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Mass Spectrometry Studies of Organometallic Compounds: Part 1. Compounds of General Formula Ph_nGeCl_{4-n}

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The mass spectra of organogermanium compounds of the type Ph_nGeCl_{4-n} (where $n=1-4$) were investigated. Positive and negative ion spectra of these compounds were recorded using conventional electron impact (EI) conditions. In common with the analogous tetra-alkyltin compound, Ph_4Ge produced no negative ion spectra under these conditions. Tandem mass spectrometry (MS–MS) was used to deduce fragmetation reaction pathways for these compounds. In the case of $PhGeCl_3$, collision-induced dissociation studies were extended to examine the ion–molecule reactions under relatively high reactant pressures of methanol and/or water vapour in the collision cell of the MS–MS instrument.

Keywords: organogermanium compounds; tandem mass spectrometry; ion–molecule reactions

1 INTRODUCTION

Conventional positive ion electron impact (EI) mass spectra of organogermanium compounds of general formula R_4Ge (where R = Me, Et, Bu, Ph, etc.) and R_3GeX (where R is as before, and X = H, Cl, Br) have been reported elsewhere.[1-3] However, whilst a detailed and comprehensive examination of the fragmentation processes for these compounds, based on metastable ion data, has been presented, not all the compounds of general formula R_nGeX_{4-n} have been reported in such detail. Much attention has been paid to organotin compounds of a similar general structure, many of which are environmental contaminants, and therefore mass spectral data for these species are readily available.[4-6] Within Group IV, the fragmentation processes of tin and germanium compounds might be expected to be similar since both elements have the same outer electronic structure (*s*, *p* and *d* electrons) whereas carbon and silicon (*s* and *p*) and lead (*s*, *p* , *d* and *f*) are different. Comparison of the fragmentation patterns of the organostannanes and organogermanes show several similarities including the production of even-electron ions which subsequently fragment by the loss of even-electron (i.e. molecular) species. In this investigation the fragmentation pathway can be uniquely defined by the preselection of a single precursor ion (fixed m/z value) in the first mass spectrometer (MS) and scanning in the second MS to determine the fragmentation products from that ion.

The mass spectral investigation of orgnogermanium compounds using EI positive and negative ion techniques in combination with MS–MS methods was therefore carried out in order to determine the extent of parallel reactions between similar tin and germanium compounds. MS–MS analyses can be used to show either the fragmentation products derived from a specified precursor ion or those precursor ions which fragment to give a selected product ion.[6] Some reactions were of specific interest, notably the formation of chlorobenzene from $PhSnCl_3$[6] and the corresponding yield of biphenyl from Ph_4Ge, Ph_3SnCl and Ph_2SnCl_2. The negative ion studies showed the propensity for nucleophilic attack on neutral R_nSnCl_{4-n} species by Cl^- to give $R_nSnCl_{5-n}^-$ even under conventional EI source conditions. Finally the ion–molecule reactions of $PhGeCl_3$, with typical HPLC solvent molecules, were examined in the collision region of the MS–MS instrument. Reactions of this type have been studied by Siu *et al.*[4] and Lawson and Ostah,[8] who reported different degrees of reaction. The differences were assigned to the much higher pressure of neutral molecules in the work carried out by Siu, with the corresponding increased potential for reaction. The comparable reactions with organogermanium compounds were investigated for comparison purposes.

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2 THEORY

2.1 Conventional positive and negative ion EI mass spectra

The general operating principles of the conventinal quadrupole mass spectrometer are well understood. Normally during the ionization process (EI) both positive and negative ions are formed in the ion source region of the mass spectrometer. However, mass spectrometers are usually tuned to detect the more abundant positive ions. Modern instruments are now provided with the facility to monitor ions of both charge signs and for electronegative compounds the yield of negative ions may approach that of the positive ions. This may be of special interest where the central atom of a molecule has available *d* or *f* orbitals which may be used to stabilize a negative charge. Reaction mechanisms for the formation of negative ions have been cited by Chapman,[9] and the nucleophilic addition of a halide anion to a neutral halogen-containing molecule, in the mass spectrometer ion source, has been reported by Dougherty.[10]

2.2 MS–MS experiments

The theory and practice of tandem MS using two quadrupole-based analyser regions has been discussed elsewhere.[6] Precursor ions are selected by the first mass spectrometer and forced to undergo collision-induced dissociation (CID) in a gas cell which precedes the second mass spectrometer, which is used to identify the products from the CID process. For non-reactive CID investigations an inert collision gas such as helium or argon is used, but for ion–molecule studies these gases are replaced by methanol and water molecules.

2.3 Ion–molecule reactions

Ion–neutral molecule reactions of organotin compounds have been investigated under atmospheric-pressure chemical ionization (APCI) and ion spray (IS) conditions.[4] This type of reaction has also been observed in the collision region of a triple quadrupole mass spectrometer. Results obtained by Lawson and Ostah[8] showed typical ion–molecule reactions occurring at relatively low pressures in a mixture of R_3SnCl and water or methanol:

Electron impact ionization processes

$$Ph_3SnCl + e^- \rightarrow Ph_3Sn^{+\cdot} + Cl^{\cdot} + 2e^-$$

$$Ph_3SnCl + e^- \rightarrow Ph_2SnCl^{+\cdot} + PhCl + 2e^-$$

Collision-induced reaction process

$Ph_3Sn^{+\cdot}$ and $Ph_2SnCl^{+\cdot}$ are sequentially selected by the first mass spectrometer (MS1) and introduced into the collision region and the second mass spectrometer (MS2) is used to identify the product ions:

$$\underset{m/z\ 341}{Ph_3Sn^{+\cdot}} + H_2O \rightarrow \underset{m/z\ 359}{Ph_3Sn^{+\cdot}(H_2O)}$$

$$\underset{m/z\ 309}{Ph_2SnCl^{+\cdot}} + H_2O \rightarrow \underset{m/z\ 327}{Ph_2SnCl^{+\cdot}(H_2O)}$$

The formation of cluster ions in a triple quadrupole mass spectrometer can be detected by monitoring ions with *m/z* values greater than that of the precursor ion.

3 EXPERIMENTAL

Authentic samples of Ph_nGeCl_{4-n} ($n = 1, 3, 4$) were obtained from Aldrich Chemicals and all were more than 98% pure. Ph_2GeCl_2 was obtained from Alfa Chemicals. The samples were introduced into the mass spectrometer via the direct insertion probe, which was heated within the range 50–250 °C until sufficient volatility was achieved. Mass spectra were recorded under conventional positive and negative EI conditions and subsequently in the MS–MS mode. All experiments were carried out on the VG TRIO 3 Instrument using the following experimental conditions.

(i) *Standard EI (positive and negative ions)*
Mass spectrometer: MS1 only operating
Scan rate: *m/z* 35–500 in 1 s
Resolution >1000

(ii) *MS–MS spectra (positive ion only)*
Set at *m/z* values selected from results of standard EI spectra
Collision gas: Argon at 3 mTorr
Ion collision energy: 5.0 eV
Scanning *m/z* 20–500 in 1 s

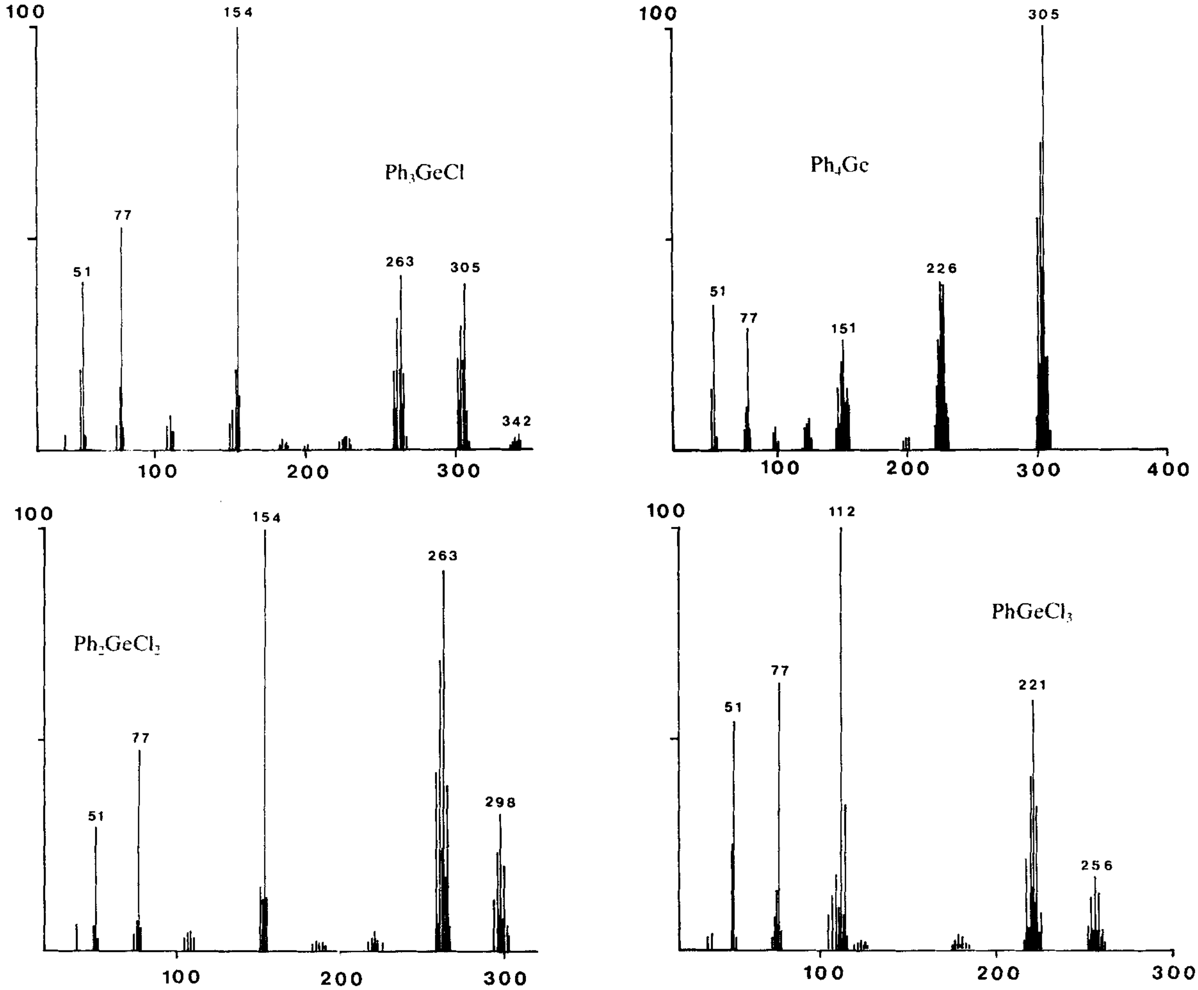


Fig. 1. Typical mass spectra obtained from compounds of general formula Ph_nGeCl_{4-n}.

(iii) *Ion–molecule reactions*

Similar to MS–MS experiments, except that methanol or water molecules at different pressures (3, 5, 6, 7, 9 and 10 mTorr), were used in the collision cell.

4 RESULTS

Each fragment ion occurs as a group of peaks due to the germanium isotopes (three major and two minor) combined with two isotopes for each chlorine atom in the molecule. In this work *m/z* values have been assigned on the basis of the ^{74}Ge and ^{35}Cl isotopes.

4.1 Positive ion EI mass spectra

The conventional mass spectra for the compounds Ph_nGeCl_{4-n} (where $n = 1–4$) are shown in Fig. 1. The most significant fragment ions are summarized in Table 1 which shows that, according to the compound, all the mass spectra have ions resulting from the loss of either a phenyl group and/or a chlorine atom from the molecular ion. Perhaps of more interest are the ions produced by rearrangement reactions leading to the formation of chlorobenzene (*m/z* 112) from $PhGeCl_3$ and biphenyl (*m/z* 154) from the other three compounds. These rearrangement reactions produce the most abundant ions for all species except Ph_4Ge, where Ph_3Ge^+ (*m/z* 305) is the most abundant. These results are very similar to those reported for the comparable organotin compounds.

Table 1. Summary of the major ions observed in the mass spectra of selected organogermanium compounds

Compound	RMM[a]	Fragment ions: m/z (RA)			Rearrangement ions	
		$-Cl^c$	$-Ph^d$	$Ph^{+\cdot}$	$Ph_2^{+\cdot}$	$PhCl^{+\cdot}$
Ph_4Ge	382 (ND)[b]	—	305 (100%)	77 (30%)	154 8%	—
Ph_3GeCl	340 (ND)	305 (42%)	263 (40%)	77 (53%)	154 (100%)	112 (ND)
Ph_2GeCl_2	298 (ND)	263 (90%)	221 (5%)	77 (48%)	154 (100%)	112 (ND)
$PhGeCl_3$	256 (20%)	221 (60%)	179 (5%)	77 (65%)	—	112 (100%)

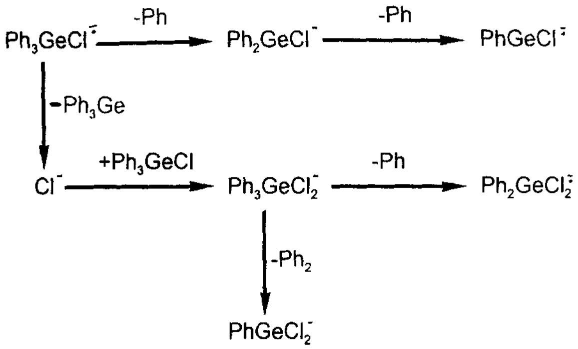
[a] RMM, relative molecular mass. [b] ND, not detected (<5%). [c] – Cl, RMM minus Cl. [d] – Ph. PMM minus C_6H_5.

4.2 Negative ion EI mass spectra

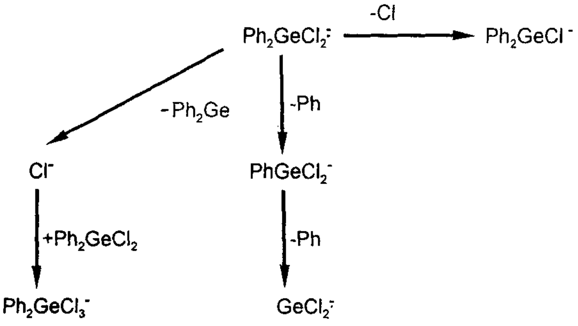
In general, the negative ion mass spectra from $PhGeCl_2$, Ph_2GeCl_2 and Ph_3GeCl showed that the most abundant ion was the chloride anion at m/z 35 and 37. The tetraphenylgermanium compound produced no signal under the conventional conditions utilized in these experiments.

4.2.1 Triphenylgermanium chloride

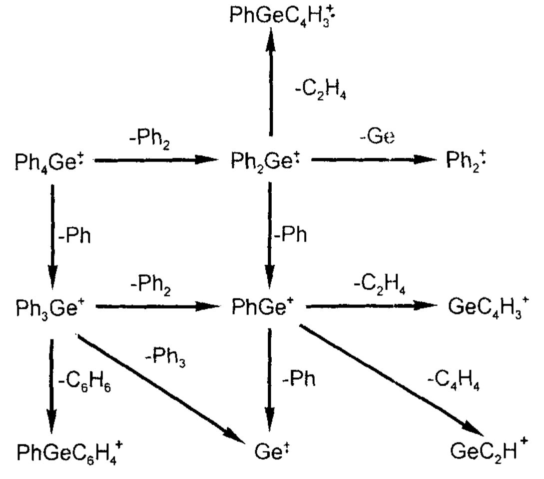
Fragment ions observed in the mass spectrum were derived from the loss of a phenyl group from the molecular ion to give the species Ph_2GeCl^- (m/z 263) and the subsequent loss of a second phenyl group to give $PhGeCl^-$ at m/z 186. Two other significant ions which were detected at m/z 221 and m/z 298 formed as a result of nucleophilic attack by Cl^- on the neutral molecule Ph_3GeCl followed by the loss of Ph_2 and Ph respectively from the resultant adduct ion $Ph_3GeCl_2^-$. Scheme 1 shows a possible fragmentation/reaction



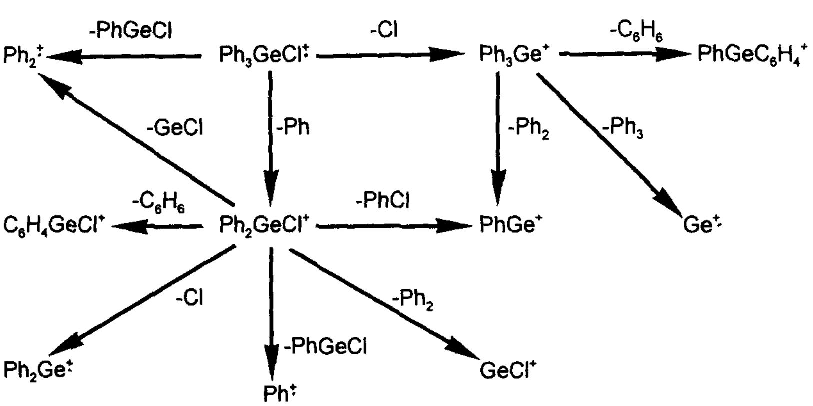
Scheme 1. Fragmentation/reaction scheme derived from the negative ion EI mass spectrum of Ph_3GeCl.



Scheme 2. Fragmentation/reaction scheme derived from the negative ion EI mass spectrum of Ph_2GeCl_2.



Scheme 3. Fragmentation pathway derived for the EI positive ion mass spectrum of Ph_4Ge.



Scheme 4. Fragmentation pathway derived for the EI positive ion mass spectrum of Ph_3GeCl.

sequence for the ions observed in the negative ion mass spectra of Ph_3GeCl.

4.2.2 Diphenylgermanium dichloride

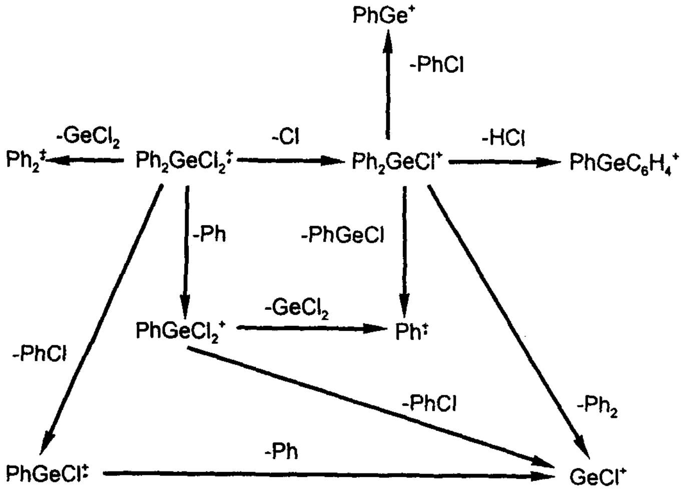
The parent molecular ion was the most abundant species observed, with *m/z* 221 (loss of one phenyl group) and *m/z* 144 (loss of two phenyl groups) being the next most abundant ions. Other ions detected included Ph_2GeCl^- (*m/z* 269) and $Ph_2GeCl_3^-$ at *m/z* 333. A possible fragmentation pathway for these ions is shown in Scheme 2.

4.2.3 Phenyltrichlorogermane

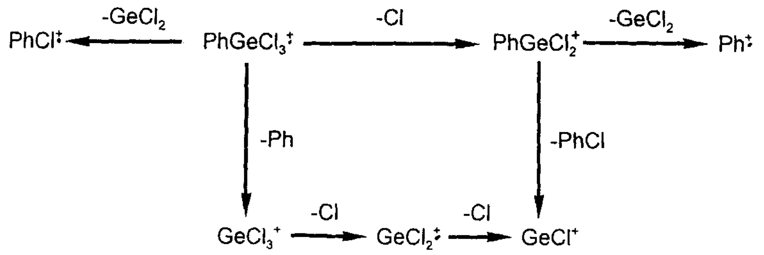
The negative ion mass spectrum of this compound is dominated by the peak at *m/z* 179 corresponding to $GeCl_3^-$ (cf $SnCl_3^-$). There is only one other significant ion produced, the chloride anion. $PhGeCl_3$ therefore has a very simple fragmentation process involving the loss of the phenyl group and also the production of the Cl^- anions.

4.3 Positive ion MS–MS spectra

MS–MS techniques have been used to elucidate and confirm the fragmentation pathways for a range of organotin compounds[11] and the approach has now been applied to this current series of compounds. Fragmentation pathways were established by monitoring the CID products from preselected ions, i.e. those most dominant in the EI mass spectra shown in Fig. 1. Using this method it is possible to follow a fragmentation process through several stages. Inspection of the mass spectra for Ph_4Ge (Fig. 1) suggests a very simple sequence of losses, whereas the MS–MS data show a more complicated series of steps (Scheme 3): they confirm the assignments made by Glockling and Light[3] for the formation of Ph_2Ge^+ and Ph_3Ge^+, but there are several points of disagreement concerning the subsequent fragmentation products, particularly those in which the



Scheme 5. Fragmentation pathway derived for the EI positive ion mass spectrum of Ph_2GeCl_2.



Scheme 6. Fragmentation pathway derived for the EI positive ion mass spectrum of $PhGeCl_3$.

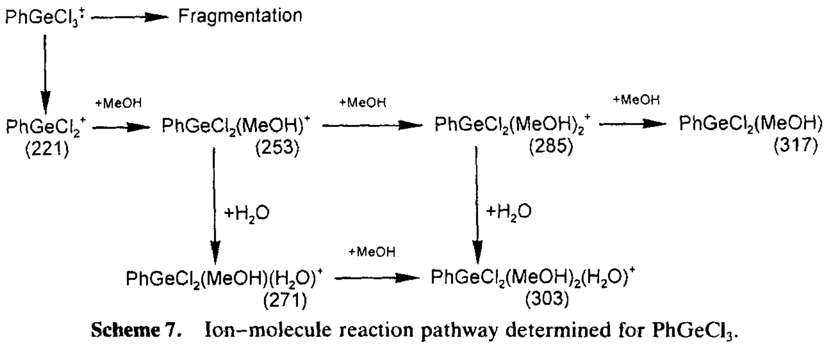
aromatic ring has been fragmented. The loss of even-electron groups in the fragmentation processes is evident from the data in Scheme 3. The MS–MS results obtained from Ph_3GeCl did not, however, show such good agreement. Pathways to the formation of Ph_2GeCl^+ and Ph_3Ge^+ (postulated by Glockling and Light[3]) were observed directly (see Scheme 4) whilst several of the subsequent fragmentation processes suggested for Ph_3GeCl^+ were not observed in this study. The elimination of molecular species from Ph_2GeCl^+, for example biphenyl, benzene and chlorobenzene, was observed in both investigations but the other processes suggested,[3] for example the loss of HCl and molecular hydrogen, were not detected by MS–MS methods. The loss of molecular species was even more pronounced in the fragmentation pattern for Ph_2GeCl_2 (Scheme 5); chlorobenzene, hydrogen chloride and biphenyl are all evident but there is no apparent loss of benzene. $PhGeCl_3$ is the only member of the group of compounds studied to produce a significant peak for the molecular ion followed by a rearrangement fragmentation process leading to the formation of chlorobenzene (*m/z* 112), the most abundant peak in the mass spectrum. The fragmentation processes for this compound were found to be much less complex (Scheme 6) than for the other compounds investigated.

In each case the pathways were confirmed using the *m/z* values appropriate to different isotopic combinations within the particular ions. This use of different isotopic species is very valuable because the same difference in mass, associated with a particular isotope, must be transmitted through the reaction sequence.

4.4 Ion–molecule reactions

The interactions of ions derived from $PhGeCl_3$ with relatively high pressures (3–10 mTorr) of either methanol or water vapour in the MS–MS collision cell were investigated. Methanol and water were chosen since they are commonly used as HPLC eluents and it is important to ensure that any interactions between a potential analyte and a solvent, particularly for example in a mass spectrometer interface, are well understood.

In parallel with the experiences from organotin compounds,[8] ion–molecule reaction products were readily observed between $PhGeCl_2^+$, i.e. a three-coordinate ion, and neutral solvent molecules. When the molecular ion $PhGeCl_3^{+\cdot}$ is preselected by MS1 the initial reaction in the collision cell appears to be the loss of a chlorine atom to give $PhGeCl_2^+$, which then reacts with water or methanol molecules to form clusters of the type $PhGeCl_2(H_2O)_n^+$ or $PhGeCl_2(MeOH)_n^+$. In this current investigation the largest value observed for *n* was 3 and mixed adducts were observed as well as those based on a single solvent system. In the analogous tin system *n* had a maximum value



Scheme 7. Ion–molecule reaction pathway determined for $PhGeCl_3$.

of 2 and the mixed adducts were also observed. Scheme 7 summarizes the reaction sequence for $PhGeCl_3^+$ introduced into the collision cell when the gas pressure was 10 mTorr, the maximum that can be tolerated by the vacuum system.

5 DISCUSSION

Positive and negative ion EI spectra of organogermanium compounds of the type Ph_nGeCl_{4-n} follow patterns similar to those of the corresponding tin compounds.[6, 11] Miller and Fulcher[2] have reported that for this group of compounds the loss of a phenyl group is dominant, whereas in this work the molecular ions (*M*) minus phenyl ions with relative abundances (RA) as low as 5% have been observed. With the exception of Ph_4Ge, the most abundant ions result from rearrangement/fragmentation reactions leading to either the biphenyl cation or the molecular ion derived from chlorobenzene. Somewhat surprisingly the yield of $Ph^{+\cdot}$ from Ph_4Ge is only 8% (RA) whereas this ion constitutes 100% RA for both Ph_3GeCl and Ph_2GeCl_2. Inspection of the fragmentation pathways may explain these results since for Ph_4Ge there are two processes which require the elimination of neutral biphenyl molecules and only one secondary process leading to the formation of $Ph^{+\cdot}$. For Ph_3GrCl and Ph_2GeCl_2 there are two and one routes respectively leading to the direct formation of $Ph_2^{+\cdot}$, with a similar number requiring the loss of the neutral molecule. These latter two compounds would therefore be expected to show higher relative abundances of the $Ph_2^{+\cdot}$ ion. Similar arguments can be used to explain why $PhCl^{+\cdot}$ is only observed for $PhGeCl_3$. For Ph_3GeCl only the neutral PhCl molecule is involved in the observed processes and for Ph_2GeCl_2 there are three routes utilizing the expulsion of PhCl and no route where $PhCl^{+\cdot}$ was the identified product. For $PhGeCl_3$ a clear direct route to the formation of $PhCl^{+\cdot}$ was noted.

Several fragmentation processes also required the loss of a neutral benzene molecule which may be comparable with the loss of alkenes from alkyl-substituted tin cations.[8] The transfer of a hydrogen atom to a neighbouring group may be a consequence of the closer proximity of these groups around germanium compared with tin. The mechanism of this process and the formation of the hexacoordinate ion–molecule reaction products are the subject of futher investigation.

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