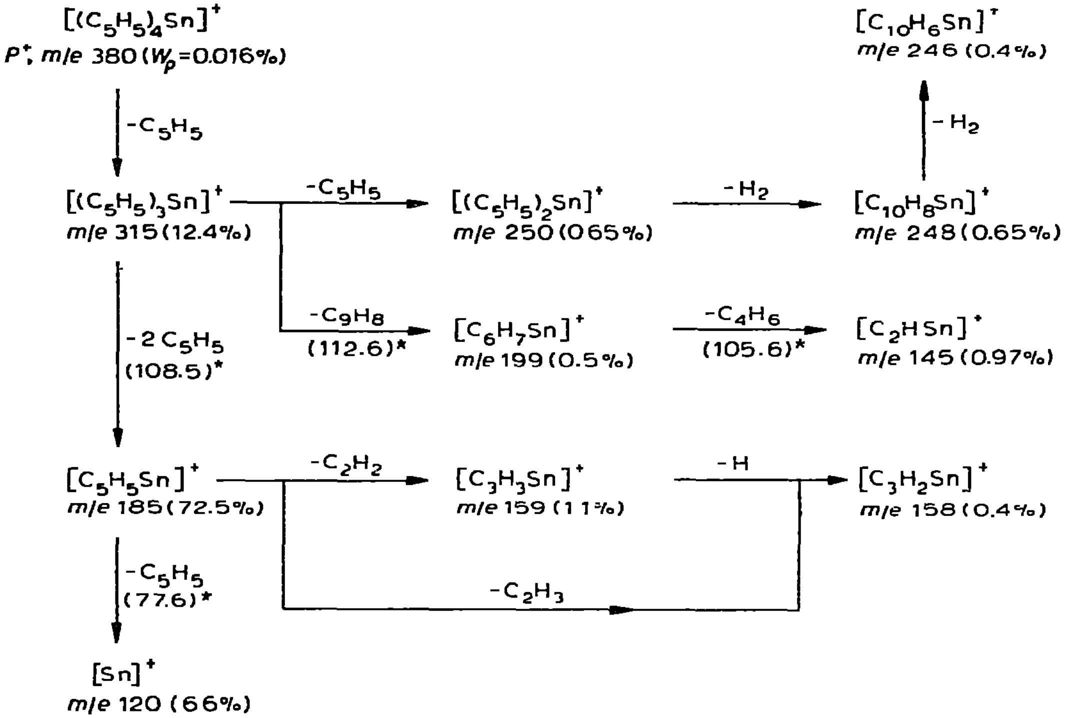


TABLE 1

STABILITIES AGAINST DECOMPOSITION (W_P^+) AND PROBABILITIES OF THE C_5H_5—M AND R—M BOND FISSIONS IN SPECTRA OF I-VI

Compound	N_A(%)	N_B(%)	N_A/N_B	W_P^+ (%)	Electron energy (eV)
h^1-$C_5H_5Si(CH_3)_3$ (I)	71	19.7	3.6	8.9	50
h^1-$C_5D_5Si(CH_3)_3$ (d_5-I)	73	19.5	3.7	6.7	50
h^1-$C_5H_5Si(CH_3)_2Cl$ (II)	74.4	11.1 (P^+—CH_3 6.6; P^+—Cl 4.5)	7.4	8.9	50
h^1-$C_5H_5Si(CH_3)_2OCH_3$ (III)	79	9.8 (P^+—CH_3 8.4; P^+—OCH_3 1.4	8.1	9.1	50
h^1-$C_5H_5Ge(CH_3)_3$ (IV)	66	28	2.4	5.6	50
h^1-$C_5H_5Sn(CH_3)_3$ (V)	61	31	2	7.5	30
h^1-$C_5D_5Sn(CH_3)_3$ (d_5-V)	66.5	28.3	2.4	5.4	50
(h^1-$C_5H_5)_4Sn$ (VI)	99.4	—	—	0.016	70
CH_2=CH-$Si(CH_3)_3$	93	6.4	14.6	1.2	—
h^5-$C_5H_5Pt(CH_3)_3$	8.9	86	0.1	4.6	—

There are other specific features in the spectra of h^1-$C_5H_5MR_3$ compounds, of which the most striking is the absence of any P^+ fragmentations leading to C—C bond fission in the C_5H_5 ring, a process so typical of h^5-complexes [22-24]. In contrast, the ions P^+—CH_3 produced by h^1-C_5H_5 compounds (except for V) decompose in this manner very readily although they are not subject to a C_5H_5—M bond fission. Consequently, the C_5H_5—M bond in the ions $[C_5H_5MR_2]^+$ is much stronger than it is in the initial molecular ions, and its stability is close to that in molecular ions of h^5-C_5H_5 compounds. However, this bond can hardly be thought of as greatly different from the bond in h^1-molecular ions. There are no data to suggest that $[C_5H_5MR_2]^+$ ions are h^5-structured: such an assumption would require more detailed investigations to be carried out.

There are a number of interesting degradations found which open new paths of study. To begin with, there is the unusual decomposition of $[(C_5H_5)_3Sn]^+$ described above. The compounds to be studied in detail are $(h^5$-$C_5H_5)_2Ti(h^1$-$C_5H_5)_2$, and other $(C_5H_5)_4M$ compounds. Also of interest are rearrangements in the molecular ion of IV and in $[C_5H_5Ge(CH_3)_2]^+$, giving rise to the abstraction of methylcyclopentadiene.

Dimetallated cyclopentadienes $C_5H_4M(CH_3)_3M'(CH_3)_3$

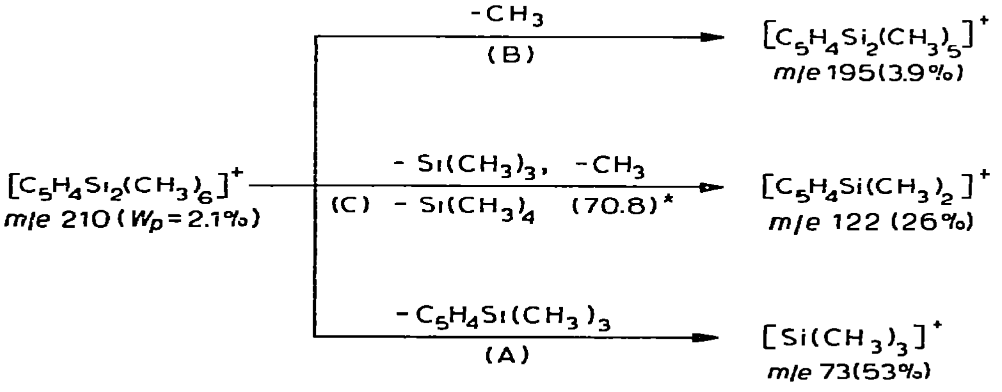
(a) $M = M' = Si$

5,5-Bis(trimethylsilyl)cyclopentadiene (VII). Photoionisation of VII at 10.2 eV gives just three peaks: P^+ (*m/e* 210, W_P 78%), $[C_5H_4Si(CH_3)_2]^+$ (*m/e* 122, 12%) and $[Si(CH_3)_3]^+$ (*m/e* 73, 10%).

Electron impact at 70 eV gives rise to three fragmentation paths of P^+, shown in Scheme 8 and Fig. 3. The C_5H_4—M bond fission (route A) predominates markedly and proceeds via two paths. The first fission is accompanied by the positive charge localisation on the fragment $[Si(CH_3)_3]^+$ (*m/e* 73). Further, this ion decomposes in a usual way as shown in Scheme 2. The second path is the abstraction of $(CH_3)_4Si$ leading to $[C_5H_4Si(CH_3)_2]^+$ (*m/e* 122). An assumption is that the process is a rearrangement accompanied with the $(CH_3)_4Si$ abstraction, but not a fast consecutive elimination of $(CH_3)_3Si$ and CH_3. The proof is that

SCHEME 8

FRAGMENTATION OF VII. ELECTRON IMPACT, 70 eV.

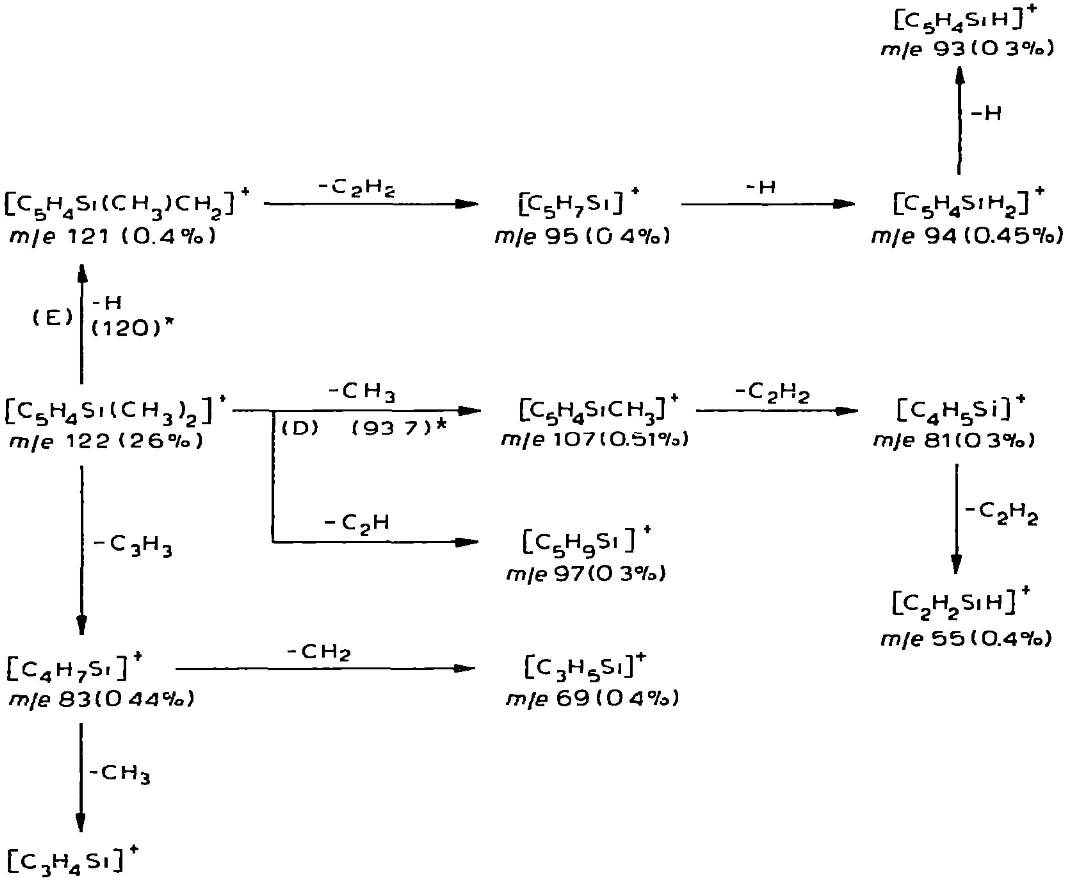


the Cooks–Williams criterion [29] is satisfied: the ratio of the intensity of $[(CH_3)_3Si]^+$ (*m/e* 73) (the ion formed through simple C—Si bond rupture) to the intensity of $[C_5H_4Si(CH_3)_2]^+$ (*m/e* 122) increases with the ionising energy. Indirect proof is also the absence of the $[C_5H_4Si(CH_3)_3]^+$ peak (*m/e* 137) from the spectrum. The fragmentation of VII involving the Si—CH_3 bond fission (route B) leads to abstraction of CH_3 groups and, finally, to $[C_5H_4Si_2]^+$ (*m/e* 120). The filial ions formed through these decompositions lie at *m/e* 195 to *m/e* 120 and are of low intensity, except for $[C_5H_4Si_2(CH_3)_5]^+$ (*m/e* 195, 3.9%).

Noteworthy of $[C_5H_4Si(CH_3)_2]^+$ is its high stability against deeper decomposition, $W_{[C_5H_4Si(CH_3)_2]} = 84\%$. The prevailing route (Scheme 9) is the CH_3 abstraction (route D) and the hydrogen abstraction from methyl (route E), *m/e* 122 → *m/e* 121, verified by a metastable peak at m^* 120. Also, ring C—C bond rupture is observed, and results in the fragments C_3H_3 and C_2H (Scheme 9).

SCHEME 9

FRAGMENTATION OF $[C_5H_4Si(CH_3)_2]^+$ (*m/e* 122) IN THE SPECTRUM OF VII.



The spectrum of the deuterated compound, d_4-VII (Fig. 3) shows that deuterium is not randomised between the methyls and the cyclopentadienyl under the action of electron impact. Peaks of all the route E ions, as well as peaks of $[C_5H_4Si(CH_3)_2]^+$ (*m/e* 122), $[C_5H_4SiCH_3]^+$ (*m/e* 107), $[C_5H_4SiH_2]^+$ (*m/e* 94), and of $[C_5H_4Si(CH_3)CH_2]^+$ (*m/e* 121), are shifted by four mass units towards higher masses, which agrees with the pattern in Scheme 9.

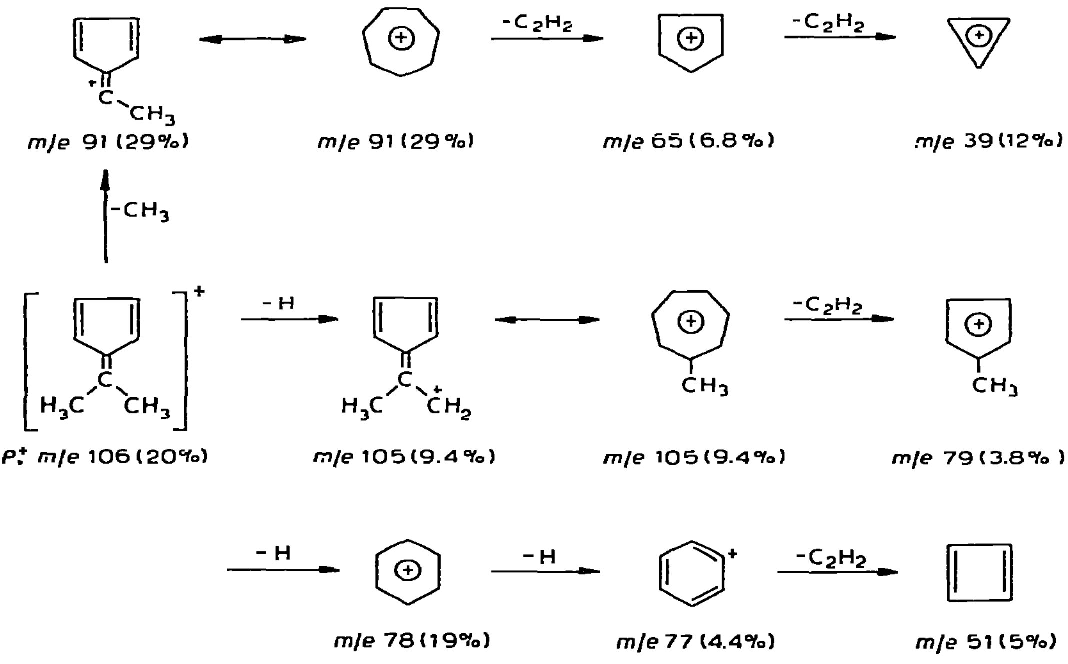
As for the $[C_5H_7Si]^+$ peak (*m/e* 95), this is shifted by three or four, but never two, mass units. Similarly, the shifts observed for $[C_4H_5Si]^+$ (*m/e* 81), $[C_4H_7Si]^+$ (*m/e* 83), $[C_3H_4Si]^+$ (*m/e* 68), $[C_3H_5Si]^+$ (*m/e* 69), and $[C_2H_3Si]^+$ (*m/e* 55) are greater than the values expected, one or two. Probably these ions result from a rearrangement while the abstraction of neutral C_2H_2 and C_3H_3 fragments involves not only the ring skeleton but also the CH_3 groups attached to silicon.

These data lead us to compare the fragmentation of $[C_5H_4Si(CH_3)_2]^+$ (*m/e* 122) in the spectrum of VII with fragmentations of fulvene molecular ions, $[C_5H_4CR_2]^+$.

Mass spectra of dimethylfulvene and other fulvenes were studied by Murata et al. [25]. Their scheme should be extended since the formation of P^+-1 (*m/e* 105, 9.4%, about 50% of the intensity of M^+) was not explained. The scheme did not include peaks at *m/e* of 79 (3.8%) and 78 (1.9%) either, while the formation of $[C_6H_5]^+$ (*m/e* 77) from $[C_7H_7]^+$ (*m/e* 91) claimed to be caused by the elimination of CH_2 does not agree with the benzyl cation fragmentation pattern [26]. In the final analysis, the pattern for dimethylfulvene may be laid down as we give in Scheme 10.

SCHEME 10

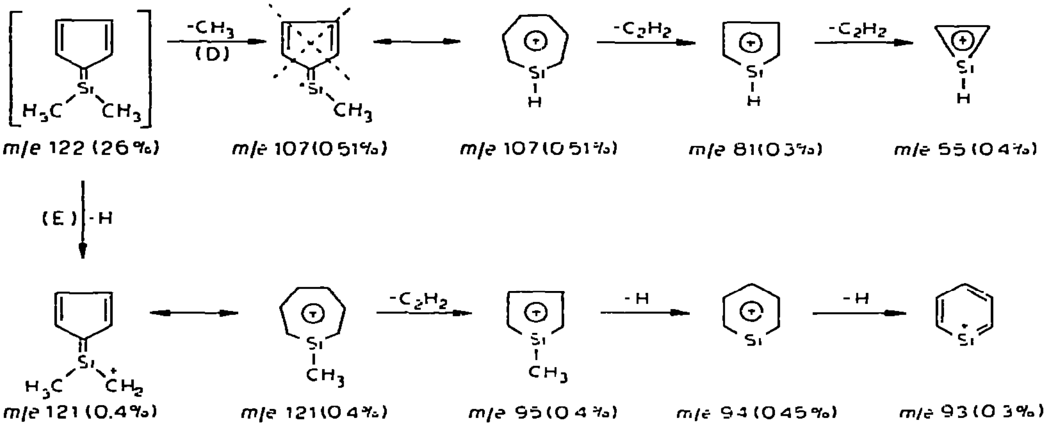
AN IMPROVED FRAGMENTATION PATTERN FOR DIMETHYLFULVENE.



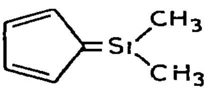
Let us remember that in fragmentation of $[C_5H_4Si(CH_3)_2]^+$ the positive charge is mainly localised on the silicon-containing fragment; then, Schemes 9 and 10 bear some resemblance. Now, when we remember the anomalous shifts of some peaks in d_4-VII we may assume that at least part of the ions resulting from $[C_5H_4Si(CH_3)_2]^+$ rearrange to merge silicon into the cycle and form silatropylium, silabenzene, and silacyclopentadienyl cations (Scheme 11). The possibility of a similar reaction was discussed earlier [27].

SCHEME 11

FRAGMENTATION OF $[C_5H_4Si(CH_3)_2]^+$ IN THE SPECTRUM OF VII.



A common assumption was that the structures were stabilised through the formation of an aromatic system much less than were their carbon analogues, or even that there was no aromatic stabilisation at all. Even if this were so, these processes should not be thought impossible. The dimethylfulvene molecular ion very easily liberates a hydrogen atom, due to the atom being in an allyl position with respect to silicon, that is, β to the double bond; therefore, the fact that the ion (*m/e* 122) observed for VII loses a hydrogen atom demonstrates that the silicon—ring bond in the ion resembles a double bond. It is evident that the hydrogen abstraction is part of a rearrangement, since the C—H bond is much stronger than C—C and C—Si bonds. Its decomposition may occur only if the energy consumed is in part compensated for by reorganisation of the molecule to a more stable structure. Ring expansion seems to be the most probable assumption. The data discussed above suggest that the ion $[C_5H_4Si(CH_3)_2]^+$ is similar in structure to the dimethylfulvene molecular ion and may be depicted as A [28].



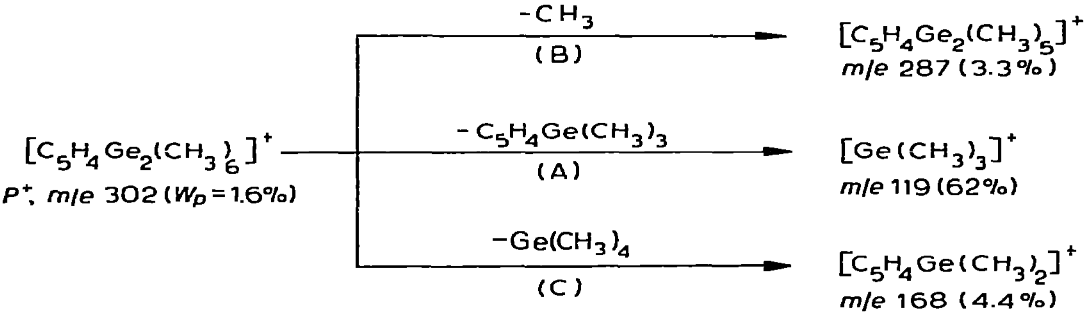
(A)

(b) M = M' = Ge

5,5-Bis(trimethylgermyl)cyclopentadiene (VIII). Fragmentation of VIII under the action of electron impact is similar to that of VII (Scheme 12). The spectrum recorded at 70 eV is shown in Fig. 3. Along with $P^+—n\ CH_3$ (n = 1-6), the spectrum contains peaks of $P^+—n\ CH_3—H_2$ (n = 2, 4 and 6). Thus

SCHEME 12

FRAGMENTATION OF VIII AT 70 eV.



$[C_5H_4Ge_2(CH_3)_5]^+$ (*m/e* 287) loses a CH_3 group, hydrogen molecules, or two CH_4 molecules while $[C_5H_4Ge_2(CH_3)_4]^+$ (*m/e* 272) may lose a $C_5H_4CH_3$ radical to result in $[Ge_2(CH_3)_3]^+$ (*m/e* 193). Fragmentation of $[Ge(CH_3)_3]^+$ (*m/e* 119) goes via a usual path (cf. Scheme 4). Unlike the similar ion in the spectrum of VII, the ion $[C_5H_4Ge(CH_3)_2]^+$ undergoes no ring C—C bond rupture, and only liberates CH_3 and CH_2 species.

$$\underset{m/e\ 168\ (4.4\%)}{[C_5H_4Ge(CH_3)_2]^+} \xrightarrow{-CH_3} \underset{m/e\ 153\ (1.1\%)}{[C_5H_4GeCH_3]^+} \xrightarrow{-CH_2} \underset{m/e\ 139\ (0.9\%)}{[C_5H_4GeH]^+}$$

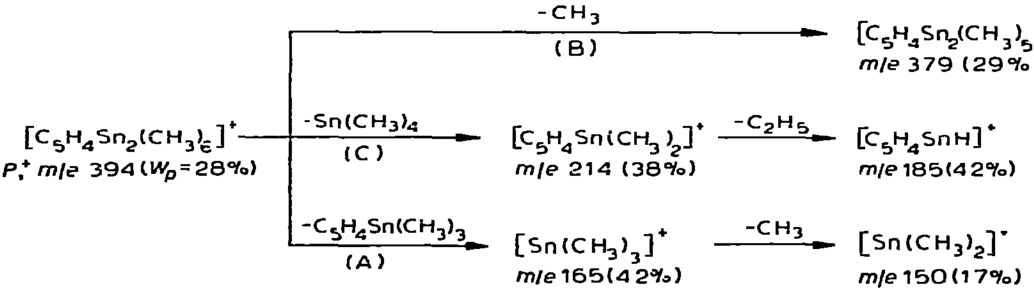
Its stability against further decomposition is markedly lower than in the case of VII.

(c) M = M' = Sn

5,5-Bis(trimethylstannyl)cyclopentadiene (IX). The fragmentation of IX at 12.6 eV is similar (Scheme 13) to that of VII and VIII.

SCHEME 13

FRAGMENTATION OF IX. ELECTRON IMPACT, 12.6 eV.



At 70 eV (Fig. 4), the stability of P^+ against decomposition W_P, falls to 5.7% and the abstraction of CH_3 or C_2H_6 from tin is sufficiently intense to result in $[C_5H_4Sn_2]^+$ (*m/e* 304), Scheme 14. Further, $[(CH_3)_3Sn]^+$ (*m/e* 165) decomposes via the usual Scheme 7. For $[C_5H_4Sn(CH_3)_2]^+$ (*m/e* 214), similar to the germanium-containing analogue, no ring C—C bond breakage is observed. The

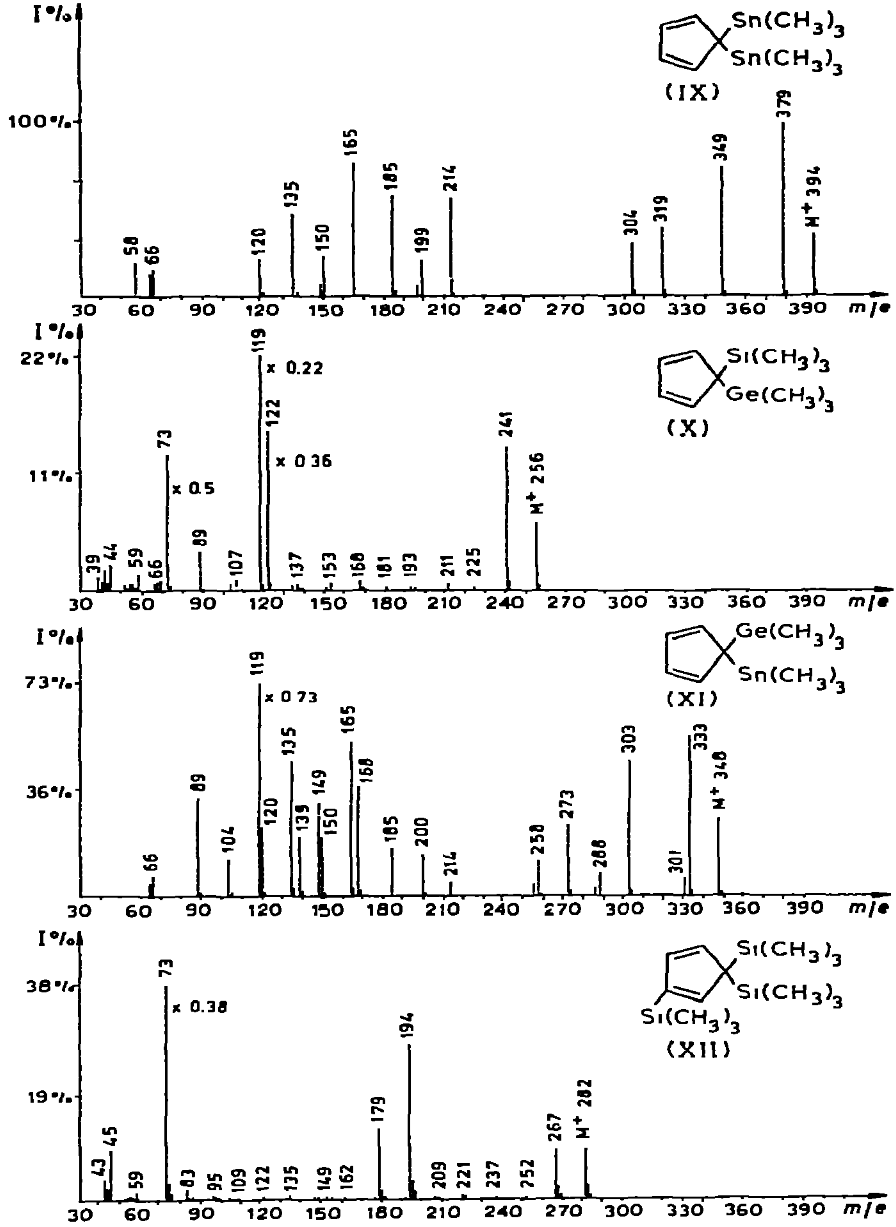


Fig. 4. Mass spectra of IX-XII.

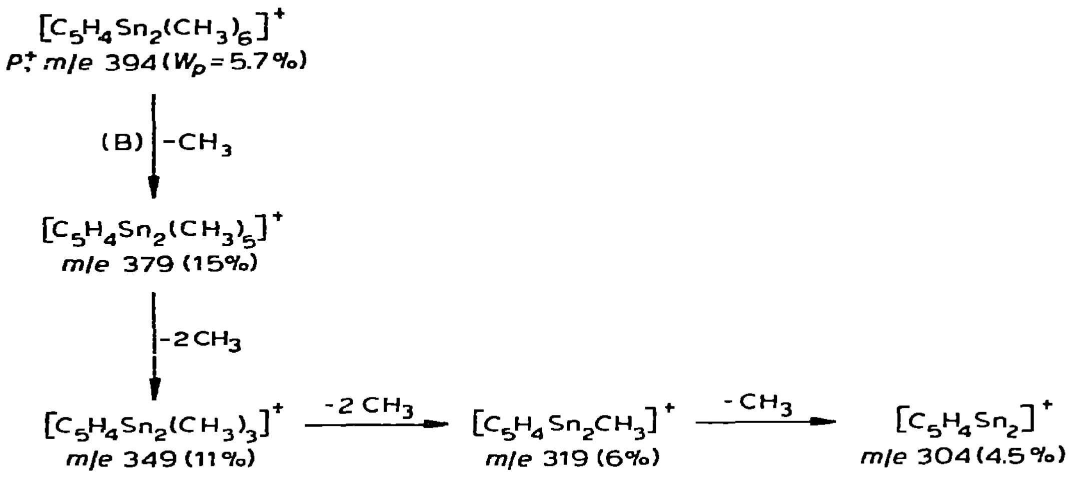
stability against decomposition is even lower. The fragmentation of $[C_5H_4Sn(CH_3)_2]^+$ is shown in Scheme 15.

(d) M = Si, M' = Ge

5-(Trimethylsilyl)-5-(trimethylgermyl)cyclopentadiene (X). The spectrum of X is shown in Fig. 4, and the molecular ion fragmentation is depicted in Scheme 16.

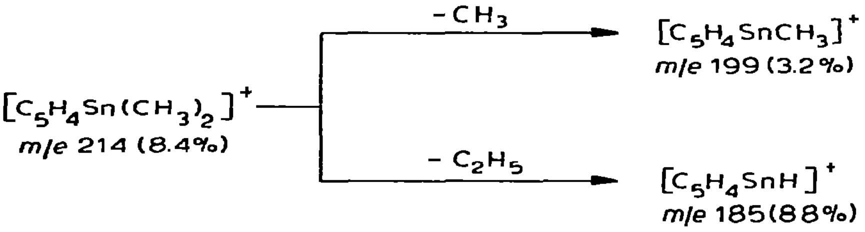
SCHEME 14

FRAGMENTATION OF IX. ELECTRON IMPACT, 70 eV, ROUTE B.



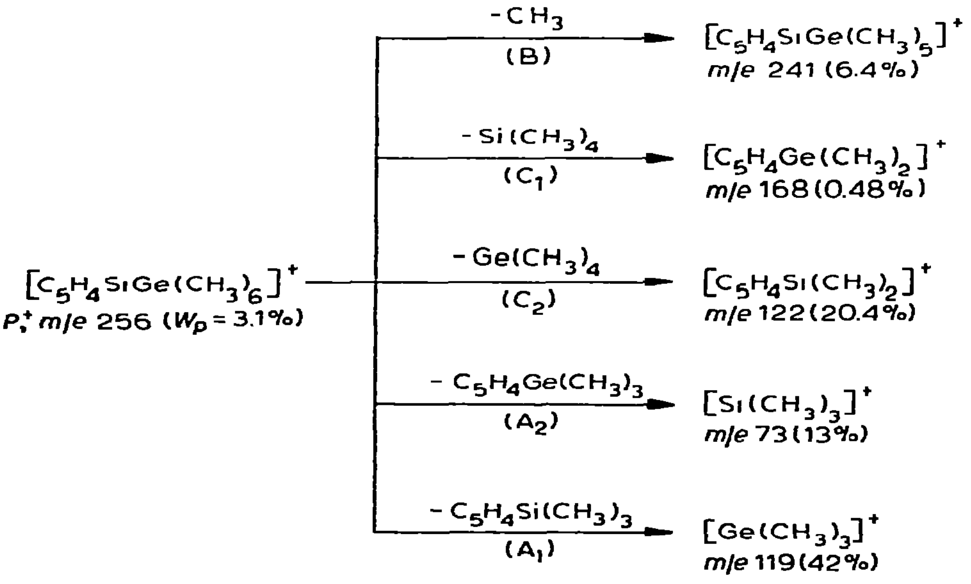
SCHEME 15

FRAGMENTATION OF $[C_5H_4Sn(CH_3)_2]^+$ (m/e 214).



SCHEME 16

FRAGMENTATION OF X. ELECTRON IMPACT, 70 eV.



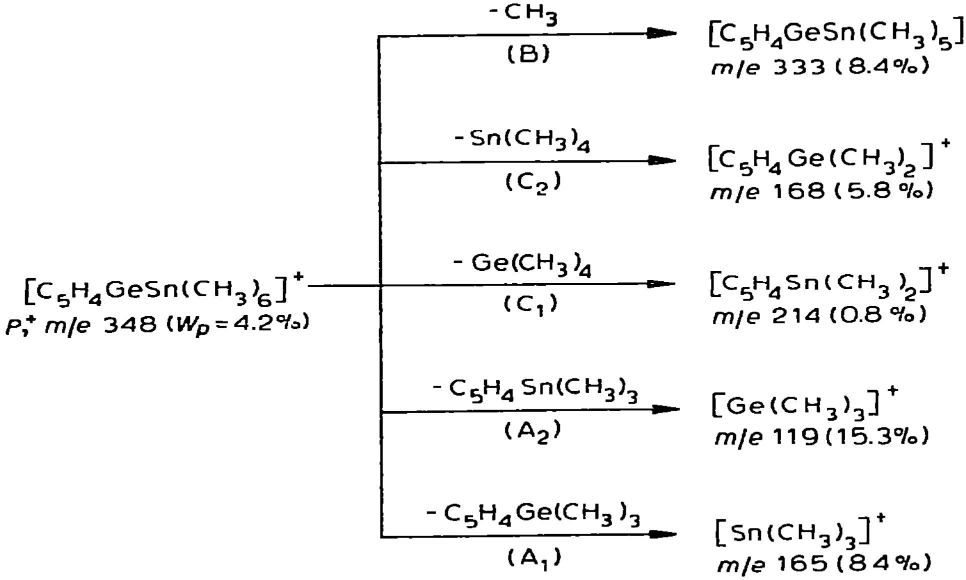
The X filial ions decompose in the same way as do the ions of VII, VIII and IX. The prevailing process is, as expected, the C_5H_4—Ge bond rupture (route A_1).

(e) M = Ge, M' = Sn

5-(Trimethylgermyl)-5-(trimethylstannyl)cyclopentadiene (XI). The spectrum of XI in Fig. 4 shows that the C_5H_4—M bond fission is predominant, and the C_5H_4—Ge bond fission does not differ much from the C_5H_4—Sn fission, see Scheme 17. The filial ions shown in Scheme 17 decompose further according to Scheme 18.

SCHEME 17

FRAGMENTATION OF XI. ELECTRON IMPACT, 70 eV.



The most probable precursor of $[CH_3SnCH_2]^+$ (*m/e* 149, 5%) is one of the ions formed via route B (methyl abstraction from the metal).

Table 2 lists degradation probabilities for molecular ions P^+ of dimetallated cyclopentadienes. The main routes are: the $M(CH_3)_3$ elimination (probability N_A), the CH_3 elimination (N_B), and the $M(CH_3)_4$ evolution (N_C). The Table also lists the stability, W_P, of molecular ions of VII-XI. As with monometallated cyclopentadienes, the first route is absolutely predominant. Comparison of Table 2 and Table 1 (monometallated cyclopentadienes) demonstrates that if two organometallic groups are present in a molecule, the fragmentation pattern will be governed by that metal whose C—M bond is weaker. E.g., C—Ge bond breakage is major for X, and C—Sn bond breakage for XI. The N_A/N_B values verify that all the dimetallated species studied have h^1 structures.

However, $N_A < N_B$ for $C_5H_4Sn_2(CH_3)_6$ (IX), and the W_P value of this compound is also increased. This may be explained by assuming that the molecular ion is stabilised through the π-component of the h^1-C_5H_5—Sn bond, i.e. through σ—π conjugation assisted by the mutual repulsion of $Sn(CH_3)_3$ groups that draws the ring to the tin atoms.

SCHEME 18

FRAGMENTATION OF IONS *m/e* 333, *m/e* 165, *m/e* 119, AND *m/e* 168 IN THE SPECTRUM OF XI.

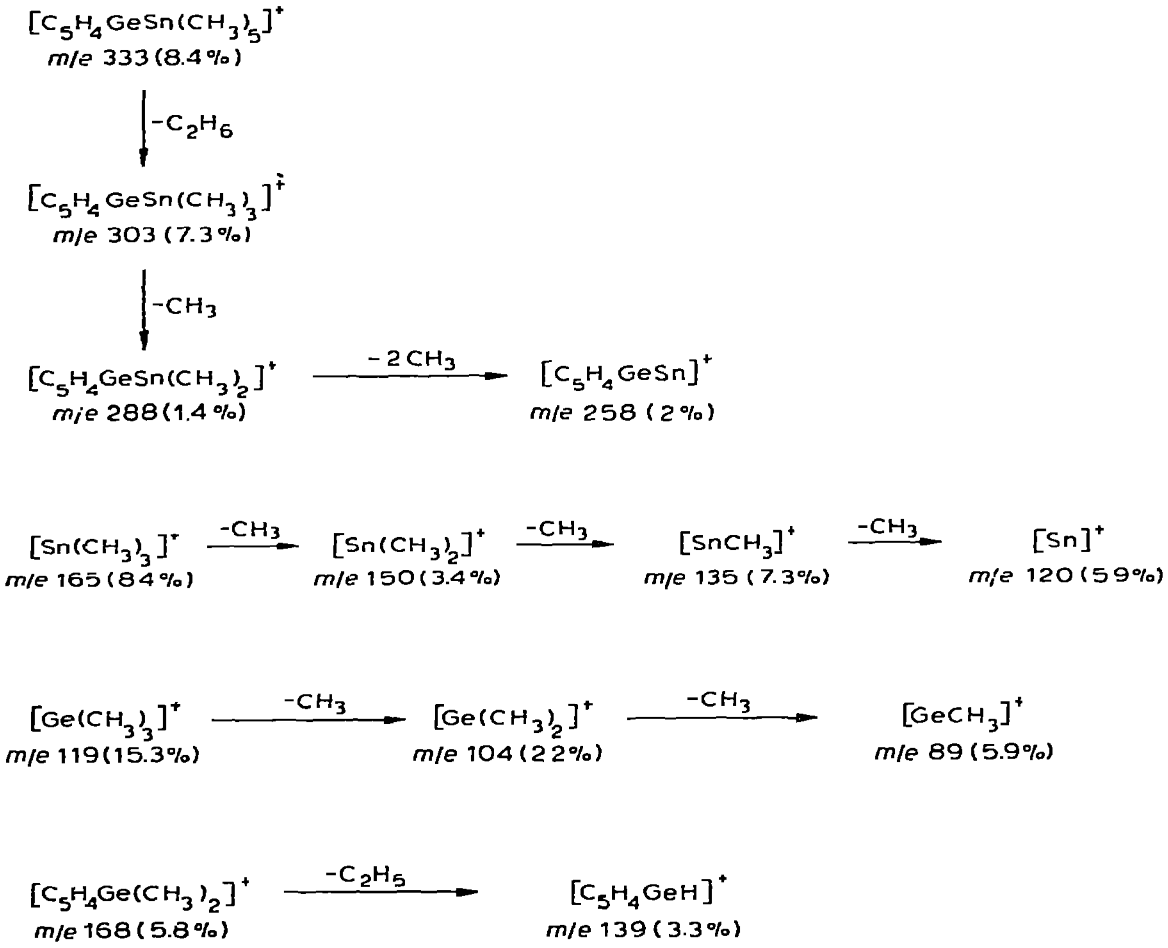


TABLE 2

STABILITY AGAINST DECOMPOSITION (W_P) AND PROBABILITIES OF THE ROUTES A, B AND C, FOR $C_5H_4M(CH_3)_3M'(CH_3)_3$

Compound	N_A (%)	N_B (%)	N_C (%)	W_P (%)
$C_5H_4[Si(CH_3)_3]_2$ (VII)	67	22	7.0	2.1
d_4-$C_5D_4[Si(CH_3)_3]_2$ (d_4-VII)	50	32	12.2	5.1
$C_5H_4[Ge(CH_3)_3]_2$ (VIII)	69	23	4.4	1.6
$C_5H_4[Sn(CH_3)_3]_2$ (IX)	26	27	39	5.7
$C_5H_4Si(CH_3)_3Ge(CH_3)_3$ (X)	Si:18 Ge:46	Si:1.2 Ge:22	8.0	3.1
$C_5H_4Ge(CH_3)_3Sn(CH_3)_3$ (XI)	Ge:25 Sn:28	Ge:4.0 Sn:10	27	4.5

A characteristic of the dimetallated species is a fragmentation to $[C_5H_4M(CH_3)_2]^+$ (M = Si, Ge, Sn), see Table 2.

The data in Table 2 suggest that the stability of $[C_5H_4M(CH_3)_2]^+$ falls across the series Si, Ge, Sn. When two different metals are present in a molecule (X, XI) the resulting ion preferentially contains the metal of lower atomic number. In other words, the formation of $[C_5H_4Si(CH_3)_2]^+$ is the most facile, the ion is the most stable against its further decomposition, and it is the only one for which we could observe hydrogen elimination and the rearrangement. Consequently, the respective neutral molecule, $C_5H_4Si(CH_3)_2$, may be assumed to be more stable than its analogues [28].

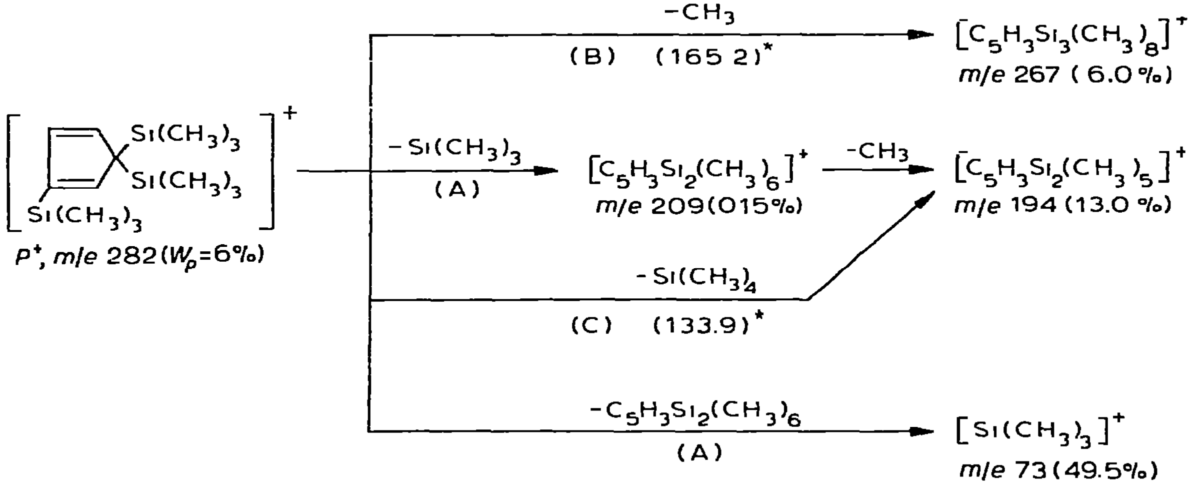
Trimetallated cyclopentadienes $C_5H_3M(CH_3)_3M'(CH_3)_3M''(CH_3)_3$

(a) $M = M' = M'' = Si$

2,5,5-Tris(trimethylsilyl)cyclopentadiene (XII). The spectra of XII and its deuterated derivative d_3-XII are shown in Figs. 4 and 5. Similar to other h^1-cyclopentadienyl compounds, the C_5H_3—Si bond rupture is the main process (Scheme 19). However, now the P^+—$Si(CH_3)_3$ (*m/e* 209) peak is present in the spectra, so $[C_5H_3Si_2(CH_3)_5]^+$ may be formed from not only the P^+—$(CH_3)_4Si$ elimination but also the successive abstraction of $Si(CH_3)_3$ and CH_3.

SCHEME 19

FRAGMENTATION OF XII. ELECTRON IMPACT, 70 eV.



The ion $[C_5H_3Si_3(CH_3)_8]^+$ (*m/e* 267) formed via route B further loses two CH_3 groups and the process is terminated after all the nine methyls have been eliminated. The respective filial peaks are of low intensity. The $[Si(CH_3)_3]^+$ fragmentation is shown in Scheme 2, and that of $[C_5H_3Si_2(CH_3)_5]^+$ (route C or A) in Scheme 20.

The most probable assumption is that the ion at *m/e* of 194 loses its first two methyls from the $Si(CH_3)_3$ group in the 2-position in the ring. Unlike mono- or di-metallated species, I or VII, the dissociative ionisation of XII is specific in that the $H_2C{=}Si(CH_3)_2$ group is eliminated from position 2 at the double

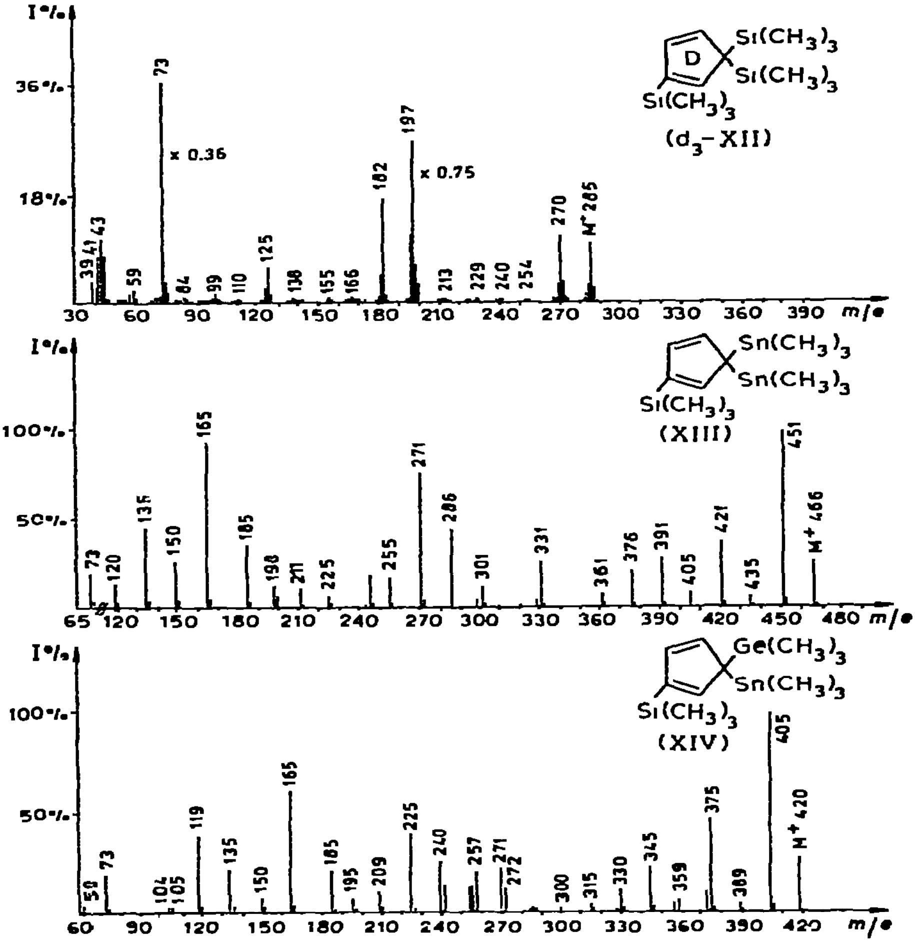
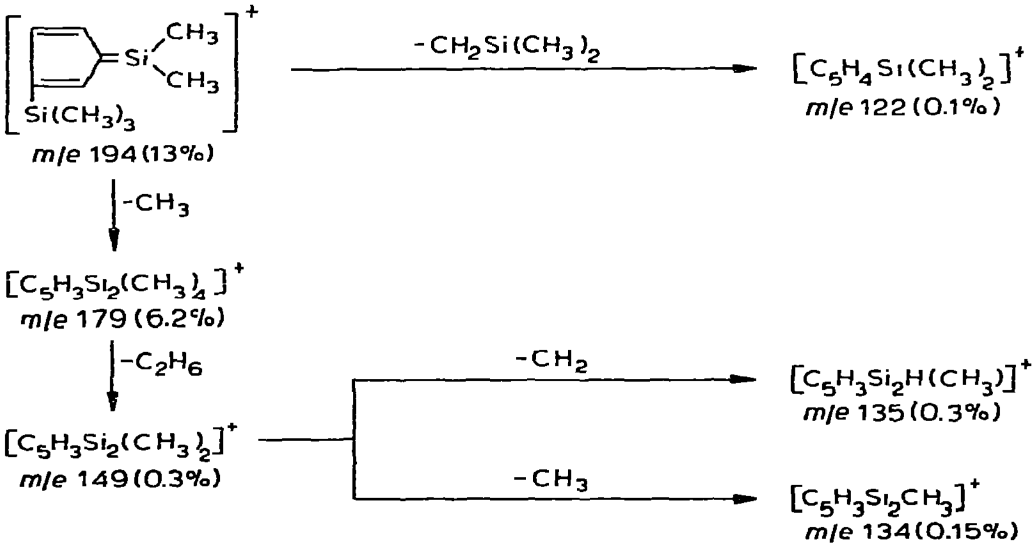


Fig. 5. Mass spectra of d_3-XII, XIII and XIV.

SCHEME 20

FRAGMENTATION OF $[C_5H_3Si_2(CH_3)_5]^+$ IN THE SPECTRUM OF XII.



bond of the ring, route D. In the spectrum of the ring-deuterated compound d_3-XII, the $P^+{-}H_2C{=}Si(CH_3)_2$ peak (*m/e* 213) is shifted by three mass units towards higher masses, so this peak is not a molecular ion of the respective dimetallated derivative that could have been an admixture to XII.

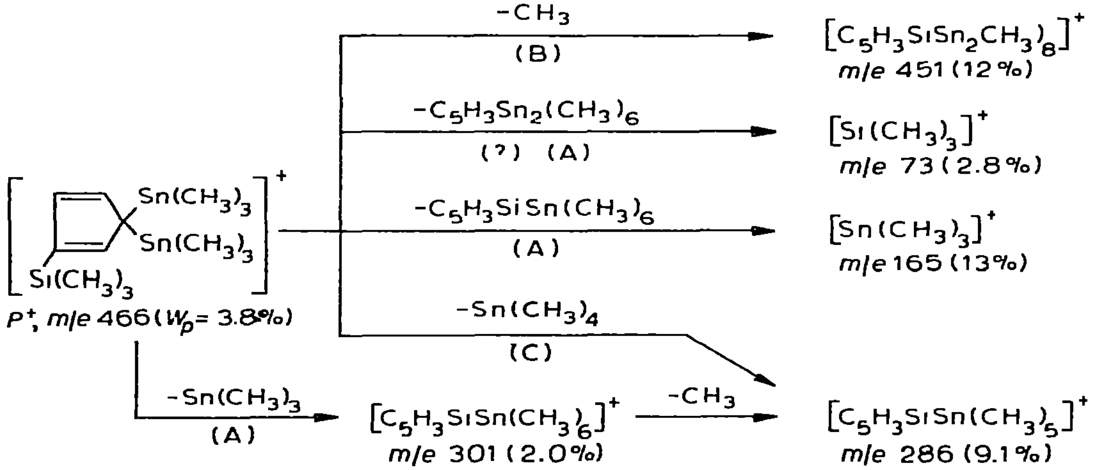
In the spectrum of d_3-XII, the $P^+{-}n$ CH_3 (n = 1-9) peaks are shifted by three mass units towards higher masses, hence there is no hydrogen randomisation between the methyls and the ring of XII.

(b) M = Si, M' = M" = Sn

2-(Trimethylsilyl)-5,5-bis(trimethylstannyl)cyclopentadiene (XIII). The spectrum of XIII is shown in Fig. 5. We observe either successive CH_3 abstractions from tin and silicon (route B), or elimination of $(CH_3)_3Sn$ followed by CH_3 abstraction from the second tin atom (Scheme 21), or the elimination of $Sn(CH_3)_4$ in the course of rearrangement.

SCHEME 21

FRAGMENTATION OF XIII. ELECTRON IMPACT, 70 eV.



The spectrum contains a peak at *m/e* 73 due to $[Si(CH_3)_3]^+$. This may form both from P^+ directly and from one of the ions generated via route B. Further degradations of $[Sn(CH_3)_3]^+$ and $[Si(CH_3)_3]^+$ proceed in the usual way, Schemes 2 and 6. The $[C_5H_3SiSn_2(CH_3)_8]^+$ (*m/e* 451) degradation (Scheme 22) results in not only elimination of ethane and methyls but also abstraction of methane.

The ion at *m/e* 286 loses CH_3 and CH_2 groups. A probable pattern is shown in Scheme 23. The spectrum also contains a peak at *m/e* 255 resulting from either the methane elimination from the ion of *m/e* 271, or from hydrogen abstraction and rearrangement, from one of the methyls in the *m/e* 256. The latter fragmentation mode is observed, e.g., at *m/e* of 122 in the spectrum of VII.

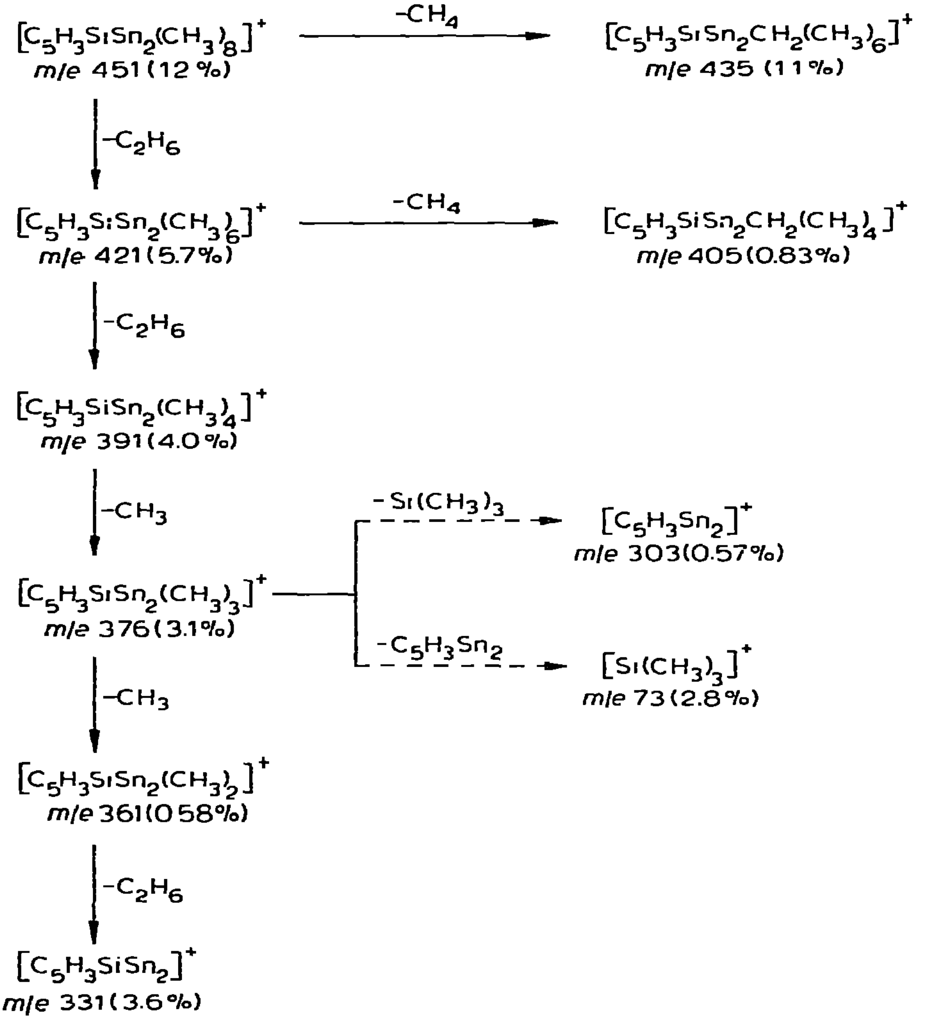
(c) M = Si, M' = Ge, M" = Sn

2-(Trimethylsilyl)-5-(trimethylgermyl)-5-(trimethylstannyl)cyclopentadiene (XIV). The spectrum of XIV is shown in Fig. 5. The molecular ion fragmentation pattern is shown in Scheme 24.

(continued on p. 62)

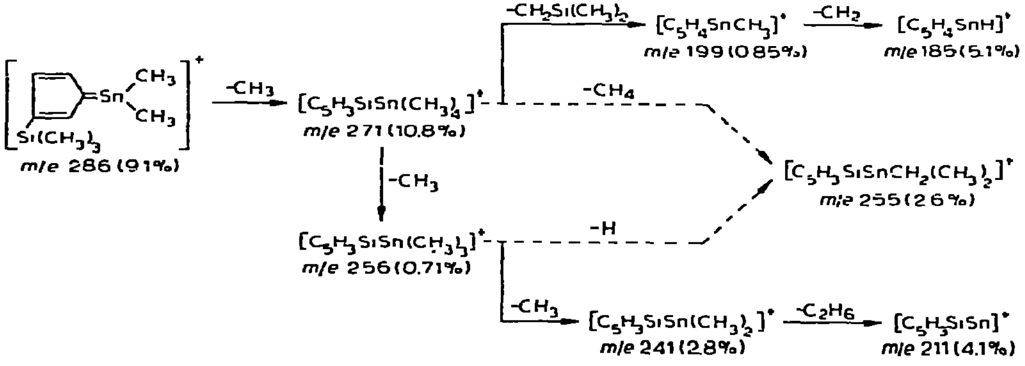
SCHEME 22

FRAGMENTATION OF $[C_5H_3Sn_2(CH_3)_8]^+$.



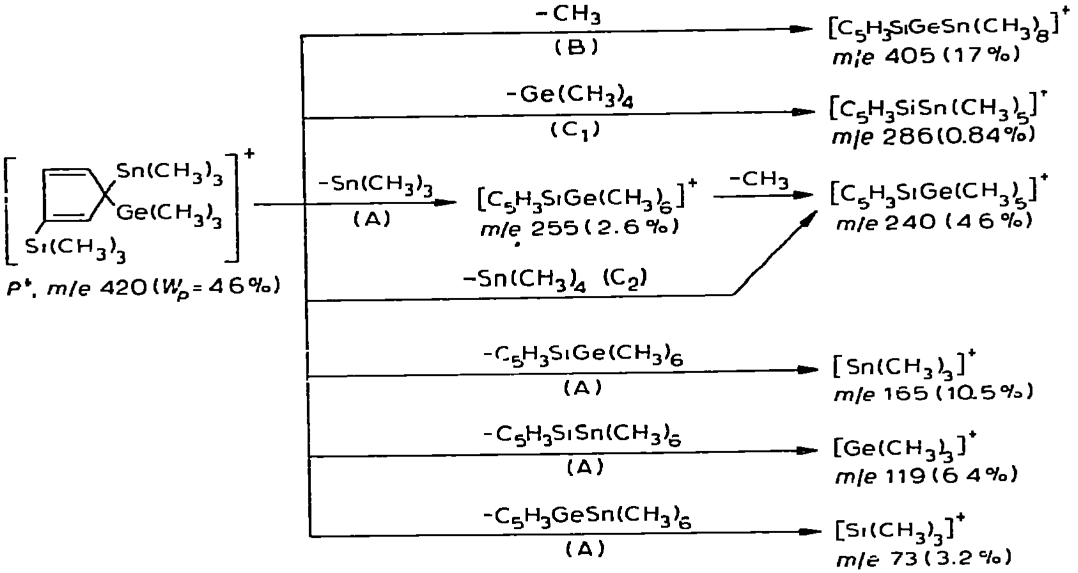
SCHEME 23

FRAGMENTATION OF *m/e* 286 IN THE SPECTRUM OF XIII.

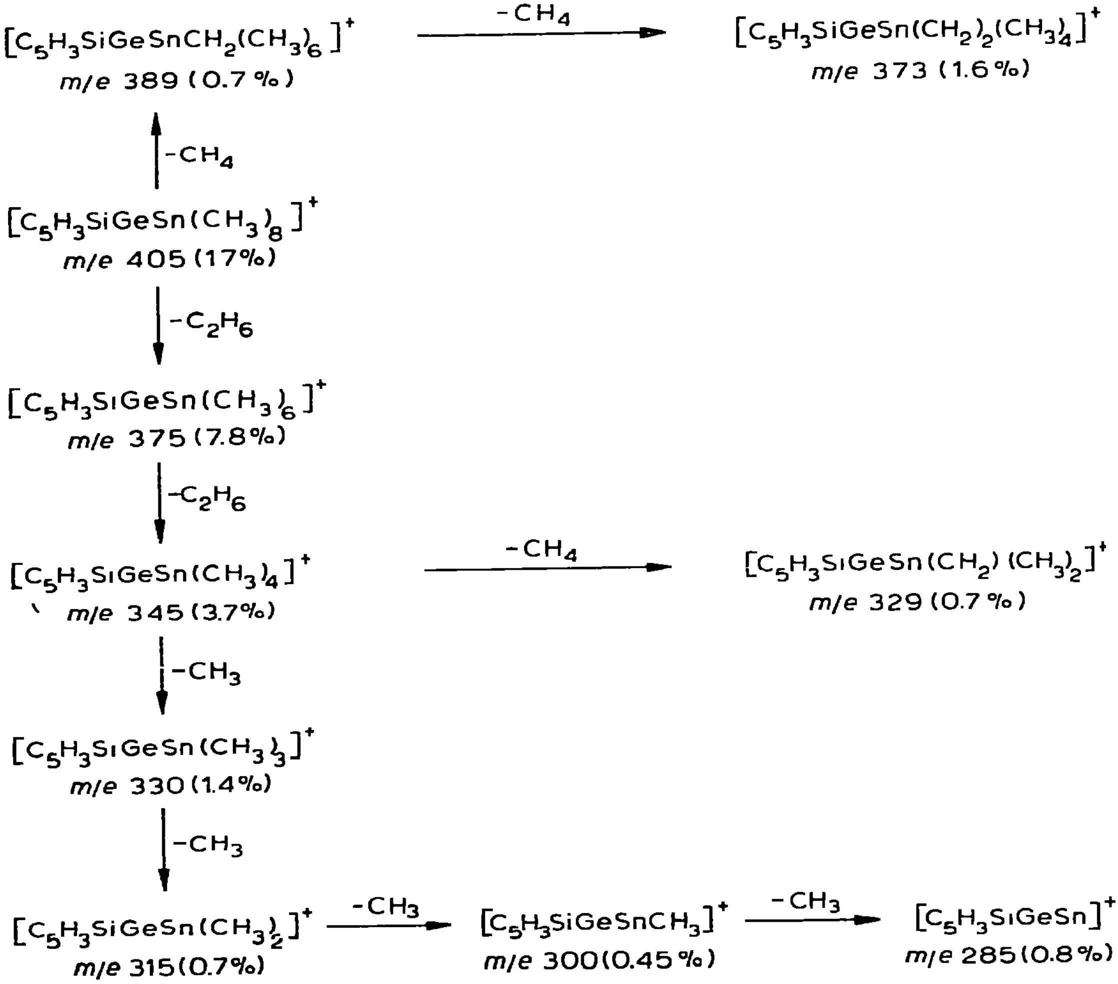


SCHEME 24

FRAGMENTATION OF XIV. ELECTRON IMPACT, 70 eV.



SCHEME 25

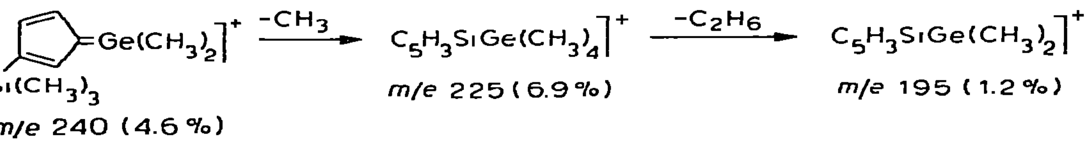


Further, $[C_5H_3SiGeSn(CH_3)_8]^+$ (*m/e* 405) decomposes chiefly via the methyl and ethane abstraction (Scheme 25).

The spectrum also contains peaks at *m/e* 389, 373 and 329 generated probably by abstraction of a methane molecule from the ions at *m/e* 405, 389 and 345 respectively.

Fragmentations of $[C_5H_3SiSn(CH_3)_5]^+$ (*m/e* 286), $[Sn(CH_3)_3]^+$ (*m/e* 165), $[Ge(CH_3)_3]^+$ (*m/e* 119) and $Si(CH_3)_3$ (*m/e* 73) follow the usual course. The *m/e* 240 fragmentation is shown in Scheme 26.

SCHEME 26



The main fragmentation routes observed for trimetallated cyclopentadienes are similar to those found for the mono- and di-metallated compounds. Again, the cyclopentadienyl—metal bond fission is a prevailing process, indicative of h^1-structures. The group $M(CH_3)_3$ is abstracted from the position 5; consequently mass spectral techniques may be employed as a method of discovering the arrangement of the substituents in a cyclopentadienyl compound containing more than one MR_3 group.

Ionisation potentials of metallated cyclopentadienes

An important problem in the chemistry of h^1-cyclopentadienyl derivatives of Group IVB elements consists in rationalising electronic effects responsible for anomalies in physical and chemical properties of the molecules and, in particular, for metallotropic and prototropic rearrangements. A priori, two electronic effects may be singled out, namely, σ—π conjugation of the C_5H_5—M bond with the ring diene system, leading to partial delocalisation of electrons of the bond, and d_π—p_π interaction of ring π-orbitals with vacant *d* orbitals of the metal. Both the possibilities have been discussed [13, 30, 31]. Ionisation potentials of the molecules allow one to clarify the role of these effects in the ground state of the molecules, as was shown recently by Rakita et al. [2] who studied a series of silicon, germanium, and tin indenyls.

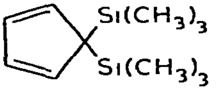
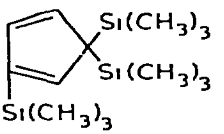
We have measured photoionisation potentials for I, IV, V, VII and XII. The results are listed in Table 3.

For monometallated cyclopentadienes I, IV and V, ionisation potentials gradually decrease, the decrease being at its most significant ($\approx$ 0.72 eV) in going from cyclopentadiene to trimethylsilylcyclopentadiene. The values obtained are in good accord with the difference in energy between the occupied upper π-orbitals (0.75 eV) calculated by us through the CNDO/2 technique [33] neglecting vacant 3*d* orbitals of silicon.

The decrease in the ionisation potentials is a strong indication that a contribution of σ—π conjugation into ground states of the $C_5H_5MR_3$ is significant. d_π—p_π interaction plays no significant role, otherwise the ionisation potential would have slightly increased. h^1-Cyclopentadienyls somewhat differ

TABLE 3

PHOTOIONISATION POTENTIALS OF METALLATED CYCLOPENTADIENES

Compound	IP
C_5H_6	8.70[a], 8.57[b]
$C_5H_5Si(CH_3)_3$ (I)	7.93 ± 0.03
$C_5H_5Ge(CH_3)_3$ (IV)	7.86 ± 0.05
$C_5H_5Sn(CH_3)_3$ (V)	7.72 ± 0.05
 (VII)	7.72 ± 0.03
 (XII)	7.57 ± 0.03

[a] From ref. 32. [b] From ref. 35.

from the respective h^1-indenyls in that the decrease of their ionisation potentials observed in going from silicon to germanium and tin is less pronounced.

Introduction of the second $(CH_3)_3Si$ into position 5 of the ring (VII) leads to some additional decrease of potential in comparison with I. The effect, however, is less pronounced than with the introduction of the first substituent and amounts to just 0.21 eV instead of the 0.72 eV observed when C_5H_6 is replaced by I. The third substituent leads to a still lower increment, 0.15 eV.

Apparently, just σ—π conjugation of the C_5H_5—M bond with the ring diene system controls rates of metallotropic rearrangements in the compounds under discussion; indeed, the IP values are paralleled by the free energies of activation in the series C_5H_6, $C_5H_5Si(CH_3)_3$, $C_5H_5Ge(CH_3)_3$, $C_5H_5Sn(CH_3)_3$ [13].

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