

MASS SPECTRAL STUDIES OF SOME  
PENTAFLUOROPHENYL DERIVATIVES OF  
GROUP V

by

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A thesis submitted in partial fulfillment of the  
requirements for the degree of Master of Science  
(Chemistry) at Brock University.

1969

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The work described in this dissertation was carried out in the chemistry department of Brock University from April 1968 to August 1969. The author wishes to thank Professor J. M. Miller for his helpful advice and stimulating encouragement throughout the course of this work. He wishes to thank Professor E. A. Cherniak for the provision of the facilities and the staff and colleagues in the laboratories for their advice and helpful discussions, particularly Mr. J. Ross who serviced the mass spectrometer. He also thanks Dr. D. J. Nichols at the University of Edinburgh for the provision of the samples of  $(C_6F_5)_2SbPh$  and  $Ph_2SbCl$ . Thanks are also due to the National Research Council of Canada and Brock University for the maintenance grants which made this work possible.

Except where otherwise indicated it is believed that this work is entirely original and has not been presented in whole or in part for a degree at any other university.

ABSTRACT

The mass spectra of compounds of the series  $(C_6F_5)_{3-n}MPh_n$  ( $n = 1, 2, 3$ ,  $M = P$  and  $As$ ),  $(C_6F_5)_3Sb$ ,  $Ph_3Sb$  and  $(C_6F_5)_2SbPh$  have been studied in detail and the important modes of fragmentation were elucidated, aided by metastable ions. Various trends attributed to the central atom and or the substituent groups have been noted and, where applicable, compared to recent studies on related phenyl and pentafluorophenyl compounds of groups IV and V. The mass spectra of fluorine containing organometallic compounds exhibit characteristic migrations of fluorine to the central atom, giving an increasing abundance of  $MF^+$ ,  $MF_2^+$ , and  $RMF^+$  ( $R = Ph$  or  $C_6F_5$ ) ions on descending the group. The mass spectra of pentafluorophenyl, antimony, and arsenic compounds show a greater fragmentation of the aromatic ring than those of phosphorus. The mixed phenyl pentafluorophenyl derivatives show a characteristic pattern depending on the number of phenyl groups present but show the general characteristics of both the tris(phenyl) and tris(pentafluorophenyl) compounds. The diphenyl pentafluorophenyl derivatives show the loss of biphenyl ion as the most important step, the loss of phenyl to give the ion  $PhMC_6F_5^+$  being of secondary importance. The bis(pentafluorophenyl) phenyl derivatives fragment primarily by loss of  $PhC_6F_5$  to give  $C_6F_5M^+$  ions, the abundance of these increasing rapidly from phosphorus to arsenic. This species then, exhibits a characteristic fragmentation observed in the tris(pentafluorophenyl) compounds. However, the abundance of  $(C_6F_5)_2M^+$

species in these compounds is small. Ions of the type  $C_6H_4MC_6F_4^+$  and tetrafluorobiphenylene ions  $C_6H_4C_6F_4^+$  also are observed on substitution of a phenyl group for a pentafluorophenyl group. The fully fluorinated species  $(C_6F_4)_2M^+$  is not observed, although octafluorobiphenylene ions,  $(C_6F_4)_2^+$ , are evident in several spectra.

The appearance potentials of the major ions were obtained from the ionisation efficiency curves. Attempts were made to correlate these to the effect of the central atom in substituent groups, but the large errors involved prevented the reaching of quantitative conclusions, although it would appear that the electron is removed from the ligand in the ionisation of the parent molecule.

## INTRODUCTION

## Mass Spectrometry of Organometallic Systems

Although the use of mass spectrometry in organic chemistry has long been established only comparatively recently have the mass spectra of organometallic compounds been studied. This is perhaps due to some of the difficulties encountered in the handling of metal containing compounds in older conventional instruments, such as air sensitive compounds or those with low volatility. Decomposition of some compounds to leave the free metal as a conducting film in the ion source also presented problems. These have been perhaps overemphasised in the past and improved instrumentation and sample handling techniques have promoted a rapid growth in this field.

The three main fields of interest are: 1) the determination of the apparent molecular weight, and from exact mass measurements, its empirical formula. Detailed studies of the isotopic patterns can also give information about the composition of the molecule. Some difficulties may be encountered here, for although in most cases the peak or group of peaks at the higher mass is assumed to be the molecular (parent) ion, this is not always true. However, where there is no parent ion it is sometimes possible to deduce the molecular weight of the compound from a detailed study of the remainder of the spectrum. In addition, the relatively high temperature of up to 300°C needed to volatilise some samples

may be enough to cause either decomposition or polymerisation of the sample in the probe.

2) A detailed study of the relationship of the fragmentation pattern to the structure of the molecule. This is often facilitated by complex isotope patterns, which are evident in all but twenty of the elements likely to be encountered by organometallic chemists. The expected isotope patterns for two or more polyisotopic elements are easily calculated, but the spread of these give complex patterns that may be difficult to interpret, especially when hydrogen is present. The relative abundance of the ions arising by rearrangement processes can be used as a rough indication of their stability, but it is not always possible to write specific structures for such ions as valency changes are often invoked.

Information concerning the mode of fragmentation is derived by analysis of the metastable peaks observed in the mass spectrum. The intensity of these diffuse peaks is related to the intensity of the ion from which they arise, and although the more intense metastable transitions are readily observed, weaker peaks are often difficult to see at all. The type of ion source and mode of operation of the instrument also affects the intensity of the metastable transition and, in order to carry out a thorough analysis of the breakdown patterns, spectra at very high gain must be

obtained.

Metastable peaks arise from ions formed on electron bombardment having lifetimes long enough so that a significant number will reach the analyser to be recorded at the expected  $m/e$  ratio, but short enough so that many of them will dissociate in the analyser and result in diffuse peaks at non-integral masses. In a Nier-Johnson double focusing mass spectrometer, these ions which break down in the field free region between the electrostatic and magnetic analyser will be recorded as peaks of mass  $m^*$  and arise from an ion of mass  $m_1$  breaking down into another mass  $m_2$  and an uncharged fragment of mass  $(m_1 - m_2)$ , such that  $m^*$  is given by  $m_2^2/m_1$ . Fragmentation modes have been described solely on the evidence of metastable transitions, but although a transition has been found it does not mean that the process occurs in a single step.

3) The study of the appearance and ionisation potentials of similar ions produced from similar molecules will give a very approximate indication of the relative bond energies in these molecules. The appearance potentials of a large number of transition metal ions together with some estimates of their heats of formation have been reported. There has been little correlation of these values due to the lack of necessary thermodynamic data. Some recent theoretical calculations show that in a few cases the observed trends

can be explained in terms of the type of bonding present.

The mass spectra of some metal carbonyl compounds has been recently reviewed by Lewis and Johnson (1), and a coverage of the organometallic field in general has been given by Bruce (2).



## Mass Spectrometry of Perfluoroaromatic Compounds

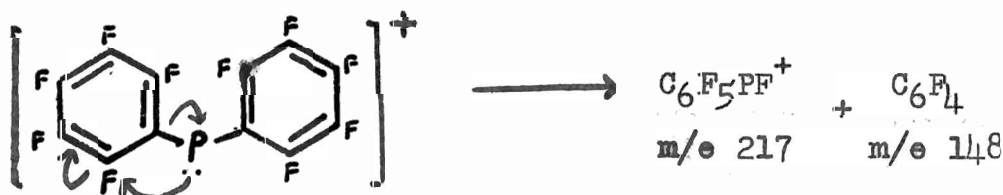
Before 1966, there were no systematic studies made on these compounds, but the appearance potentials of a few pentafluorophenyl derivatives were reported by Cotter (3), Majer and Patrick (4), and Dibeler et al (5). The mass spectra of the series  $C_6F_5X$  ( $X = H, Cl, Br$  and  $I$ ) have been reported (6) (7) along with that for hexafluorobenzene (5). Recently, some organic pentafluorophenyl compounds have had their mass spectra determined (8).

For the simple halides  $C_6F_5X$  the abundance of the ion  $C_6F_5^+$  increases along the series  $F < Cl < I < Br$ , and the major process in each case is loss of  $CF_3$  to form an ion retaining the halogen atom. The major ions are  $C_3F_3^+$  and  $C_5F_2^+$ , the former of these being formed by loss of  $C_2F_2$  and  $CX$  from  $[C_6F_5X]^+$ . The formation of  $C_5F_5^+$  is only observed in the case of hexafluorobenzene and arises by loss of  $CF$ . Most polyfluorinated compounds show intense peaks resulting from fragmentation of the ring by loss of  $CF$ ,  $CF_2$ , and  $CF_3$ , the loss of  $CH$ ,  $CH_2$ , and  $CH_3$  from the analogous hydrocarbons not being observed. In addition, most aromatic hydrocarbons show intense peaks due to loss of a proton, but in fluorocarbons the peak due to loss of a fluorine atom is very weak.

Inorganic pentafluorophenyl derivatives usually show loss of a metal fluoride species, either as a neutral fragment or

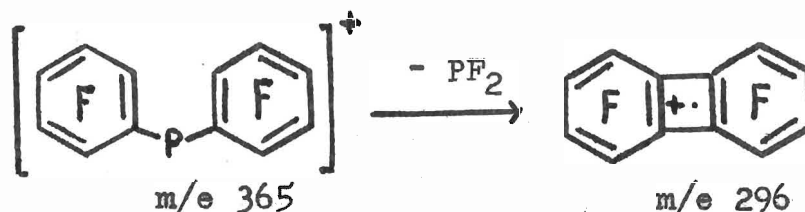
radical as one of the main features in their mass spectrum. This usually originates not from the parent ion but from the ion corresponding to the loss of one pentafluorophenyl group. Thus, in the mass spectrum of  $(C_6F_5)_3P$  (9), the loss of  $PF_2$  and  $PF_3$  is observed, and similarly for the tetrakis(pentafluorophenyl) derivatives of group IV, the loss of  $MF_3$  from the ion  $(C_6F_5)_3M^+$  is also reported (10). No loss of any neutral  $M - H$  species has been observed in any hydrocarbon analogue. This phenomenon is not confined to main group elements, for Bruce (11) and King (12) have shown that various fluorocarbon complexes of transition metals also lose metal-fluorine species. In the case of some iron and ruthenium complexes it appears as a neutral fragment or radical but in some of manganese it appears as the ion  $MnF^+$ .  $FeF_2^+$  is also observed to be lost from  $[ (C_6F_5)_2PF_2(CO)_3 ]_2$  under electron bombardment. (9)

Fluorine is also observed to migrate in these compounds from the aromatic ring to the central atom. Again, this is found for  $(C_6F_5)_4M$  ( $M = Ge$  and  $Sn$ ) to give species such as  $(C_6F_5)_2MF^+$  and  $C_6F_5MF_2^+$  from the ion  $(C_6F_5)_3M^+$  by successive loss of  $C_6F_4$  (10). It is also observed in the mass spectrum of  $(C_6F_5)_3P$  (9) for which Miller gives a possible reaction mechanism as

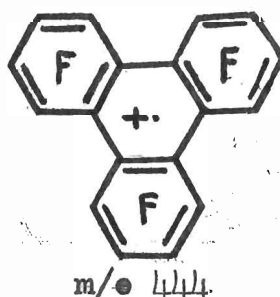


The product formed by a fluorine transfer may also be ejected as neutral species. Thus in the mass spectrum of  $[(C_6F_5)_2PF_2(CO)_3]_2$ , a metastable is found corresponding to the loss of a  $C_6F_5FeF$  species. Loss of  $C_5H_5COF$  is also seen in the mass spectrum of  $C_5H_5COC_{14}H_{14}F_6$ . (12)

The loss of a metal fluoride species in pentafluorophenyl derivatives of the main group elements gives rise to a strong peak at  $m/e$  296 which can be considered to be ionised octafluorobiphenylene, and could arise by two simultaneous steps of the scheme above. This is only observed when there are two or more pentafluorophenyl groups in the molecule. Thus, for the ion  $(C_6F_5)_2P^+$  observed in the mass spectrum of  $(C_6F_5)_3P$ :



The pentafluoro- derivatives of group IV, in addition to giving the perfluorobiphenylene ion above, also give quite appreciable amounts of perfluorotriphenylene ion, which has the structure:



by loss of  $MF_3$  from the abundant ion  $(C_6F_5)_3M^+$  ( $M$  = group IV).

The loss of  $\text{MF}_3$  from the ion  $(\text{C}_6\text{F}_5)_2\text{M}^+$  ( $\text{M}$  = group IV and V) gives the ion  $\text{C}_{12}\text{F}_7^+$ , presumably having a similar structure to that for perfluorobiphenylene but minus a fluorine atom. The remainder of the spectrum of these compounds is usually composed of fluorocarbon fragments derived from the perfluorophenylene type ions by loss of  $\text{CF}$ ,  $\text{CF}_2$ , and  $\text{CF}_3$ . Fluorine migrations have also been observed in trifluoromethyl phosphines and arsines but not in tris(trifluoromethyl)amines (13-15).

Where there is also hydrogen present the loss of  $\text{HF}$  becomes significant. King (12) has found that this is a common process in a variety of species containing fluorine and hydrogen.

The formation of perfluorophenylene ions is not a result of thermal decomposition of the sample or the dimerisation of tetrafluorobenzene in the ion source for in the mass spectra of compounds where there is only one pentafluorophenyl group, no ions due to  $\text{C}_{12}\text{F}_8^+$  are observed although a tetrafluorobenzene intermediate has been postulated to arise by lithium fluoride abstraction from pentafluorophenyl lithium (16-18). In addition, the mass spectrum of decafluorobiphenyl (19) shows only small amounts of octofluorobiphenylene, and since the abundance of the former is very small in the compounds studied, the formation of  $\text{C}_{12}\text{F}_8^+$  from this is thought unlikely. Rearrangements in the ion

source, however, do occur in pentafluorophenyl compounds, for it has been shown that  $(C_6F_5)_2PX$  and  $C_6F_5PX_2$  ( $X = Cl$  and  $Br$ ) give the ions  $(C_6F_5)_3P^+$  and  $(C_6F_5)_2PX^+$  respectively (9).

The mass spectra of similar compounds in a group often show regular trends as one descends the group. Thus, for the tetrakis (pentafluorophenyl) derivatives of group IV (10) the amount of metal fluoride ion observed increases in going from silicon to lead; the intensity of the molecular ion showing a parallel decrease. Only lighter atoms show fragments still containing the metal atom after partial fragmentation of the aromatic ring has taken place. Thus, the mass spectrum of  $(C_6F_5)_4Si$  shows a weak peak due to  $(C_6F_5)_2SiC_5F_3^+$ . For the tin and lead derivatives the loss of a complete pentafluorophenyl ring and the elimination of the metal fluoride species are the dominant features in the mass spectra. The modes of fragmentation become increasingly more complex as one proceeds to lighter atoms, due to the increasing strength of the metal-carbon bond. Derivatives of pentafluorophenyl compounds show a dependence of their fragmentation patterns on structure. Thus, tris(pentafluorophenyl) phosphine sulphide,  $(C_6F_5)_3PS$ , loses a sulphur atom as the first step but the oxide  $(C_6F_5)_3PO$ , loses a fluorine atom and a  $C_6F_5$  group more easily, and is then followed by the species  $C_6F_5O$  (9). The most favoured process is usually an odd electron ion fragmenting to an even electron ion, which in turn gives rise to other even electron ions. This

process is also the predominant one for phenyl derivatives of group IV (20-22), but other similarities between these and pentafluorophenyl derivatives are few.

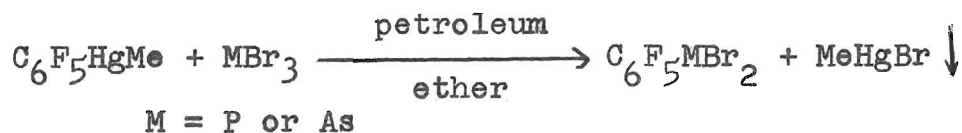
#### The Pentafluorophenyl Derivatives of Group V

Other fluorocarbon derivatives of Group VB elements have been studied in considerable detail, but the pentafluoro derivatives have not received much attention until recently.

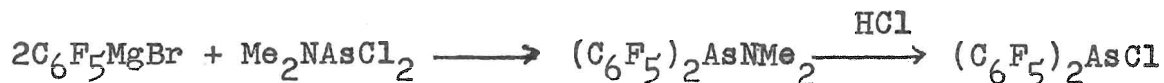
The tertiary phosphines  $(C_6F_5)_3M$  ( $M = P, As$  and  $Sb$ ) have been prepared by the Grignard method (23,24) in fair yield but higher yields are obtained by the use of the more reactive pentafluorophenyl lithium (25). The phosphine is also the only product of the reaction of  $C_6F_5MgBr$  with  $PSCl_3$  (26). Recently, Massey et al (36) have prepared tris(pentafluorophenyl) phosphine and stibine by the direct reaction of pentafluoroiodobenzene with the corresponding element. The antimony derivative is claimed to be more susceptible to hydrolysis than either the arsine or phosphine, slowly losing a pentafluorophenyl group (34). Increasing fluorine substitution in triphenyl phosphine results in a stronger interaction between the unshared electron pair on the phosphorus atom and the  $\pi$  electrons on the aromatic ring, thus decreasing the basicity of the molecule as a whole. Tris(pentafluorophenyl) phosphine does not form a phosphorus

salt with methyl iodide (23) and is more thermally stable than its hydrocarbon analogue, whereas tetrakis(pentafluorophenyl) silane is of lower thermal stability than tetraphenyl silane (23). The compounds in the series  $(C_6F_5)_nPR_{3-n}$  ( $n = 1, 2$   $R = Me$  Et and Ph) have been reported by the reaction of the corresponding organochlorophosphine with  $C_6F_5MgBr$  (25).

The series of phosphorus halides  $(C_6F_5)_2PX$  and  $(C_6F_5)PX_2$  ( $X = Cl$  and  $Br$ ) have been prepared by the reaction of pentafluoromagnesium bromide with the stoichiometric quantity of the phosphorus halide (26,27). The bromides  $C_6F_5MBr_2$  ( $M = P$  and  $As$ ) can also be readily obtained by the cleavage of methyl (pentafluorophenyl) mercury by the reaction (28)



Recently, the two pentafluorophenyl chloroarsines  $C_6F_5AsCl$  and  $(C_6F_5)_2AsCl$  have been obtained; the former by reaction of pentafluorophenyl magnesium bromide with a large excess of the trihalide and the latter by either further reaction with pentafluorophenyl magnesium bromide or more conveniently by the reaction of the Grignard reagent with dimethyl aminoarsenous dichloride. (29)



This latter reaction was also found to give improved yields over that described above for the preparation of the analogous phosphorus halide (30).

The two fluorophosphines  $C_6F_5PF_2$  (9) and  $(C_6F_5)_2PF$  (31) have been reported by the fluorination of the corresponding chlorides with anhydrous potassium fluoride in sulfolone or with antimony trifluoride (32); the latter preparation giving higher yields. Miller investigated ~~the reaction of~~ tris(pentafluorophenyl) phosphine with sulphur to give the sulphide and with chlorine to give tris(pentafluorophenyl) dichlorophosphorane  $(C_6F_5)_3PCl_2$  (33). The series of fluorophosphorones  $(C_6F_5)_nPF_{3-n}$  and their corresponding oxides  $(C_6F_5)_nP(O)F_{3-n}$  ( $n = 1, 2$ ) are also described (32).

Pseudo halide derivatives  $(C_6F_5)_nPX_{3-n}$  ( $n = 1, 2, X = CN, NCO$  and  $NCS$ ) and  $Ph(C_6F_5)PX$  are also known (34). The preparation of pentafluorophenyl phosphine and tris(pentafluorophenyl) phosphine has been reported by the reduction of the corresponding halides with lithium aluminum hydride (27).

The preparations and chemical reactions of some compounds containing a P-P bond have been investigated. Tetrakis(pentafluorophenyl) diphosphine  $(C_6F_5)_4P_2$  has been prepared by reaction of  $(C_6F_5)_2PCl$  with metallic mercury (35). The mixed diphosphine  $\angle(C_6F_5)PhP\angle_2$  and the cyclic compound  $(C_6F_5)_4P_4$  are also reported (37). Tetrakis(pentafluorophenyl) diphosphine reacts with chlorine to give bis(pentafluorophenyl) trichlorophosphorane and forms a complex with iron pentacarbonyl to give  $\angle(C_6F_5)_2PFe(CO)_3\angle_2$  (35). Analogous complexes are formed with the corresponding diarsine and  $Fe(CO)_5$  (38).



Hydrolysis of the mono and dihalides of phosphorus give the corresponding phosphinous and phosphonous acids respectively (26) and alcoholysis gives the corresponding alkoxides (38). Primary amines and ammonia react with the bis(pentafluorophenyl) phosphorus halides to give the derivatives  $(C_6F_5)_2PNHR$  ( $R = MePhCH_2$  and  $t-Bu$ ) (30), and the phosphamide  $(C_6F_5)_2PNH_2$  (26) respectively. Dimethylamine, however, gave tris(dimethylaminotetrafluorophenyl) NN dimethyl phosphinamide by nucleophilic displacement of a ring fluorine (26). The expected product of the reaction of  $(C_6F_5)_2PX$  with dimethyl (30) and diethylamine (27) has, however, been reported.

Pentafluorophenyl phosphorus dichloride gives the expected compound on treatment with various amines and the compounds  $C_6F_5P(NHR)_2$  ( $R = MeCH_2Ph$  and  $Bu-t$ )  $C_6F_5P(NMe_2)_2$  and  $C_6F_5PClNMe_2$  have been prepared. (30) The cyclic compound, bis(pentafluorophenyl) phosphonitrile  $\left[ (C_6F_5)_2PN \right]_x$  (26) is also reported.

Green and Kirkpatrick (29) have described some of the chemistry of the two (pentafluorophenyl) arsenous halides and prepared the corresponding oxides by hydrolysis and the sulphides  $(C_6F_5AsS)_4$  and  $\left[ (C_6F_5)_2As \right]_2S$  by reaction with silver sulphide from which the corresponding chlorides may be reformed by treatment with mercuric chloride. Mercuration of  $(C_6F_5)_2AsCl$  and  $\left[ (C_6F_5)_2As \right]_2S$  gives separable isomeric mixtures of  $\left[ (C_6F_5)_2As \right]_2$ , this also being the product of the reaction of bis(pentafluorophenyl) chloroarsine with phosphine and trimethylsilane. Mercuration of  $C_6F_5AsCl_2$  pro-

duces the four membered ring compound  $(C_6F_5As)_4$ .

Chambers and Chivers (39) have prepared bis(pentafluorophenyl) antimony chloride by the fluoridation of pentafluorophenyl boron dichloride with antimony trifluoride above  $25^\circ C$ .

The series of compounds  $(C_6F_5)_nMPh_{3-n}$  ( $n = 1, 2, 3$   $M = P, As$  and  $Sb$ ) has been reported by Kenneth Nichols and Peacock (25) from the reaction of pentafluorophenyl lithium with the corresponding halide. Yields are higher than those reactions reported using Grignard reagents but the yields fall into the order  $P < As < Sb$ .

Appearance Potentials Studies on Some Inorganic Systems

Assuming that the species considered are in their respective ground state and that there is no excess kinetic energy involved, the appearance potential (AP) of the ion  $A^+$  formed by the reaction:



equals the heat of reaction ( $\Delta H_R$ ), and is thus

$$AP(A^+) = \Delta H_R^\circ = \Delta H_f^\circ(A^+) + \Delta H_f^\circ(B) - \Delta H_f^\circ(AB)$$

where  $\Delta H_f^\circ(A^+)$ ,  $\Delta H_f^\circ(B)$  and  $\Delta H_f^\circ(AB)$  are the mean heats of formation in the gas phase of the respective species. The appearance potential is also related to the bond dissociation energy  $D(AB)$  and the ionisation potential (I) by the equation:

$$AP(A^+) = D(A-B) + I(A) = I(A-B) + D(A-B^+)$$

Where the ionisation potentials of radicals are not immediately available they can sometimes be found by considering the process



The difference in the appearance potentials of the processes (1) and (2) gives the heat of reaction for the overall process



If the ionisation of A is known, the ionisation potential of B can be found.

Thus from a study of appearance potentials one can sometimes determine the two fundamental quantities necessary

to understand chemical reactions, i.e. the heat of formation and the bond dissociation energy. Unfortunately the heats of formation and ionisation potentials<sup>of</sup> organometallic compounds and ions are not usually available, and although various theoretical calculations have been made to determine the quantities for some organic molecules (40) they are of little value in dealing with organometallic compounds.

The determination of appearance potentials for some organometallic species has only been of recent interest. The available data suggests that although workers have claimed that their results, are reproducibly accurate, there appears to be no theory, as yet, to explain the observed trends in all the classes of compounds studied. The lack of correlation may be due to several factors. It appears that some ions are formed in excited states and hence have higher appearance potentials than those in the ground state, and the various results reported for some metal carbonyls (2) show that they are not at all in agreement with each other, this perhaps being due to differing experimental conditions.

Recently some tris ( $\beta$ -diketonate) metal III complexes (41, 42, 43, 44) have been studied for which it is found that although the theory of Koepmans (45) should be applicable, this is not the case. The theorem states that the eigen value of the highest occupied molecular orbital approximates to

the negative of the molecular ionisation potential. In these complexes it is the ligand and not the metal atom that determines the ionisation potential, although some molecular orbital calculations support Koepmans theorem and are quantitatively consistent with the accepted electronic structure of these molecules (42). There is also a remarkable parallel between the appearance potential of the ion  $M(acac)_2^+$  and the highest occupied molecular orbital of  $M(acac)_3$  (41). This is the only trend to be observed, the values of the appearance potentials themselves showing few explainable trends. In these compounds it appears that the unpaired electron resulting from the ionisation of the molecule is localised mainly on the ligand although localisation on the metal is not ruled out.

Foffani et al (46) has related the donor power of the ligand to the measured ionisation potential in some transition metal carbonyl nitrosyl complexes. The ionisation potentials are significantly lowered when  $PCl_3$  or  $P(OEt)_3$  is substituted for a carbonyl group and this lowering is attributed to the greater donor capacities of  $PCl_3$  or  $P(OEt)_3$  relative to CO, and hence to the ionisation potential of the ligand itself. Some studies on metal carbonyls (47) on the other hand show, that the metal atom tends to dominate the ionisation potential of these molecules but variations within a group are anomalous with respect to the metal atom and are often within the limits of experimental reproducibility. Average ionic bond energies

have been calculated from appearance potential data for the manganese and rhenium pentacarbonyl halides (48) and show only very general conclusions about the metal carbonyl bond strengths although the general conclusions of Foffani are valid in this case. However a shift of 20% of the difference in the ionisation potential of two free ligands is noticed on the exchange of one ligand in the metal carbonyl for another. A similar shift is noticed on exchanging the metals and tends to support the conclusion that in these cases the primary ionisation is from the metal orbital and not from the ligand.

Some calculations of bond dissociation energies from appearance potentials have been made in organosilanes (49) (50) trimethyl tin derivatives (51) and some alkyl aryl stannanes (52,22). Although conclusive evidence is lacking it appears that in the latter case, the electron that is removed in the primary ionisation is derived from the Sn-C bond and not from the metal atom. The removal of a non-bonding d electron from the tin atom would result in the Sn-C bond energy being approximately equal in both the ion and the molecule which is not observed, the Sn-C bond energy in the ion being some 30 kcal/mole lower than that found in the unionised molecule. Davidson (50) in an investigation of the appearance potentials of the class of compounds  $\text{Me}_3\text{Si X}$  ( $\text{X} = \text{Me}_3\text{Si}, \text{Me}, \text{H}, \text{Cl}, \text{Br}, \text{and I}$ ) has shown that a plot of the dissociation energy of these against those obtained from

$\text{Me}_3\text{CX}$  ( $\text{X} = \text{Me}_3\text{C}, \text{Me}, \text{H}, \text{Cl}, \text{Br}, \text{and I}$ ) consists of two distinct parallel lines one for silicon carbon and silicon hydrogen bonds and one for silicon halogen bonds. A similar plot of the dissociation energy of  $\text{Me}_3\text{C-X}$  [ $\text{D}(\text{Me}_3\text{Si-X})$ ] against  $\text{MeX}$  shows only a single straight line. The interpretation is that although silicon hydrogen bonds and silicon carbon bonds are weaker than their carbon analogues silicon halogen bonds are stronger. Using the method to calculate the apparent electronegativity proposed by Pauling (53) it has been also shown that the electronegativity of silicon is approximately equal to that of carbon and hydrogen. There is also a relationship between  $\text{D}(\text{Me}_3\text{Si-X}) - \text{D}(\text{Me-X})$  and the difference between the ionisation potential and electron affinity of  $\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), from which it is suggested that there is an increase in ( $\text{p} \rightarrow \text{d}$ ) bonding in trimethyl silyl halides in the order  $\text{Cl} > \text{Br} > \text{I}$ .

There have been few appearance potential studies made on aromatic fluorine compounds. The appearance potential of several fluorobenzenes (3) (54) and some pentafluorobenzene derivatives have been reported (4) along with the appearance potential measurement of the major ions occurring in hexafluorobenzene (5). The ionisation potentials of the molecular ions suggest that there are both large inductive and resonance effects operating in these compounds, but are of opposite signs to each other (54).

Cullen and Frost (55) have studied the ionisation potentials of the series  $(\text{CF}_3)_{3-n}\text{AsX}_n$  ( $n = 1, 2, 3$   $X = \text{Me}, \text{H},$  and  $\text{Cl}$ ) and  $\text{Me}_{3-n}\text{AsX}_n$  ( $n = 1, 2$   $X = \text{H}$  and  $\text{Cl}$ ). In the latter series an irregular decrease in ionisation potential occurs as the number of methyl groups is increased and can be attributed to the inductive effect of the methyl group and the electron withdrawing effect of the chloro group raising or lowering the energy of the lone pair. However, in the former series although a similar trend is observed where  $X = \text{Me}$  or  $\text{H}$  it is not observed for  $(\text{CF}_3)_2\text{AsCl}$  and  $\text{AsCl}_3$  where the ionisation potential of  $\text{AsCl}_3$  is higher than that of  $(\text{CF}_3)_2\text{AsCl}$  and perhaps indicated that the electron withdrawing power of the  $\text{CF}_3$  group is less than that of the chloro group.

The aim of this work is to examine in detail the mass spectra of the series  $(\text{C}_6\text{F}_5)_{3-n}\text{MPh}_n$  ( $n = 0, 1, 2, 3$   $M = \text{P}, \text{As}$  and  $\text{Sb}$ ) and to attempt to correlate the appearance potentials of the major ions to the central atom and substituent groups.



EXPERIMENTAL

### Techniques

Standard ground glass apparatus was used for all preparations. Vacuum sublimations were carried out in a standard sublimation apparatus equipped with a central cold finger at vacuums of better than  $10^{-2}$  mm of mercury and at temperatures a little above the melting point of the sample. Cooling of the cold finger with a mixture of dry ice and acetone was sometimes necessary to effect sublimation.

The identification and purity of the compounds was determined by elemental analysis melting point, infra-red and mass spectra.

### Infra-red Spectra

Infra-red spectra were recorded on a Perkin-Elmer 237 B double beam grating spectrometer in the region  $4000-625\text{ cm}^{-1}$ . All samples were examined as pressed KBr discs. The spectra were found to be constant with the published data (24).

### Mass Spectra

Mass spectra were obtained on high resolution double focusing and medium resolution single focusing spectrometers. These were AEI MS-9 and Hitachi-Perkin Elmer RMU-6 respectively both operating at an ionisation voltage of 70 ev., a current of 50mA and a resolution of about 1000. Samples were

admitted either indirectly from a heated glass storage reservoir at temperatures between 200 and 250°C or directly into the ion source via a heated probe operating at 40-80°C. Spectra from the MS-9 were recorded on UV sensitive paper at three galvanometer sensitivities in the approximate ratio 1:3:9.6 and those from the RMU-6 machine (Morgan Schaffer Corp.) were recorded similarly at four sensitivities in the ratio 1:2.5:8.5:29. The two machines gave essentially similar spectra. Mass counts were started at mass to charge ratio of 20. Internal calibrants were used for the identification of high molecular weight species and any background was subtracted where significant.

The intensities of the peaks were measured with a variable scale ruler set so that the relative intensities could be read directly. The observed metastable transitions were assigned, and the intensities of some polyisotopic ions of antimony were calculated with the aid of a computer programme (100) and were found to be the same as those observed, within experimental error.

#### Appearance Potentials

Appearance potentials were determined on a Bendix Time-of-Flight Model 12 mass spectrometer equipped with a 14-107 ion source. Samples were introduced directly into the ion source on the heated tip of a Model 843 A probe op-

ating at temperatures of 100-70 °C and monitored by a thermocouple. In general the mass spectra obtained on this machine were similar to those obtained on the higher resolution instruments, but the intensities of a few peaks were different due to a different operating mode and source geometry. In addition, the very much lower resolving power of this instrument made the resolution of consecutive masses above  $m/e$  250 difficult.

The method used for obtaining the appearance potentials of the ions is similar to that used by Loyd and Stafford (56). The ionisation voltage control was fitted with a pulley wheel and driven by a small synchronous electric motor, operating at 1/3 r.p.m., by means of a rubber O-ring. The electron energy output was connected to the X-axis terminal of a Hewlett Packard Moseley 7005 B X-Y recorder and was monitored simultaneously on a digital voltmeter, the Y axis terminal being connected to electrometer output of the spectrometer. The X scale was 1 ev per inch. The scanning gate was opened to its widest setting and moved onto the ion whose appearance potential was to be measured by use of the manual scan heliopot, which was then adjusted with the vernier control so that the recording galvanometers showed a maximum deflection. The gate was then locked in position and the ionisation voltage set two to three ev below that of the expected appearance potential. The X-axis was zeroed at some convenient point and the ionisation efficiency curves were drawn auto-

matically on inch graph paper. The recorder and analogue electrometer sensitivities and time constants were adjusted so that the ionisation efficiency curve was as steep as possible with a minimum amount of noise. The same set of operating conditions were used during each set of measurements.

Mercury and Krypton were used as calibrating standards. Krypton was admitted via the inlet system from a gas storage bulb, mercury arising as background from the diffusion pumps. The most intense peak of the isotope pattern of each was used for measurement. Where the compound under consideration had significant peaks in the mass range 196-204, the mercury was removed by liquid nitrogen and oxygen from the background spectrum substituted as the second standard. This gave less reproducible results than the mercury or krypton standards.

At **least** two standards were used for each compound and the appearance potential of these was determined immediately before and after a particular compound had been studied.

There was no variation over the time required to complete a set of experimental determinations but a drift over longer time periods was noticed.

For each ion in turn a set of eight to ten ionisation efficiency curves were obtained and the appearance potential

taken at the point where the first definite reproducible rise from the base line was observed. Errors were evaluated using the standard mean deviation method. Although efforts were made to bring the ionisation curves as parallel as possible to these of the standards some ions gave such shallow curves that an accurate determination of the appearance potential was impossible.

Wood and Waldron (57) have shown that by this method the measured appearance potential is inversely proportional to the pressure in the ion source. Accordingly, efforts were made to keep the rate of evaporation of the sample as low and as constant as possible by carefully adjusting the temperature of the probe but high enough to observe all the significant peaks in the mass spectrum.

The values of the appearance potentials were obtained by taking the difference in the values for the initial break in each curve for the ion under consideration and the standard and then adding the appropriate correction factor to each value based on the following standard values (93):

Mercury	m/e	202	10.4 ev.
Krypton	m/e	84	14.0 ev.
Oxygen	m/e	32	12.2 ev.

Ions that gave no sharp break in the ionisation efficiency curves from which an accurate determination of their appearance potential could be made where almost invariably from those that could arise by two or more processes.

Thus although the ion due to  $\text{SbF}_2$  in the mass spectrum of  $(\text{C}_6\text{F}_5)_3\text{Sb}$  is the base peak, the ionisation efficiency curve showed only in very gradual rise after increasing the voltage some 5-7 e.v. This ion can arise by several paths each having its own energetics and will thus make the determination of its appearance potential by the initial break method difficult, since a large amount of kinetic energy is probably acquired. Ionisation efficiency curves that were parallel to the standard were normally only obtained from the ions  $\text{R}_n\text{M}$  ( $n = 1, 2, 3$   $\text{R} = \text{Ph}$ ,  $\text{C}_6\text{F}_5$ ,  $\text{M} = \text{P}$ ,  $\text{As}$  and  $\text{Sb}$ ).

#### Sources of Materials

The sources of starting materials used in the preparations for this work are given in Table 1 and were used without further purification. Commercially available samples of the compounds for mass spectral study were purified by either sublimation or recrystallisation from hot ethanol. All compounds were sublimed once prior to mass spectral analysis.

#### The Preparation of bis(pentafluorophenyl) phenyl phosphine

In a three necked flask fitted with an oil sealed paddle stirrer was placed magnesium turnings (3.0 g 0.125 mole) and 50 ml of dry diethyl ether. A small crystal of

Table 1: Sources of Materials

<u>Compound</u>	<u>Supplier</u>
Pentafluorobenzene ) Bromopentafluorobenzene )	Pierce Chemical Co. Rockford, Ill.
Phenyl dichlorophosphine ) Diphenyl chlorophosphine )	Stauffer Chemical Co. New York, New York
Phenyl dichloroarsine ) Diphenyl chloroarsine ) n Butyl Lithium ) Triphenyl arsine ) Triphenyl antimony )	Alfa Inorganics Beverly, Mass.
Triphenyl phosphine ) Antimony trichloride )	British Drug Houses, Poole Dorset, England
Arsenic trichloride	Allied Chemical New York, New York
† Tetraphenyl diphosphine	Strem Chemicals Inc. Danvers, Mass.

Samples of tris(pentafluorophenyl) phosphine and tetra-  
kis (pentafluorophenyl)diphosphine previously prepared by Dr.  
J. M. Miller were available. Samples of bis(pentafluorophenyl)  
phenyl stilbene and diphenyl chlorostilbene were kindly donated  
by Dr. D. J. Nichol's from the University of Edinburgh.

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† The sample obtained showed on mass spectral analysis  
gross contamination by the oxide  $\text{Ph}_2\text{P}-\text{P}(\text{O})\text{Ph}_2$ . The melting  
point of the sample was found to be  $86-105^\circ\text{C}$ . (Lit. value  $121^\circ\text{C}$ )  
and was observed to fall to  $86-90^\circ\text{C}$  over a period of two  
weeks due to gradual oxidation by the air. Attempts to  
synthesise tetraphenyl diphosphine by literature methods (58-  
60) gave a crystalline product m.pt.  $196-198^\circ\text{C}$  which also  
showed the presence of oxygen in its mass spectra. In addition  
the mass spectra obtained from the Bendix machine was very  
different from that obtained on the RMU-6 (Morgan Schaffer  
Corp.) in that the peaks of interest  $\text{Ph}_4\text{P}_2$  and  $\text{Ph}_2\text{P}$  were of  
such low intensity that no appearance potential measurements  
could be made.



iodine was added and a solution of bromopentafluorobenzene (24.7 g, 0.1 mole) in ether (50 ml) was added dropwise with constant stirring. If the reaction did not start immediately, a few turnings of magnesium activated with a 1:1 solution of ethylene dibromide in ether (5 mls) were added. After the reaction had begun the contents of the flask turned cloudy and the rate of addition of the bromopentafluorobenzene solution was adjusted to give a reasonable rate of reflux of the ether. When the addition was complete the reaction was allowed to proceed to completion for half an hour, yielding a dark black-brown solution. The solution was decanted free of the unreacted magnesium and added dropwise to a stirred solution of phenyl dichlorophosphine (8.0 g, 0.048 mole) in dry ether (50 mls) at 0° C. When the addition was complete the solution was gently refluxed for an hour after which time it was cooled and the excess Grignard reagent hydrolysed with 50 mls of 1N hydrochloric acid. The ether layer was separated, washed three times with 50 ml portions of distilled water and dried overnight over anhydrous sodium sulphate. Evaporation of the ether gave a dark brown oil which was passed down an alumina column (85-100 mesh) with Ligroin bpt. (68-75° C). An almost colorless eluant was recovered, leaving a heavy black tar at the top of the column. The light yellow oil obtained on evaporation of the solvent slowly crystallised to give off-white needles (12.3 g 57.7%) mpt. 52-54° C, which were sublimed under high vacuum at 70-80° C to yield bis(pentafluorophenyl) phenyl phosphine (9.5 g, 44.5%) mpt 60-62° C lit value 69-70° C (24a) (25).

The preparation of tris(pentafluorophenyl) arsine, stibine, and diphenyl pentafluorophenyl phosphine were carried out in an analagous manner, and the results are summarised in Table 2.

Table 2: A Summary of the Preparations  
Using Pentafluorophenyl Magnesium Bromide

<u>Compound Prepared</u>	<u>Halide Used</u>	<u>Crude Yield %</u>	<u>Sublimed Yield %</u>	<u>Mpt. °C</u>	<u>Analysis</u>
$(C_6F_5)_3As$	$AsCl_3$ (0.06 mole)	78.9	69.5	104- 106  Lit. 106	Found C 37.4 F 49.7  Calc. C 37.4 F 49.5
$(C_6F_5)_3Sb$	$SbCl_3$ (0.06 mole)	79.1	56.0	72- 74  Lit. 74	Found C 34.5 F 45.62  Calc. C 34.7 F 45.7
$Ph_2PC_6F_5$	$Ph_2PCl$ (0.1 mole)	61.2	47.2	69- 71  Lit. 69- 70	Found C 61.54 F 27.1 P 8.72 H 2.68  Calc. C 61.36 F 26.99 P 8.8 H 2.84
$PhP(C_6F_5)_2$	$PhPCl_2$ (0.1 mole)	57.7	44.5	60- 62  Lit. 69- 70	Found C 48.68 F 42.96 P 6.87 H 1.00  Calc. C 48.86 F 42.99 P 7.01 H 1.13

Preparations Using Pentafluorophenyl Lithium

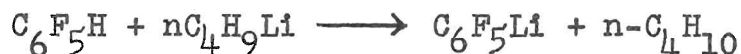
Bis(pentafluorophenyl) phenyl arsine, diphenyl pentafluorophenyl arsine and diphenyl pentafluorostibine<sup>phenyl</sup> were prepared by the action of pentafluorophenyl lithium on the corresponding chloride using the method of Kemmitt, Nichols, and Peacock (25).

The use of pentafluorophenyl lithium as a reagent for the preparation of pentafluorophenyl derivatives was discovered by Coe (63) who used a metal-halogen exchange reaction between bromo pentafluorobenzene and n-butyl lithium at  $-78^{\circ}\text{C}$ ,



Low temperatures were necessary to prevent the formation of fluoride ion through an intermediate benzyne system (63,64). Excess amounts of the halo-pentafluorobenzenes reacted with pentafluorophenyl lithium to give 2-bromo nonafluorobiphenyls which were used in the preparation of other 2-substituted

nonafluorobiphenyls (18). The preparation of pentafluorophenyl lithium was improved by Harper et al (65) who used the reaction of pentafluorobenzene with n-Butyl Lithium at  $-78^{\circ}\text{C}$ .



This has the advantage that inert butane is the only side product. The rate of formation of pentafluorophenyl lithium is however extremely dependent on the solvent used. In hexane

ether the reaction is only complete in 2 hours but with ether or ether-tetrahydrofuran as a solvent, it is complete in 5 minutes. Kemmitt et al (25) prepared compounds in the series  $(C_6F_5)_nMPh_{3-n}$  ( $n = 1, 2$  and  $3$   $M = P, As$  and  $Sb$ ) by use of this reagent and reported superior yields to those obtained via the Grignard procedure at lower cost since pentafluorobenzene is the much cheaper starting material than bromopentafluorobenzene.

Details of the preparations are summarised in Table 3 and a typical reaction is described below.

#### The Preparation of Diphenyl Pentafluorophenyl Arsine

A 500 ml three necked flask was fitted with an oil sealed paddle stirrer, an efficient water condenser and a by-pass dropping funnel. The apparatus was flushed for 10 minutes with dry nitrogen, (further dried by passing the gas through a 2 ft. tube packed with "Drierite") and a solution of pentafluorobenzene (9.25 g 0.050 moles) in anhydrous ether (100 ml) admitted to the flask, which was then cooled to  $-78^{\circ}C$  with an acetone-dry ice bath. A solution of n-butyl lithium (24 mls) of a 22 wt % solution in hexane (3.52 g , 0.055 moles) was then added dropwise to the stirred solution. When the addition was complete the solution was stirred for 2 hrs under a blanket of nitrogen.

Then a solution of diphenyl chloroarsine (13.87 g , 0.052 moles) in ether (50 mls) was added dropwise and then the contents of the flask were allowed to warm to room temperature. The solution changed from colorless at  $-78^{\circ}\text{C}$  to dark brown at room temperature and a fine precipitate of lithium chloride was observed in the flask. The solution was filtered and hydrolysed with 1N hydrochloric acid (50 ml) washed with water in two 30 ml portions and the ether layer dried over anhydrous sodium sulphate. The solvent was removed in vacuo and the dark brown oil that remained passed down an alumina column and eluted with naphtha solvent. The brown tar remained at the top and evaporation of the solvent yielded pale brown crystals (11.25 g 54.5%) of diphenyl pentafluorophenyl arsine mpt  $60-63^{\circ}\text{C}$ . Final purification was achieved by vacuum sublimation to give 9.6 g 46.5% of the pure product mpt  $62-64^{\circ}\text{C}$  Lit. value  $63-64^{\circ}\text{C}$ . (25). A similar reaction performed with dry THF as the solvent gave 8.2 g of a semi-solid mass that was difficult to crystallise or sublime, due to some unidentified by-product.

Table 3: A Summary of the Preparations  
Using Pentafluorophenyl Lithium

<u>Compound Prepared</u>	<u>Halide Used</u>	<u>Crude Yield %</u>	<u>Sublimed Yield %</u>	<u>Mpt. °C</u>
PhAs(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	PhAsCl <sub>2</sub> (0.025 mole)	49	40	73-75 Lit.73-75
Ph <sub>2</sub> AsC <sub>6</sub> F <sub>5</sub>	Ph <sub>2</sub> AsCl (0.052 mole)	54	46	62-64 Lit.63-64
Ph <sub>2</sub> SbC <sub>6</sub> F <sub>5</sub>	Ph <sub>2</sub> SbCl <sup>†</sup> (0.01 mole)			

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† The reaction was carried out in an analogous manner to that described, except that after filtration, the filtrate was not hydrolysed with water in case this removed the pentafluorophenyl group. The ethereal filtrate was evaporated to yield a small amount of an oil which did not crystallise or show any sign of pentafluorophenyl groups in its IR and mass spectra.

Previous attempts to synthesise the halide Ph<sub>2</sub>SbCl by the reported methods (66) failed and because of the small amount (3.6 g) supplied to us, another reaction could not be attempted. The reported yield of the required C<sub>6</sub>F<sub>5</sub>SbPh<sub>2</sub> is only 25%, based on the amount of Ph<sub>2</sub>SbCl used.

## RESULTS AND DISCUSSION



The figures 1-11 show the mass spectra of the compounds under study. These were drawn up from the Tables I-XI that are found in the Appendix and are plotted with the mass to charge ( $m/e$ ) ratio vs. the intensity of each peak relative to the base peak, which is normalised to 100 % relative abundance.

Figures 12-21 show the proposed fragmentation schemes for the compounds based on the observed metastable transitions and any analogies that might reasonably be drawn from their neighbors.

To facilitate comparison, tables 4 and 5 show the abundances of each ionic species (over 1 to 2% relative intensity) as a percentage of the total positive ion current. These are formed by summing all the isotopic contributions to each ion species in turn and then dividing this by the total ion current.

Table 6 shows the nature of major charge carrying species as a percentage of the total positive ion current. Where necessary the spectra is normalised so that the sum of each separate species is 100%.

Table 7 shows the observed metastable transitions. These were in the main fitted to the observed metastable peaks by a computer programme such that all peaks over 2% relative abundance were considered. Where the transition

was very broad because of polyisotopic elements, the total range was divided into 0.3 a.m.u. sections and each was considered in turn.

Figure 1: The Mass Spectrum  
of  $\text{Ph}_3\text{P}$  at 70 ev.

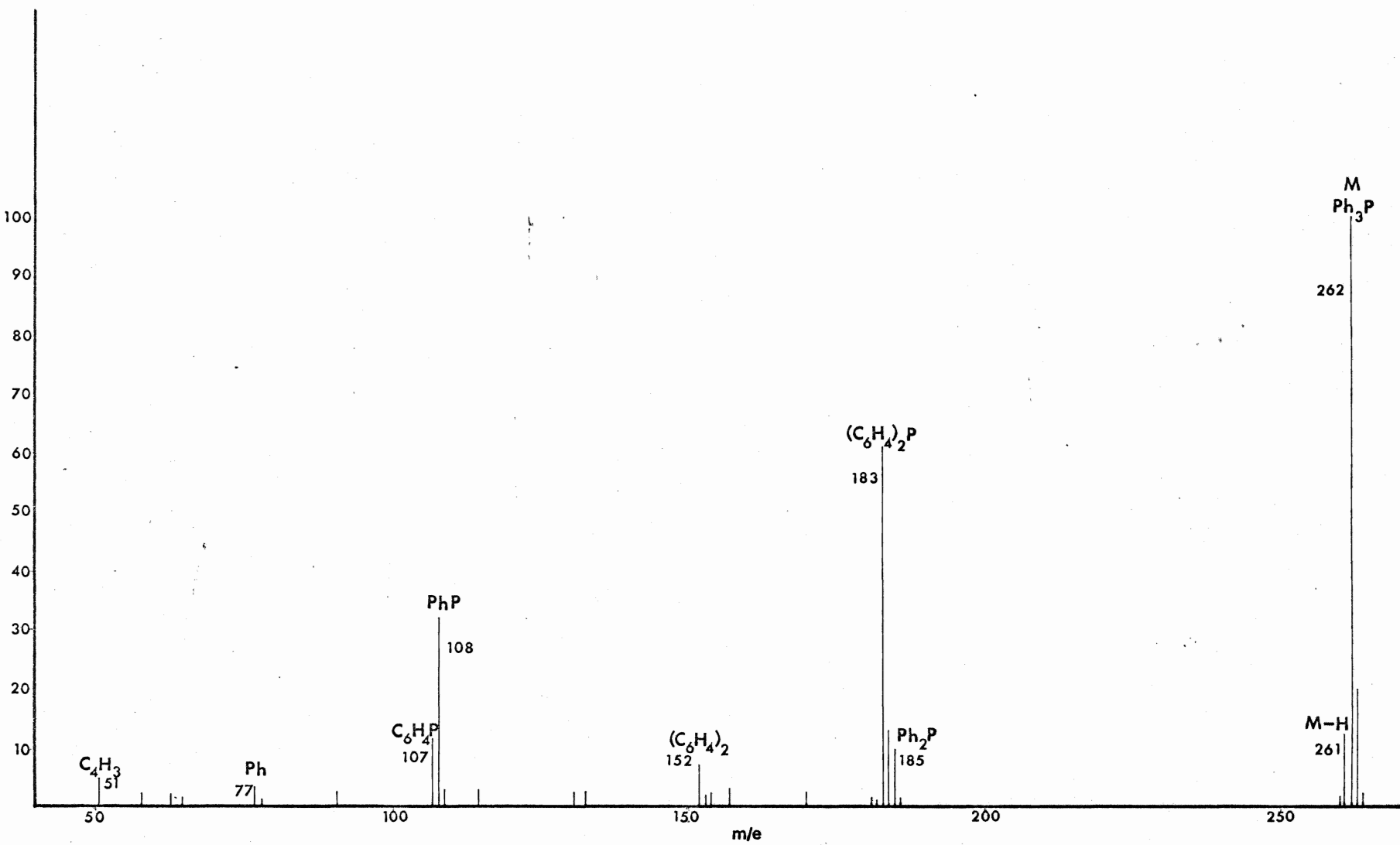


Figure 2: The Mass Spectrum  
of  $\text{Ph}_3\text{As}$  at 70 ev.

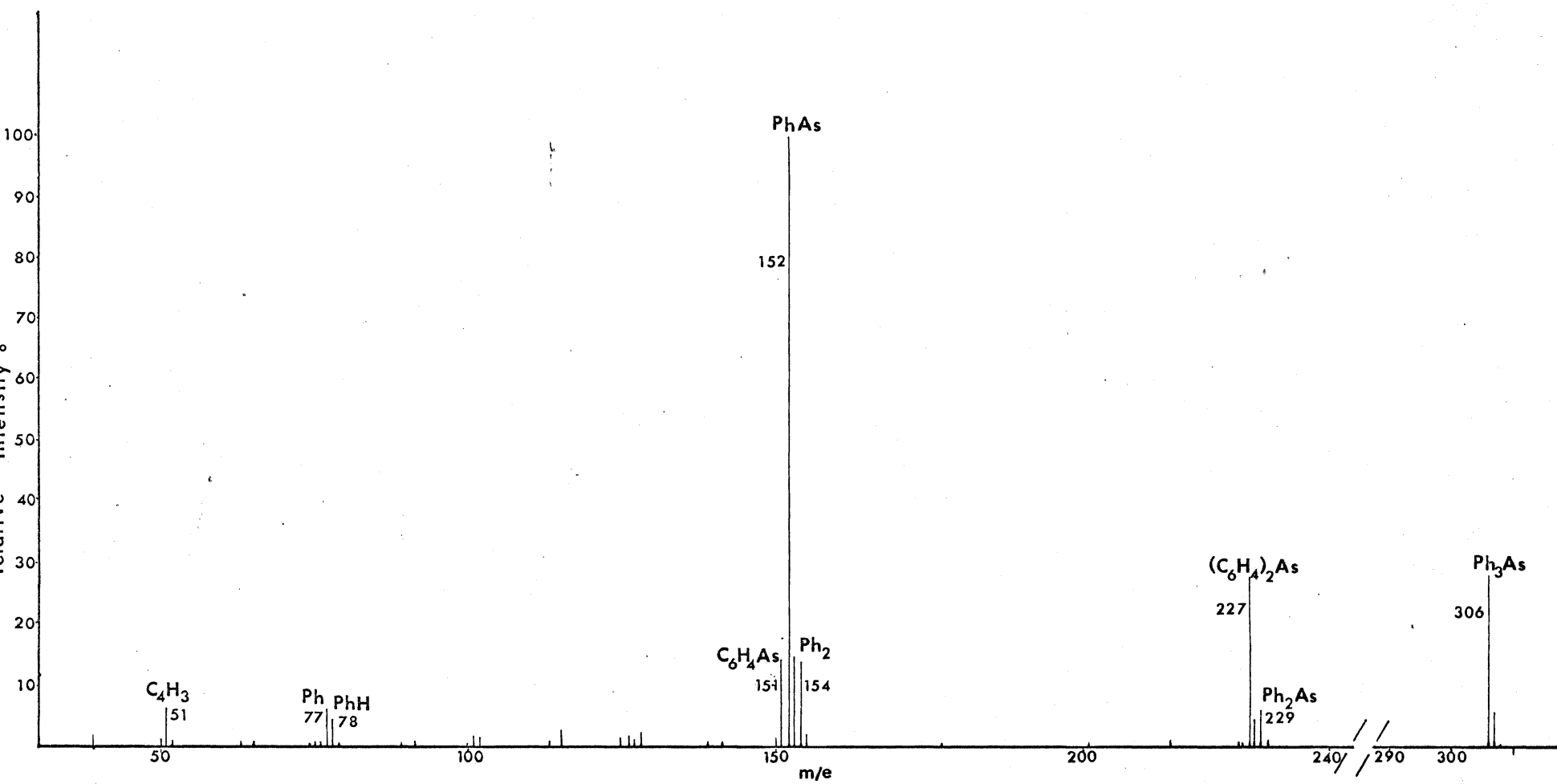


Figure 3: The Mass Spectrum  
of  $\text{Ph}_3\text{Sb}$  at 70 ev.

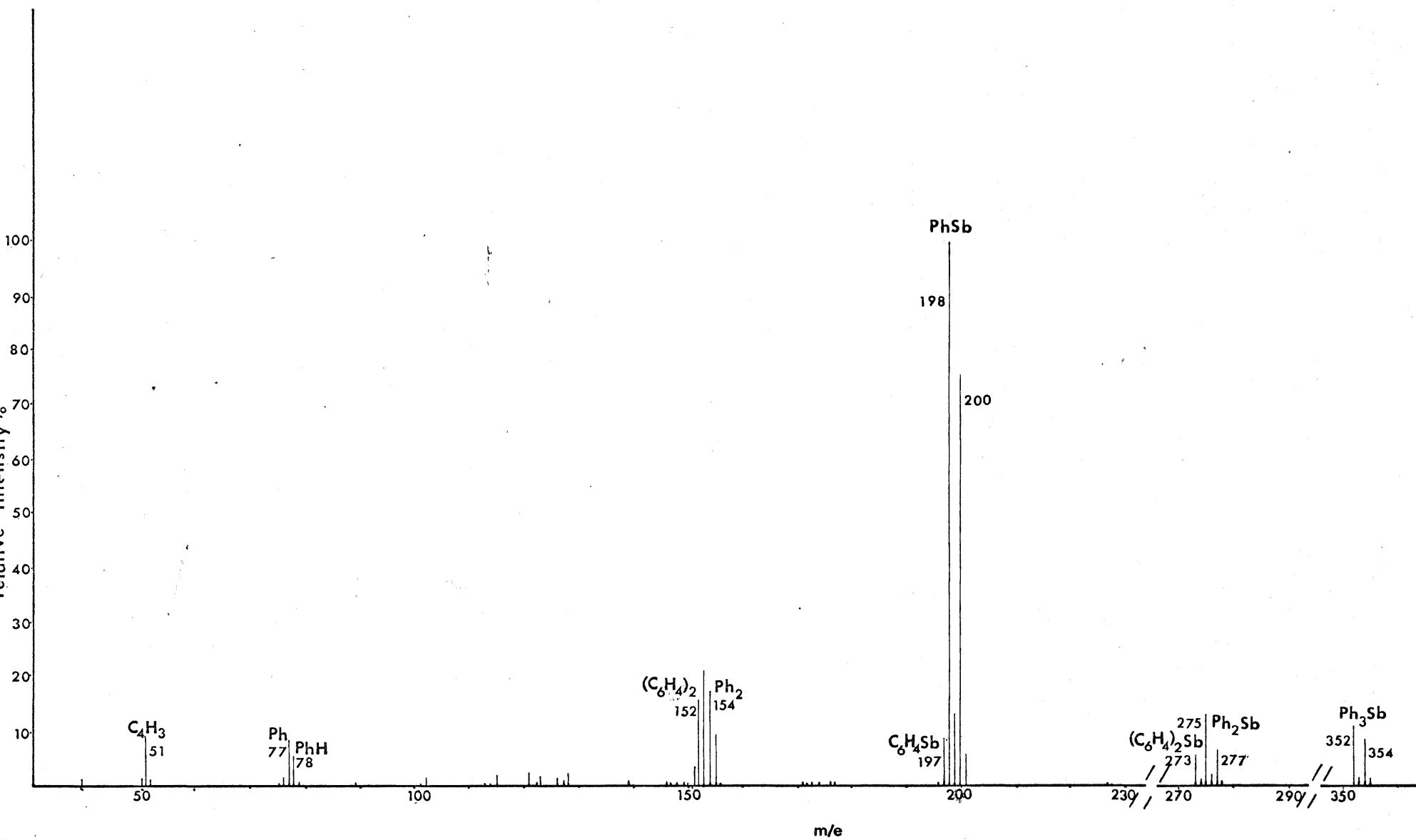




Figure 4: The Mass Spectrum  
of  $(C_6F_5)_3P$  at 70 ev.

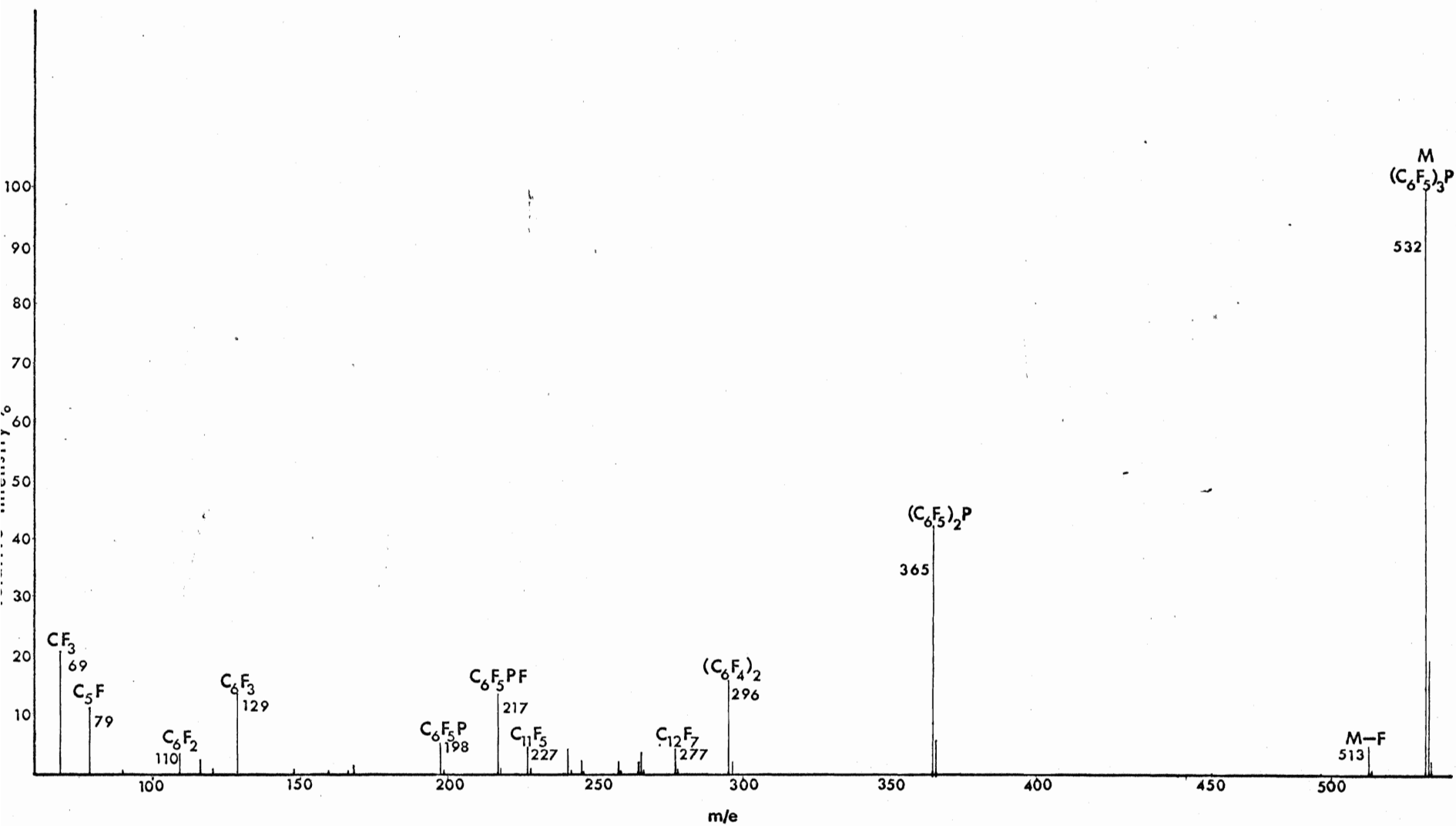


Figure 5: The Mass Spectrum  
of  $(C_6F_5)_3As$  at 70 ev.

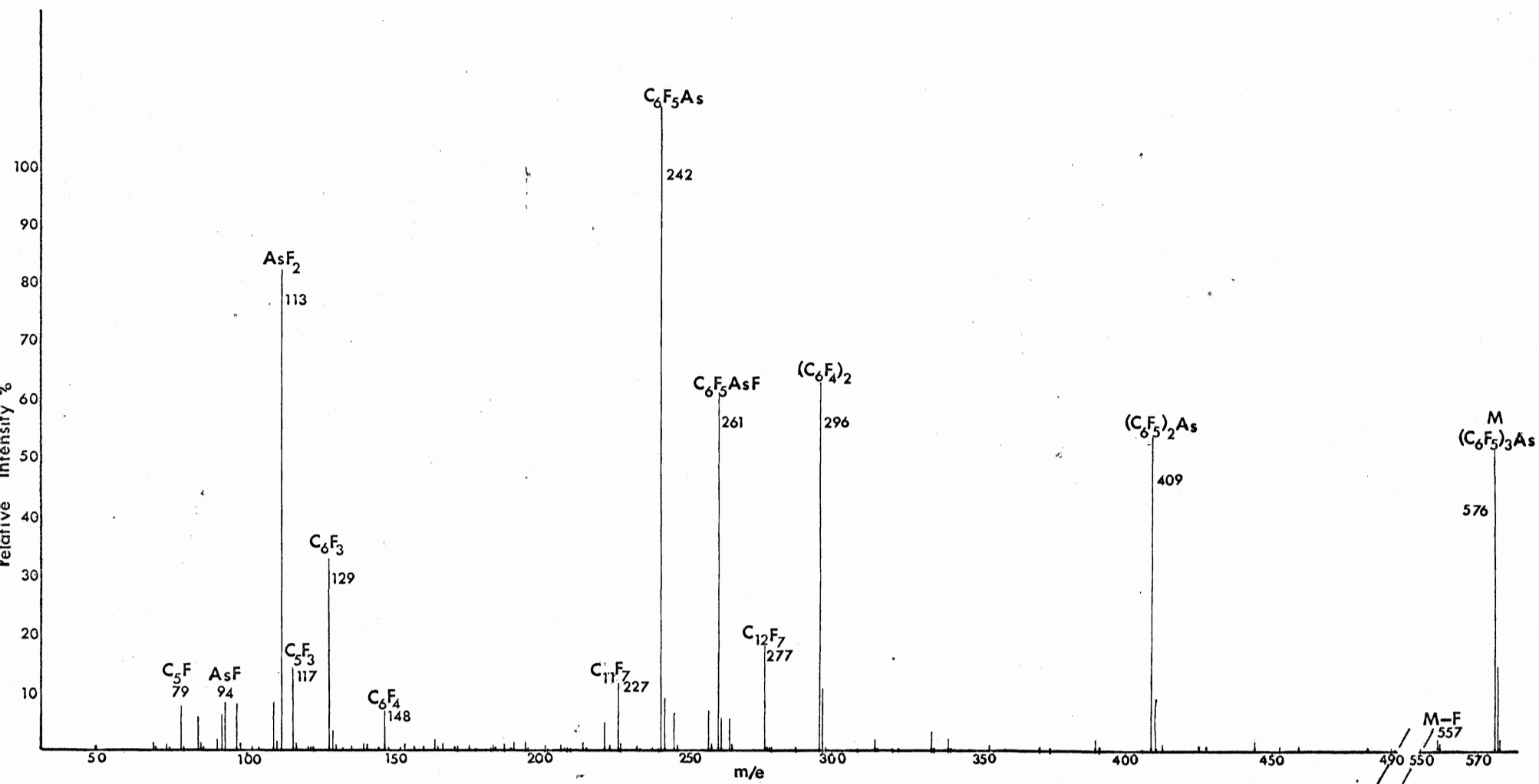


Figure 6: The Mass Spectrum  
of  $(C_6F_5)_3Sb$  at 70 ev.

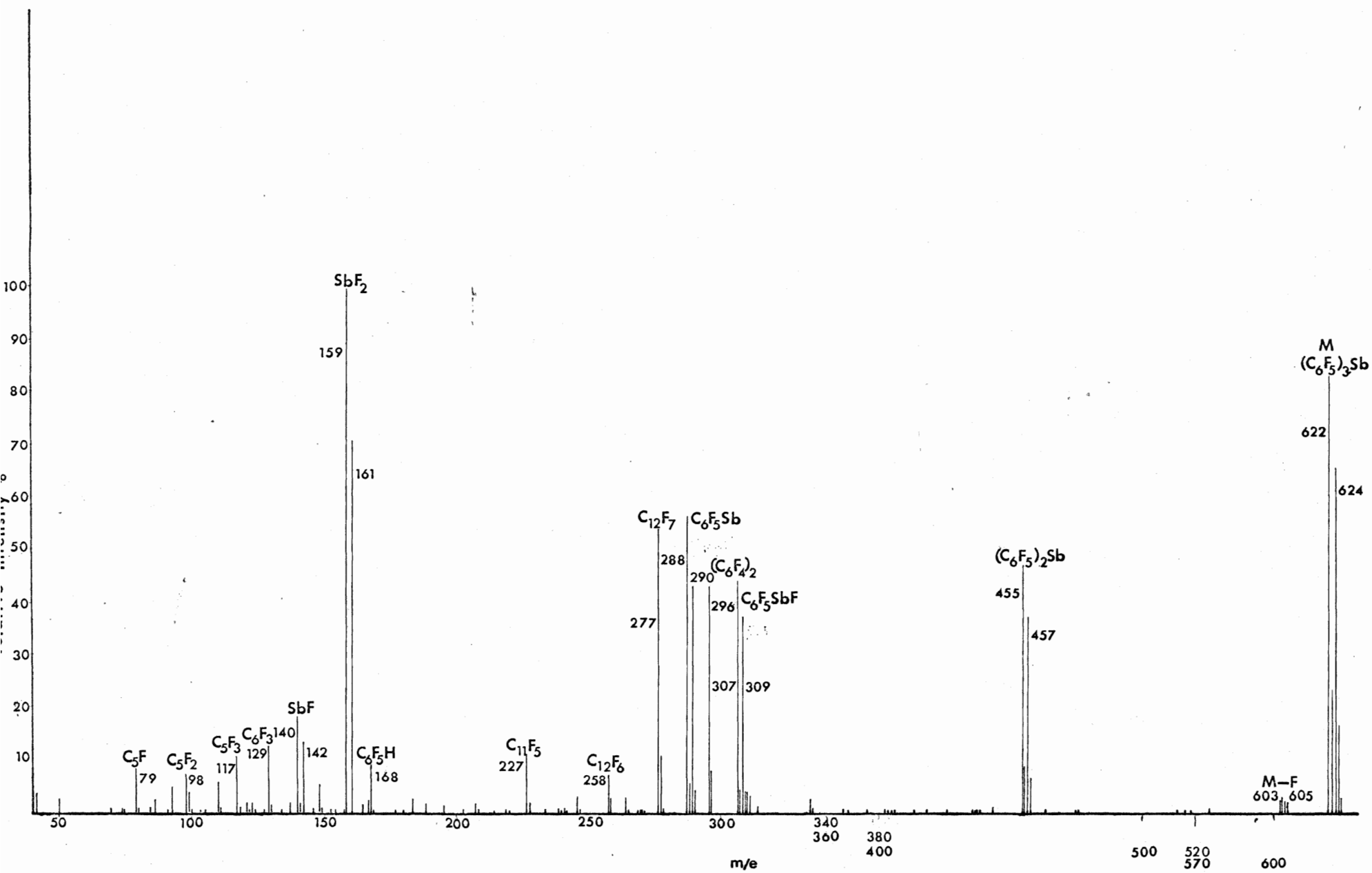


Figure 7: The Mass Spectrum  
of  $\text{Ph}_2\text{PC}_6\text{F}_5$  at 70 ev.

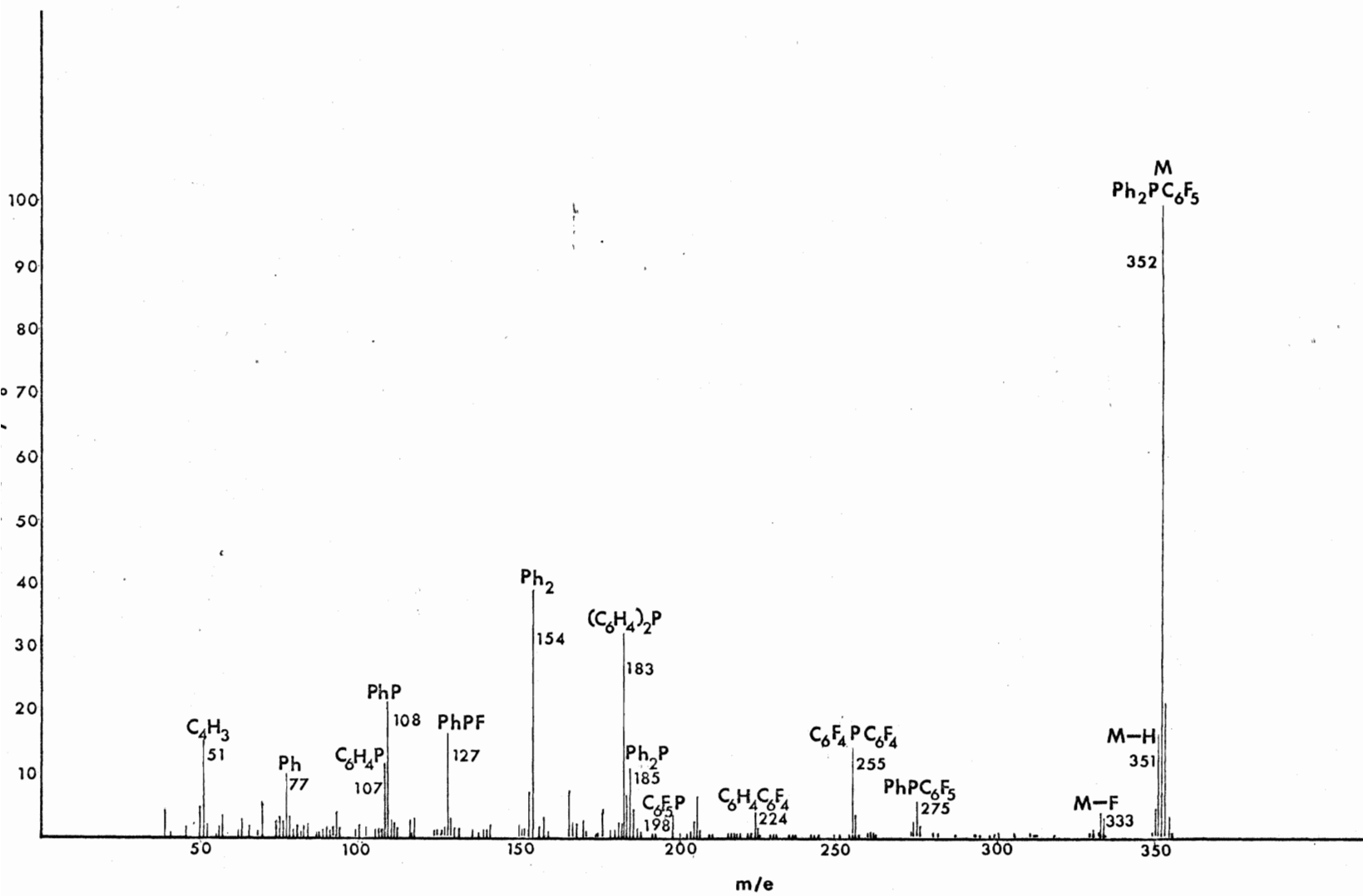




Figure 8: The Mass Spectrum  
of  $\text{Ph}_2\text{AsC}_6\text{F}_5$  at 70 ev.

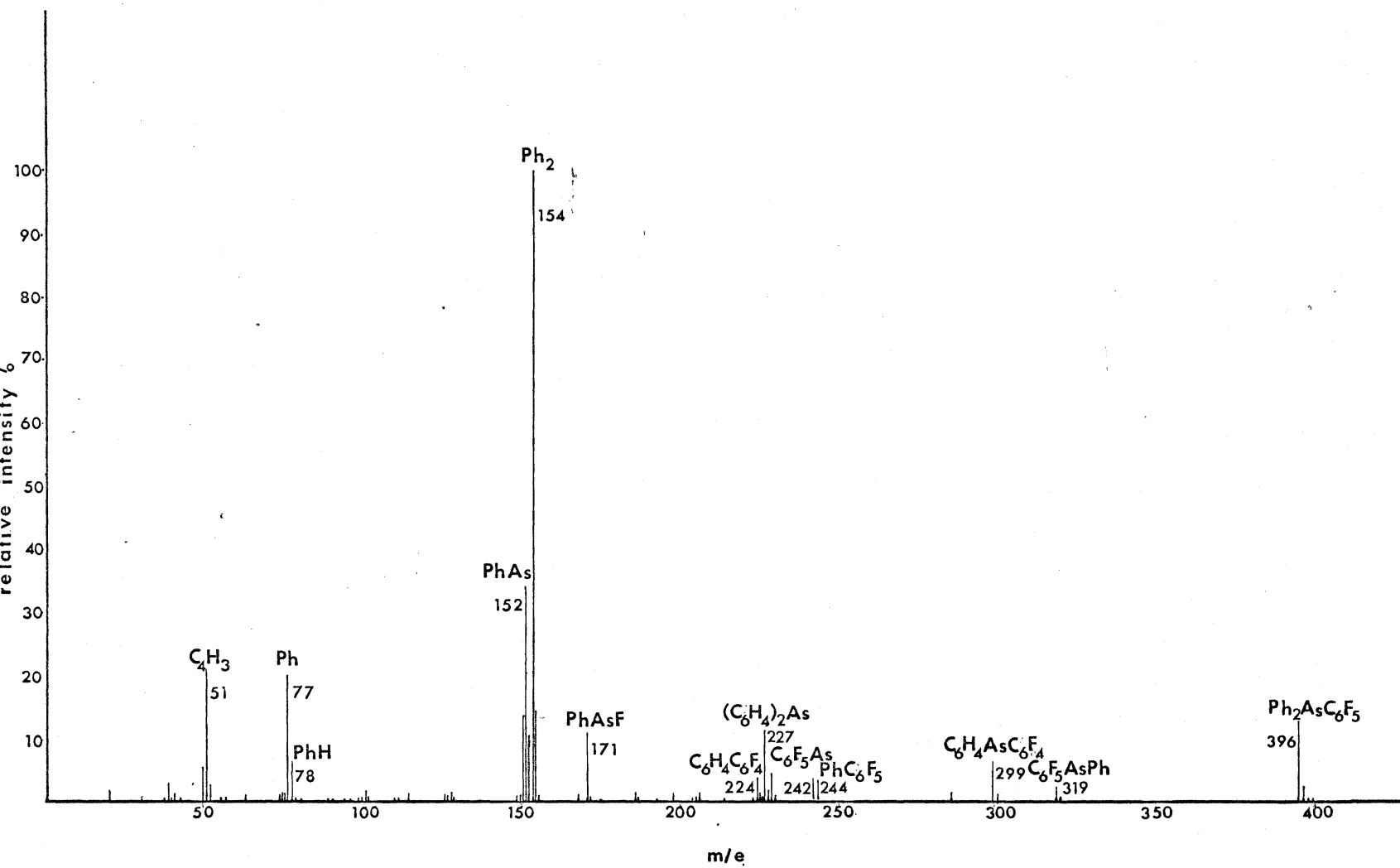


Figure 9: The Mass Spectrum  
of  $\text{PhP}(\text{C}_6\text{F}_5)_2$  at 70 ev.

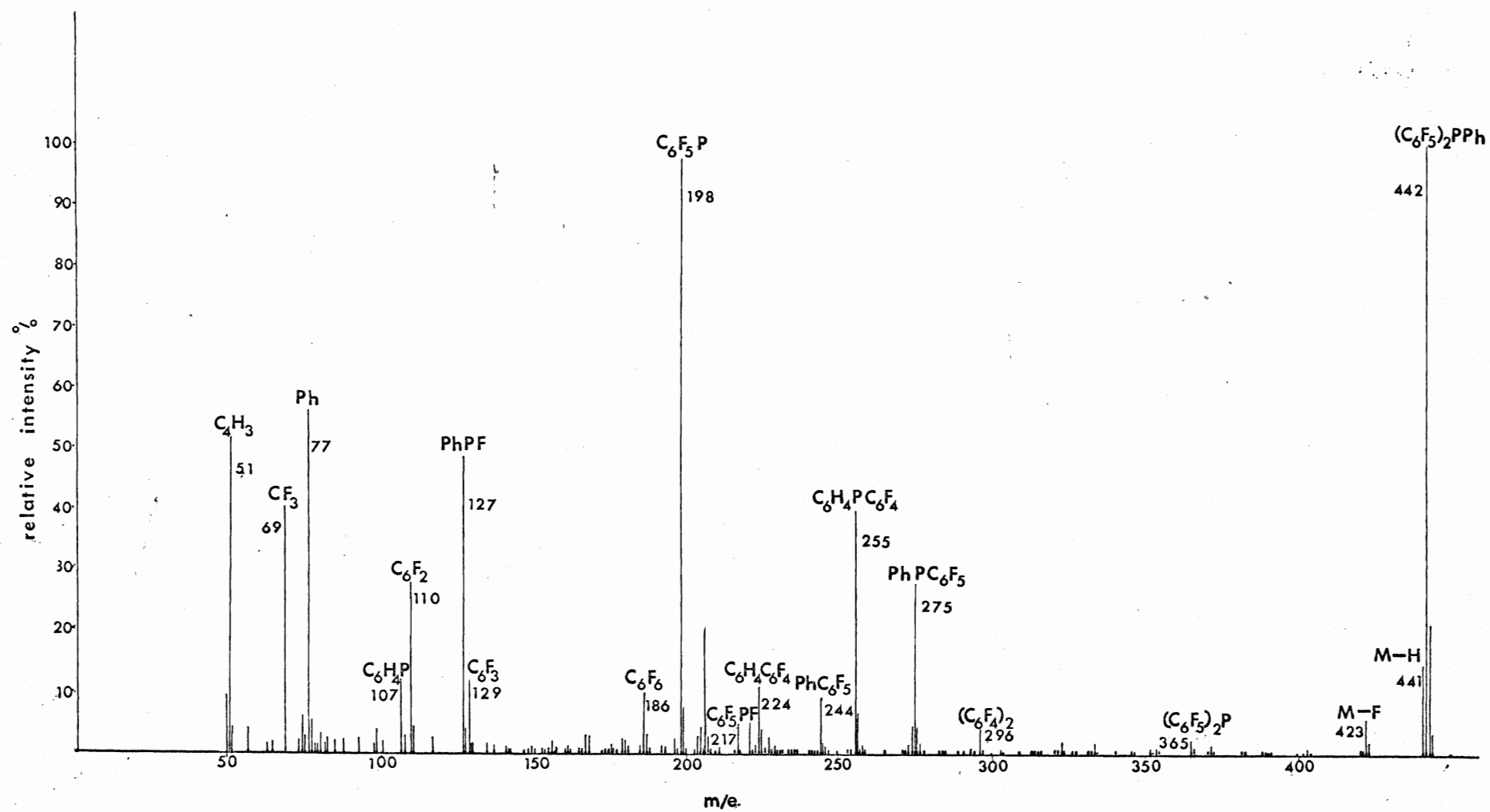


Figure 10: The Mass Spectrum  
of PhAs(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> at 70 ev.

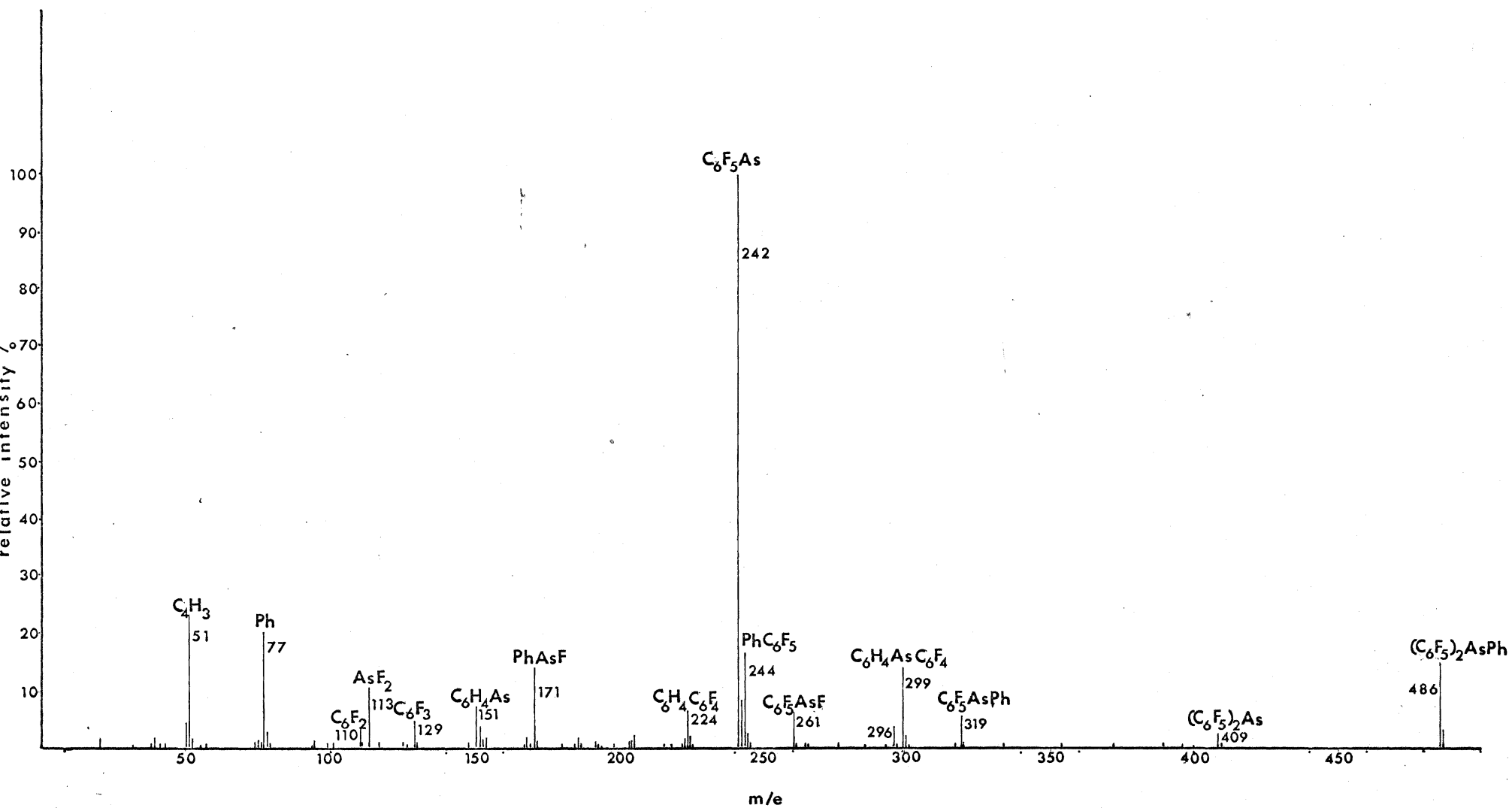


Figure 11: The Mass Spectrum  
of PhSb(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> at 50 ev.

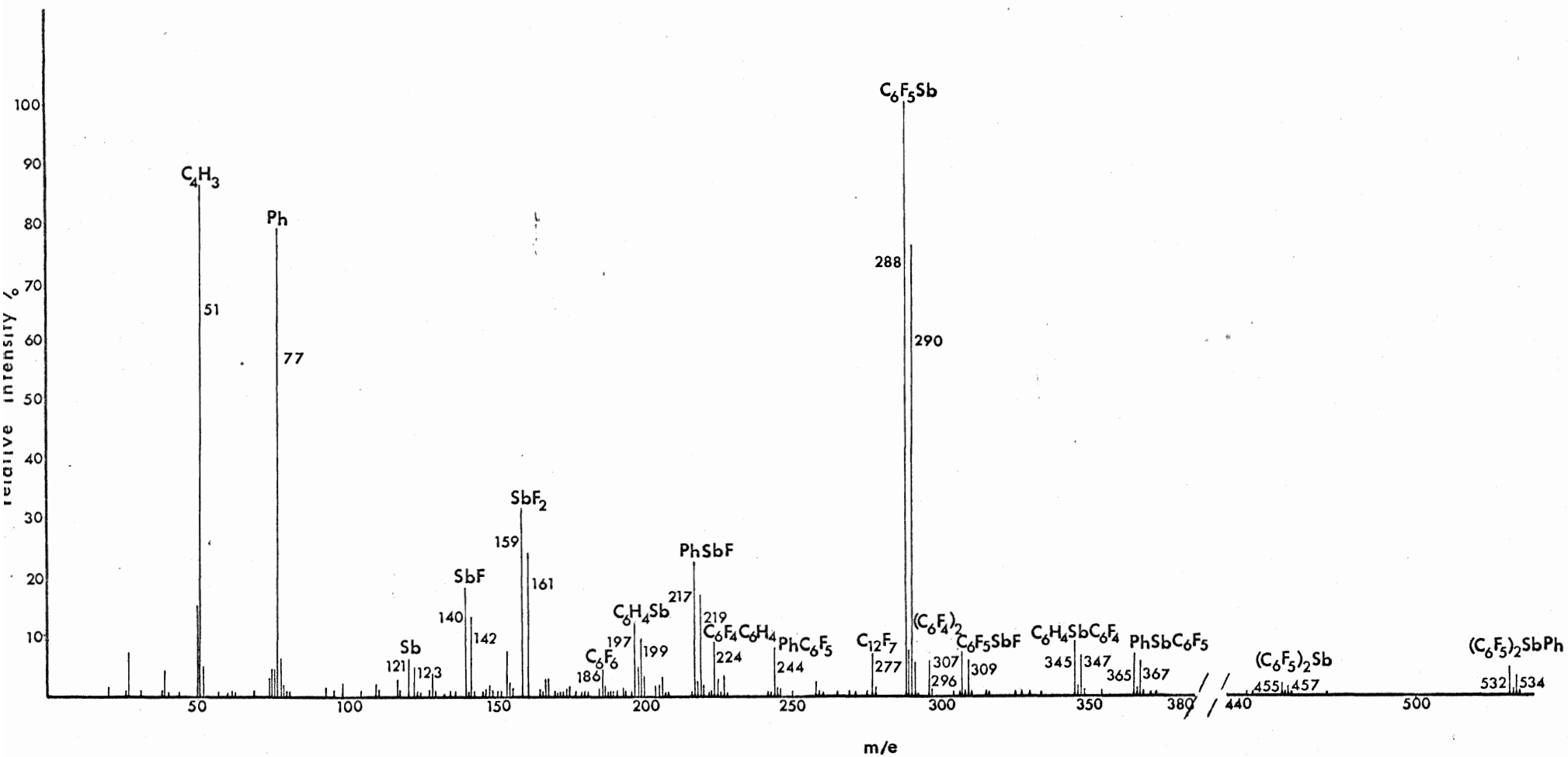




Figure 12: Fragmentation Pattern  
for  $\text{Ph}_3\text{M}$  (M = P, As, or Sb)

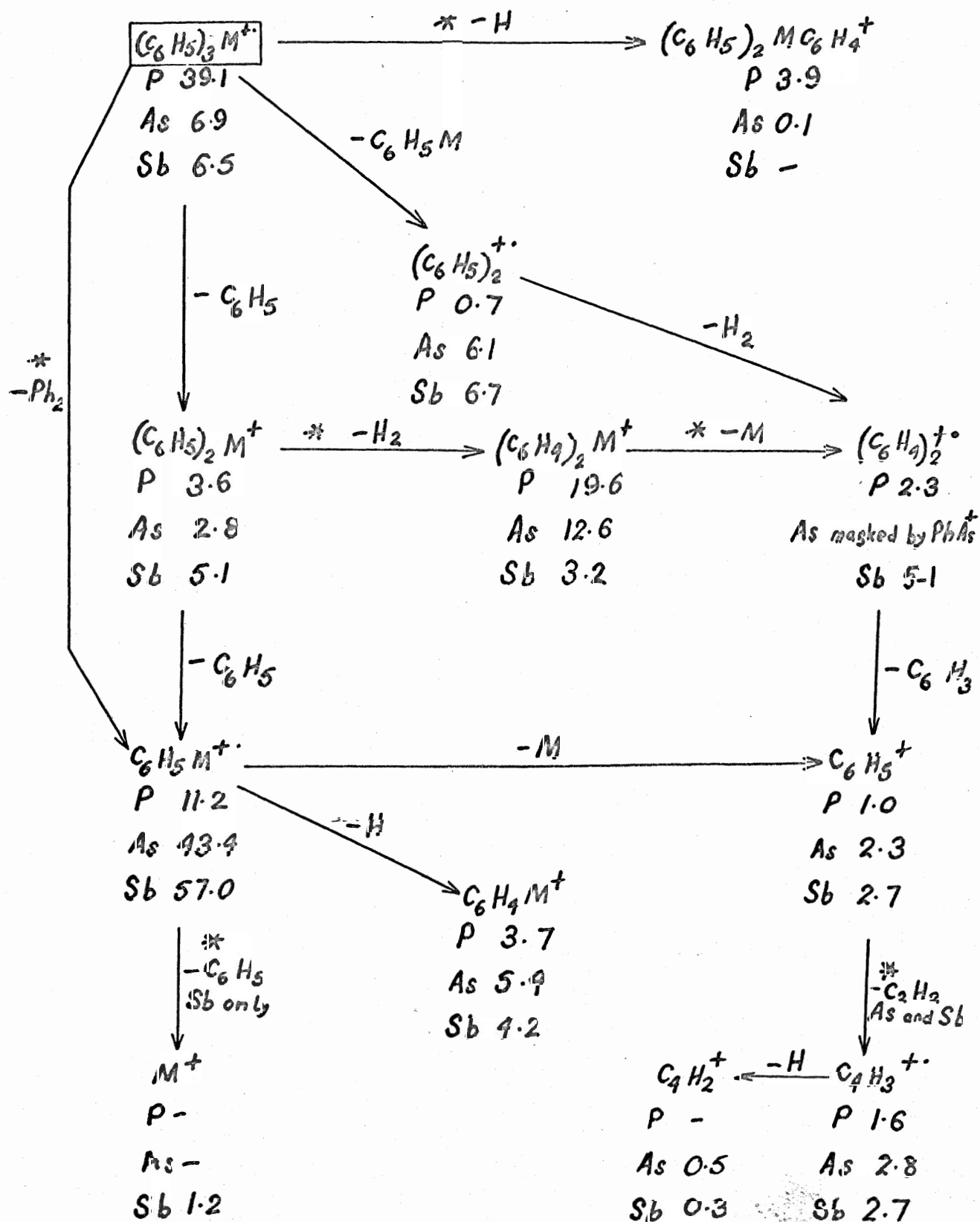


Figure 13: Fragmentation Pattern  
for  $(C_6F_5)_3P$

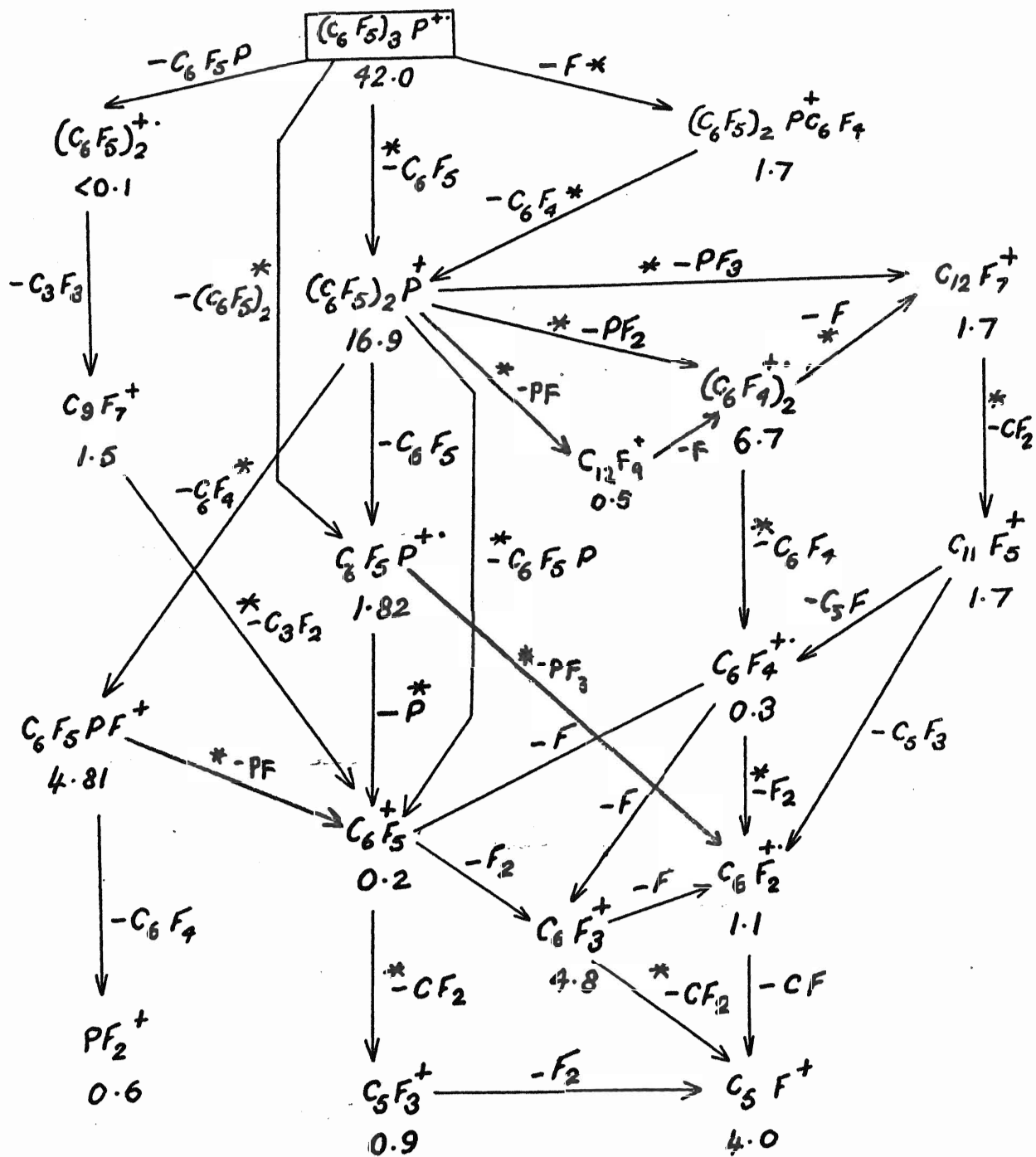


Figure 14: Fragmentation Pattern  
for  $(C_6F_5)_3As$

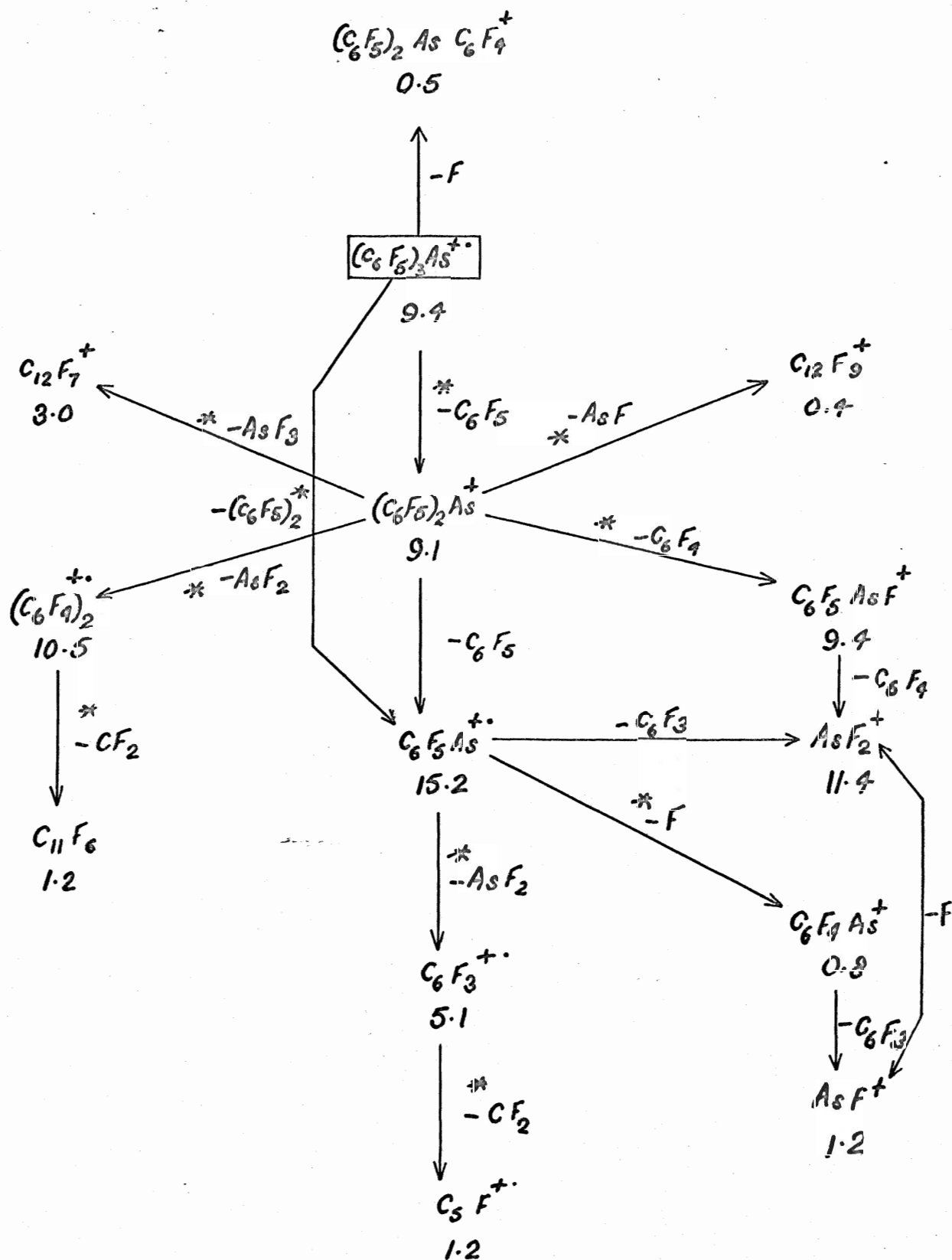


Figure 15: Fragmentation Pattern  
for  $(C_6F_5)_3Sb$

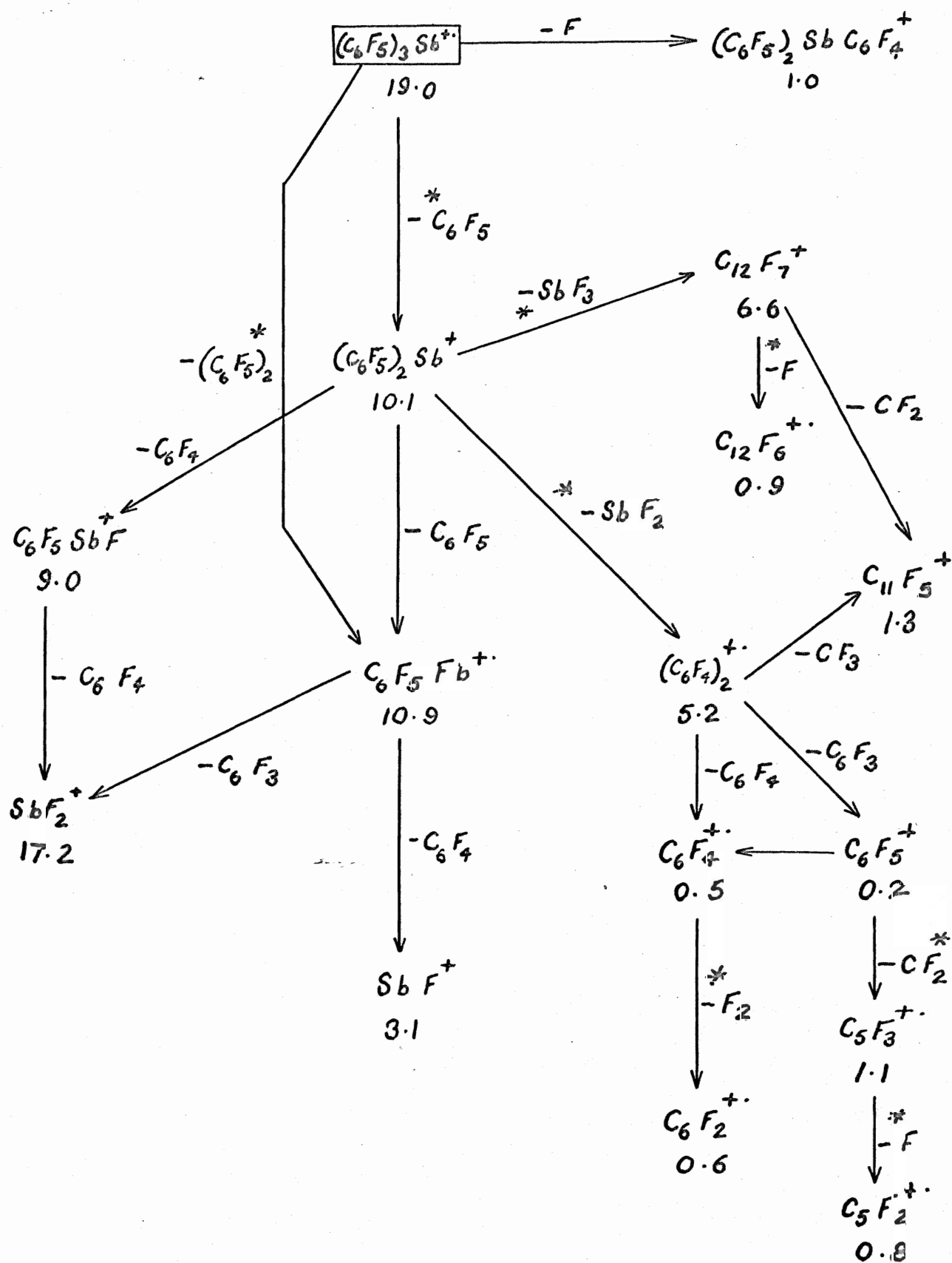




Figure 16: Fragmentation Pattern  
for C<sub>6</sub>F<sub>5</sub>PPh<sub>2</sub>

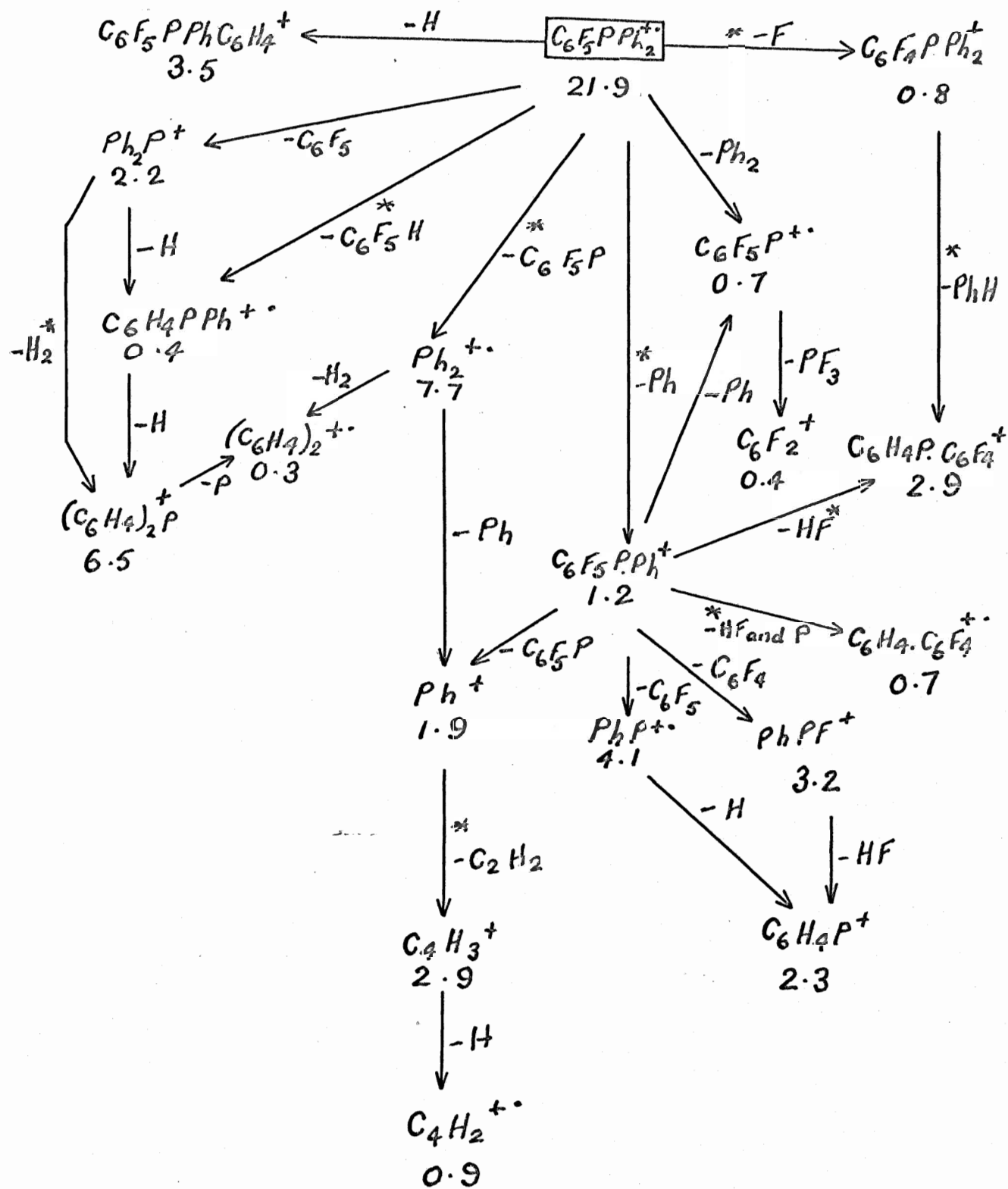


Figure 17: Fragmentation Pattern  
for C<sub>6</sub>F<sub>5</sub>AsPh<sub>2</sub>

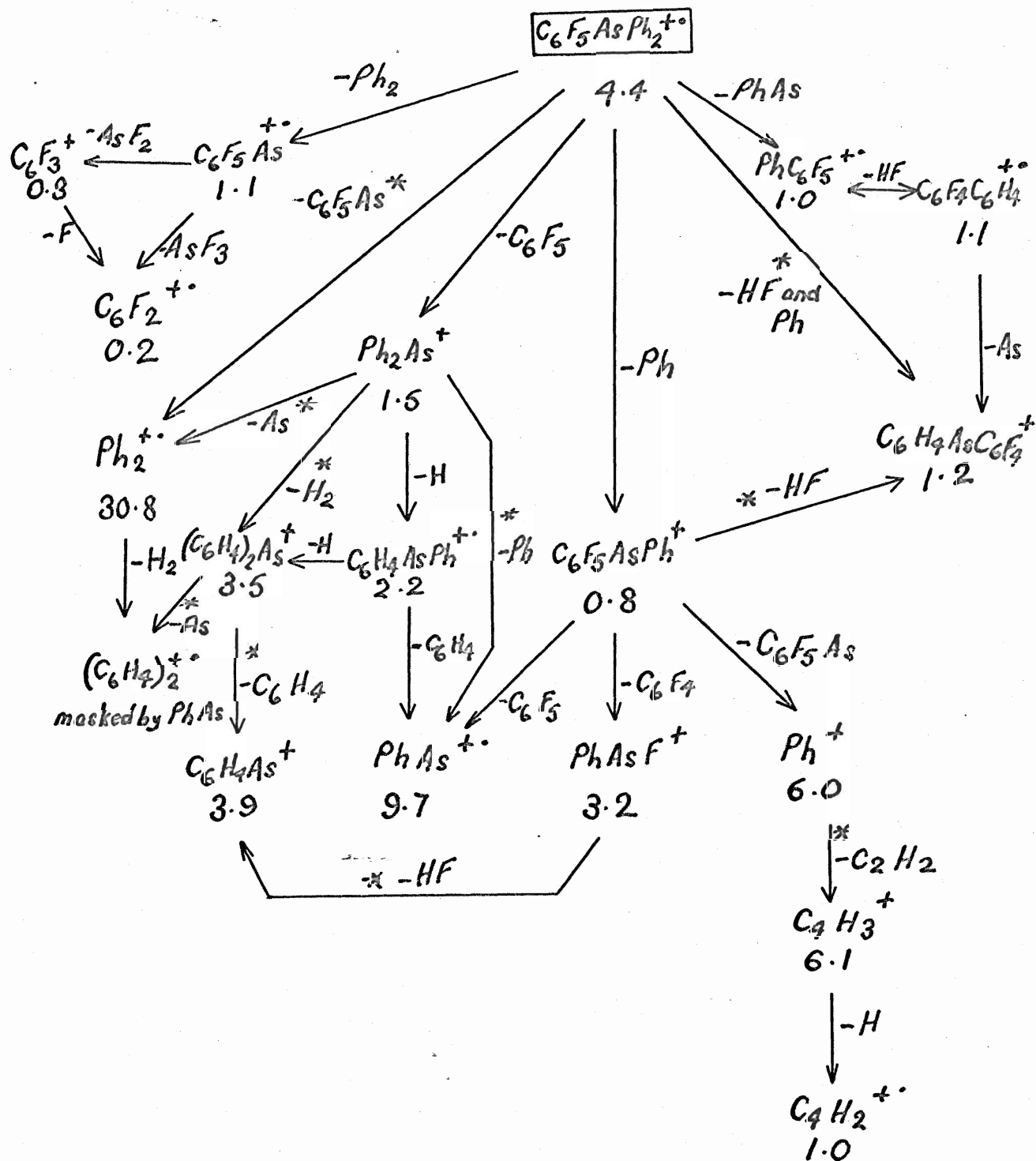


Figure 18: Fragmentation Pattern  
for  $(C_6F_5)_2PPh$

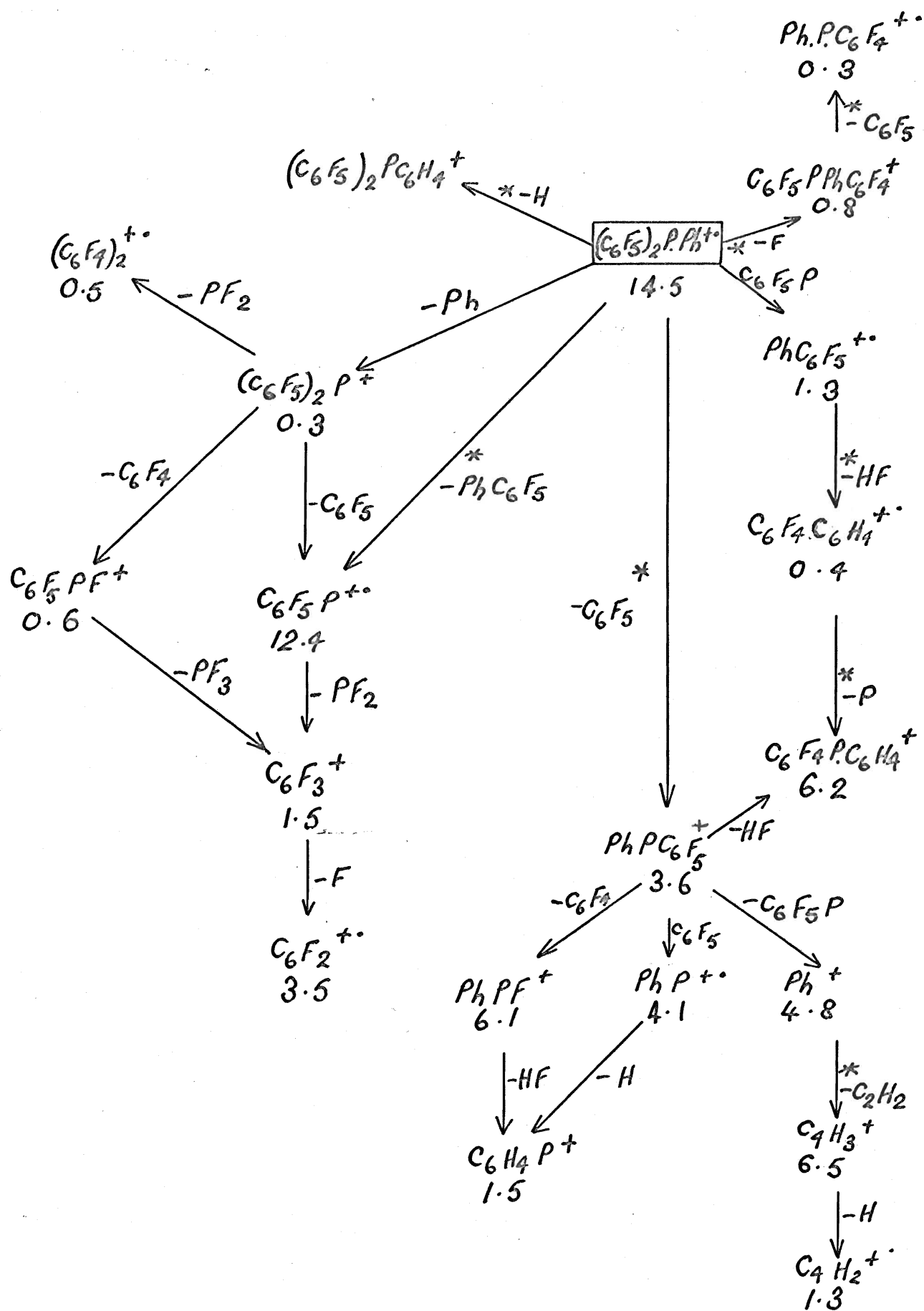


Figure 19: Fragmentation Pattern  
for  $(C_6F_5)_2AsPh$

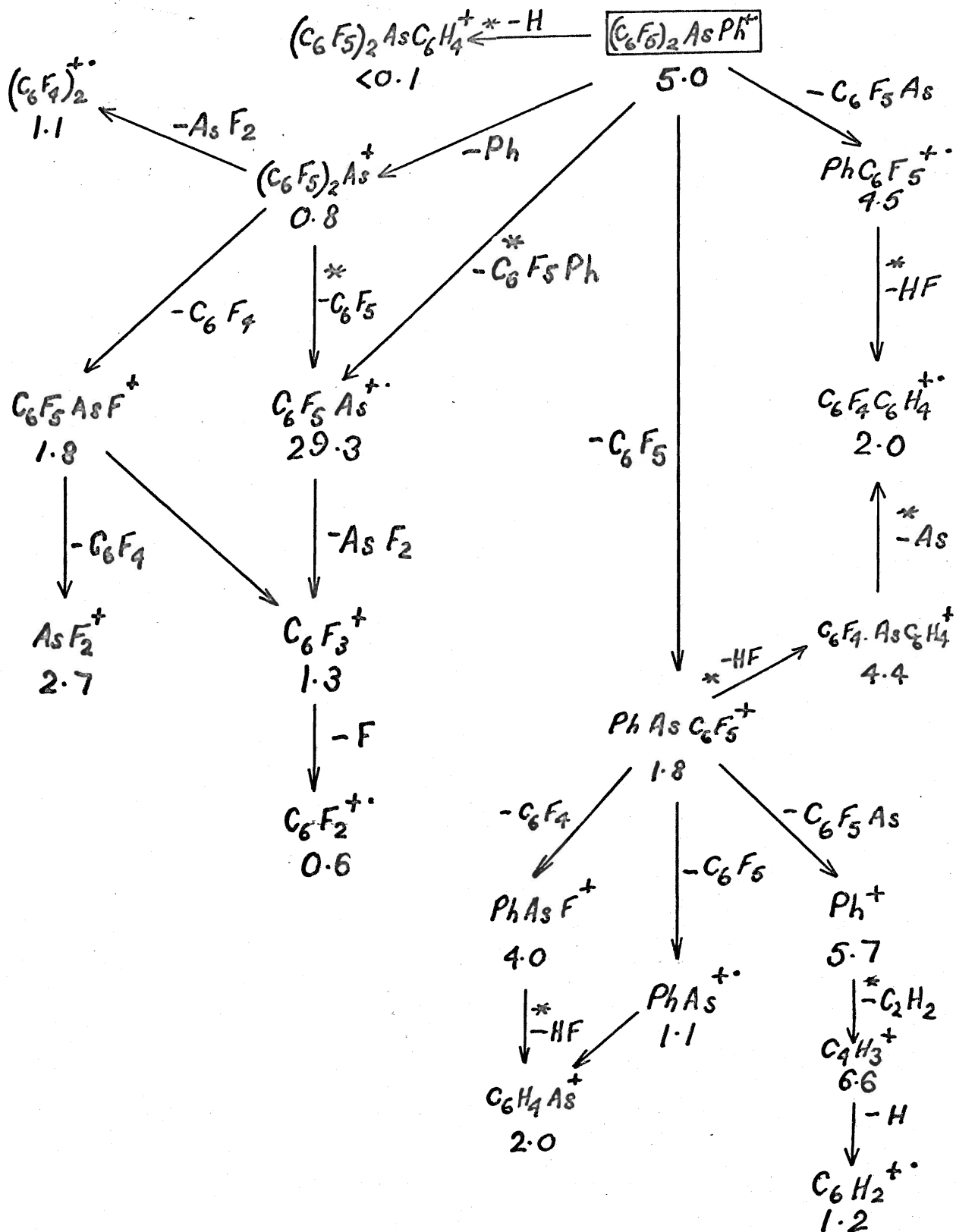




Figure 20: Fragmentation Pattern  
for  $(C_6F_5)_2SbPh$

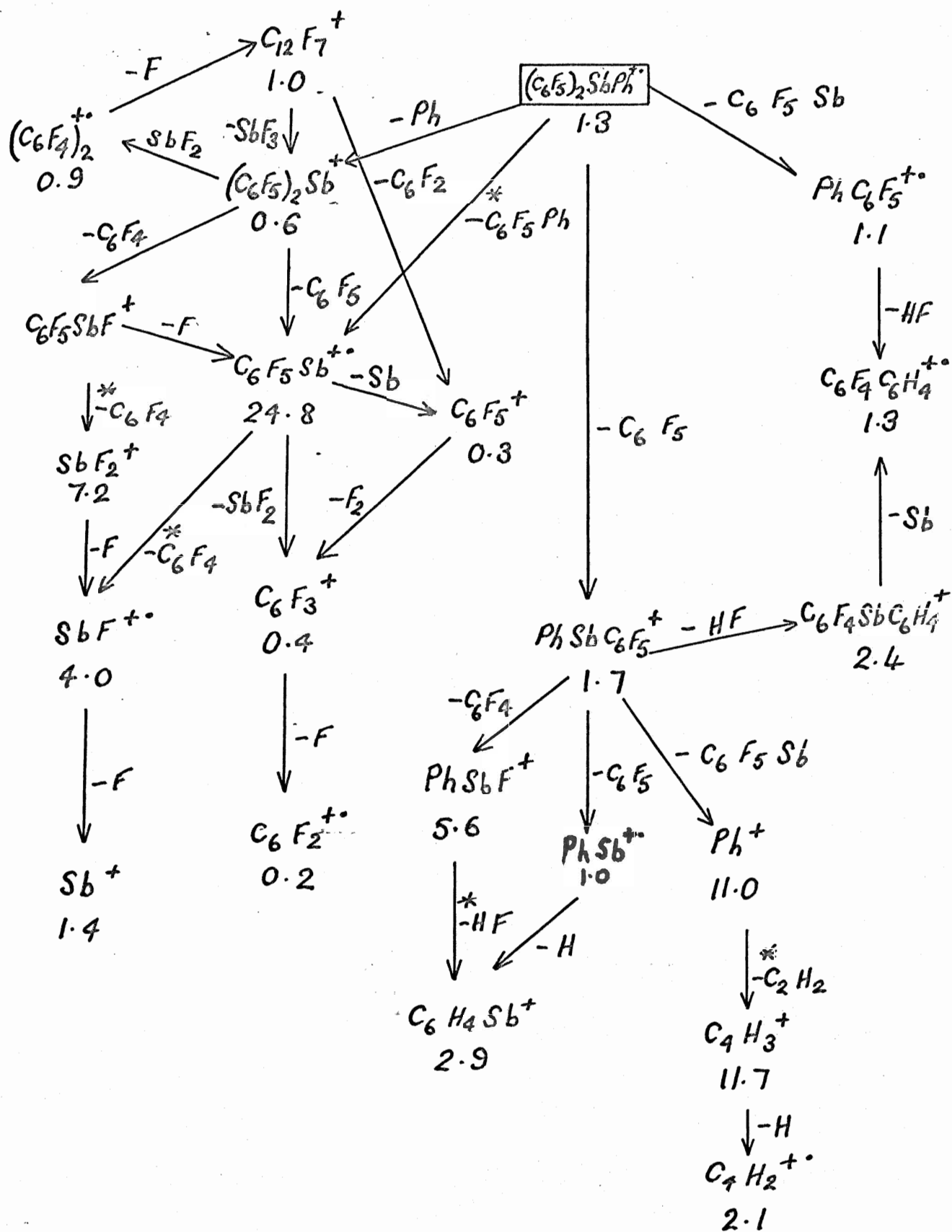


Table 4: Mass Spectra of  
 $(C_6X_5)_3M$  (X = H, F M = P, As and Sb )  
as Percentage of the Total Positive Ion Current

A. Ions Containing Central Atom

Ion <sup>+</sup>	Phosphorus		Arsenic		Antimony	
	X = F	X = H	X = F	X = H	X = F	X = H
(C <sub>6</sub> X <sub>5</sub> ) <sub>3</sub> M	42.0	39.1	9.4	6.9	19.0	6.5
(C <sub>6</sub> X <sub>5</sub> ) <sub>2</sub> MC <sub>6</sub> X <sub>4</sub>	1.7	3.9	0.5	0.1	1.0	
C <sub>6</sub> X <sub>5</sub> M(C <sub>6</sub> X <sub>4</sub> ) <sub>2</sub>		0.5				
(C <sub>6</sub> X <sub>5</sub> ) <sub>2</sub> M	16.9	3.6	9.1	2.8	10.1	5.1
C <sub>12</sub> X <sub>9</sub> M		4.2				
(C <sub>6</sub> X <sub>4</sub> ) <sub>2</sub> M		19.6	0.8	12.4		3.2
C <sub>6</sub> X <sub>5</sub> MX	4.8		9.4		9.0	
C <sub>6</sub> X <sub>5</sub> M	1.8	11.2	15.2	43.4	10.9	52.5
C <sub>6</sub> X <sub>4</sub> M		3.7	0.8	5.4		4.2
MX <sub>2</sub>	0.7		11.4		17.2	
MX			1.2		3.1	
M					0.4	1.2
Total	67.9	85.8	57.8	71.0	70.7	72.7

B. Ions Not Containing Central Atom

Ion <sup>+</sup>	Phosphorus		Arsenic		Antimony	
	X = F	X = H	X = F	X = H	X = F	X = H
(C <sub>6</sub> X <sub>5</sub> ) <sub>2</sub>		0.7	0.5	6.1	0.3	7.7
C <sub>12</sub> X <sub>9</sub>	0.5	0.6	0.4	2.8	0.2	5.6
(C <sub>6</sub> X <sub>4</sub> ) <sub>2</sub>	6.7	2.3	10.5	masked by PhAs <sup>+</sup> masked by C <sub>6</sub> H <sub>4</sub> As <sup>+</sup>	5.2	5.1
C <sub>12</sub> X <sub>7</sub>	1.7	0.3	3.0		6.6	0.9
C <sub>11</sub> X <sub>7</sub>	0.5		0.9		0.3	
C <sub>12</sub> X <sub>6</sub>	0.9		1.1		0.9	
C <sub>11</sub> X <sub>6</sub>	0.6		1.2		0.9	
C <sub>9</sub> X <sub>7</sub>	1.5		1.1		0.3	
C <sub>11</sub> X <sub>5</sub>	1.7		1.8		1.3	
C <sub>10</sub> X <sub>4</sub>	0.2		0.3		0.1	
C <sub>11</sub> X <sub>3</sub>			0.2		0.2	
C <sub>6</sub> X <sub>6</sub>		0.4	0.1	1.9	0.2	1.4
C <sub>6</sub> X <sub>5</sub> H	0.6		0.2		0.9	
C <sub>6</sub> X <sub>5</sub>	0.2	1.0	0.4	2.3	0.2	2.7
C <sub>6</sub> X <sub>4</sub>	0.3		1.1	0.3	0.5	0.5
C <sub>6</sub> X <sub>3</sub>	4.8		5.1	0.2	1.3	0.2
C <sub>6</sub> X <sub>2</sub>	1.1		1.4		0.6	
C <sub>5</sub> X <sub>5</sub>		0.5			1.1	
C <sub>5</sub> X <sub>3</sub>	0.9	0.7	2.0		1.1	
C <sub>5</sub> X <sub>2</sub>			1.1		0.8	
C <sub>4</sub> X <sub>3</sub>		1.6		2.8		2.7
C <sub>4</sub> X <sub>2</sub>				0.5		0.3

Ion <sup>+</sup>	Phosphorus		Arsenic		Antimony	
	X = F	X = H	X = F	X = H	X = F	X = H
$C_3X_3$	0.5		0.8	0.6	0.5	0.3
$C_4X_2$					0.2	
$C_6X$	0.1		0.3		0.2	
$C_5X$	4.0		1.2		0.9	
$C_3X_2$			0.2		0.1	
$CX_3$	6.5		0.2		0.1	
$CX_2$			0.1		0.3	
$CX$			0.7		0.4	
Total	33.3	8.1	36.2	17.5	25.7	27.4

Table 5: Mass Spectra of  
 $\text{Ph}_n\text{M}(\text{C}_6\text{F}_5)_{3-n}$  ( $n = 1, 2$   $\text{M} = \text{P}$  or  $\text{As}$ )  
and  $\text{PhSb}(\text{C}_6\text{F}_5)_2$  as Percentage of the  
Total Positive Ion Current

A. Ions Containing Central Atom

Ion	$\text{Ph}_2\text{PC}_6\text{F}_5$	$\text{PhP}(\text{C}_6\text{F}_5)_2$	$\text{Ph}_2\text{AsC}_6\text{F}_5$	$\text{PhAs}(\text{C}_6\text{F}_5)_2$	$\text{PhSb}(\text{C}_6\text{F}_5)_2$
Parent $^+$	21.9	14.5	4.4	5.0	1.3
Parent - H $^+$	3.5				
Parent - 2H $^+$	0.6				
Parent - F $^+$	0.8	0.8			
$(\text{C}_6\text{F}_5)_2\text{M}^+$		0.3		0.8	0.6
$\text{C}_6\text{F}_5\text{MPh}^+$	1.2	3.6	0.8	1.8	1.7
$\text{C}_6\text{F}_4\text{MPh}^+$	0.4	0.3			
$\text{C}_6\text{F}_5\text{MC}_6\text{H}_4^+$	0.5				
$\text{C}_6\text{F}_4\text{MC}_6\text{H}_4^+$	2.9	6.2	1.2	4.4	2.4
$\text{C}_6\text{F}_5\text{MF}^+$		0.6		1.8	1.8
$\text{C}_6\text{F}_5\text{M}^+$	0.7	12.4	1.1	29.3	24.8
$\text{C}_6\text{F}_4\text{M}^+$		0.3		0.5	0.2
$\text{Ph}_2\text{M}^+$	2.2		1.5		
$\text{PhMC}_6\text{H}_4^+$	0.4		0.1		
$(\text{C}_6\text{H}_4)_2\text{M}^+$	6.5		3.5		
$\text{PhMF}^+$	3.2	6.1	3.2	4.0	5.6
$\text{PhM}^+$	4.1		9.7	1.1	1.0
$\text{C}_6\text{H}_4\text{M}^+$	2.3	1.5	3.9	2.0	2.9
$\text{MF}_2^+$			0.4	2.7	7.2
$\text{MF}^+$				0.3	4.0
$\text{M}^+$					1.4
Total	51.2	46.6	29.8	53.7	53.9



B. Ions Not Containing Central Atom

<u>Ion<sup>+</sup></u>	<u>Ph<sub>2</sub>PCF<sub>5</sub></u>	<u>PhP(CF<sub>5</sub>)<sub>2</sub></u>	<u>Ph<sub>2</sub>AsCF<sub>5</sub></u>	<u>PhAs(CF<sub>5</sub>)<sub>2</sub></u>	<u>PhSb(CF<sub>5</sub>)<sub>2</sub></u>
(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>		0.1			
(C <sub>6</sub> F <sub>4</sub> ) <sub>2</sub>	0.4	0.5		1.1	0.9
C <sub>12</sub> F <sub>7</sub>					1.0
PhC <sub>6</sub> F <sub>5</sub>	0.1	1.3	1.0	4.5	1.1
C <sub>6</sub> F <sub>4</sub> ·C <sub>6</sub> H <sub>4</sub>	0.7	0.4	1.1	2.0	1.3
C <sub>6</sub> F <sub>6</sub>	0.6	1.3	0.4	0.5	0.6
C <sub>6</sub> F <sub>5</sub> H	0.4	0.4	0.3	0.5	0.3
C <sub>6</sub> F <sub>5</sub>	0.5	0.4		0.1	0.3
Ph <sub>2</sub>	777		30.8		1.0
PhC <sub>6</sub> H <sub>4</sub>	1.4		2.2		
(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub>	0.3		masked by PhAs <sup>+</sup>		
C <sub>6</sub> F <sub>3</sub>	0.2	1.5	0.3	1.3	0.4
C <sub>6</sub> F <sub>2</sub>	0.4	3.5	0.2	0.6	0.2
C <sub>3</sub> F <sub>3</sub>	0.3	0.3	0.1		0.1
C <sub>6</sub> H <sub>6</sub>	0.6	0.2	1.5	0.7	0.1
C <sub>6</sub> H <sub>5</sub>	1.9	4.8	6.0	5.7	11.0
CF <sub>3</sub>	1.0	4.9	0.1		0.1
C <sub>4</sub> H <sub>3</sub>	2.9	6.5	6.1	6.6	11.7
C <sub>4</sub> H <sub>2</sub>	0.9	1.3	1.0	1.2	2.1
C <sub>3</sub> H <sub>3</sub>	0.8	1.1	1.0	0.5	0.5
HF			0.4	0.5	0.1
Total	21.1	28.5	52.5	25.8	32.8

Table 6: Nature of the Charge Carrying Species as a Percentage of the Total Positive Ion Current.

Ion Type	M = P		As		Sb	
	X=F	H	F	H	F	H
$N^+$	68	86	58	71	71	83
$MC_mX_n^+$	67	86	45	71	51	72
$MX_n^+$	1	-	13	-	20	-
$M^+$	-	-	-	-	0.5	1
$C_mX_n^+$	33	14	42	29	29	27
$C_mX_nMF_a^+$	5	-	9	-	9	-

N = Total metal containing species

Compound	$N^+ \ddagger$	$C_mX_n^+ \ddagger$	$C_mX_nMF_a^+ *$
$Ph_2PC_6F_5$	71	29	3
$PhP(C_6F_5)_2$	62	38	7
$Ph_2AsC_6F_5$	36	64	3
$PhAs(C_6F_5)_2$	68	32	6
$PhSb(C_6F_5)_2$	66	34	7

\* mostly  $PhMF^+$

‡ Spectra renormalised from Table 5 so that the sum of  $N^+$  and  $C_mX_n^+ = 100\%$

Table 7: Observed Metastable Transitions

Ph<sub>3</sub>P<sup>+</sup>

		<u>calc.</u>	<u>found</u>
Ph <sub>3</sub> P <sup>+</sup> → Ph <sub>2</sub> P C <sub>6</sub> H <sub>4</sub> <sup>+</sup> + H		260.0	260.0
m/e 262	m/e 261		
Ph <sub>3</sub> P <sup>+</sup> → PhP <sup>+</sup> + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>		44.5	44.5
m/e 262	m/e 108		
Ph <sub>2</sub> P <sup>+</sup> → (C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P <sup>+</sup> + H <sub>2</sub>		180.7	180.9
m/e 185	m/e 183		
(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P <sup>+</sup> → (C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> <sup>+</sup> + P		126.2	126.4
m/e 183	m/e 152		

For a complete assignment of all the metastables that have been observed, see reference (67).

Ph<sub>3</sub>As

		<u>calc.</u>	<u>found</u>
Ph <sub>3</sub> As <sup>+</sup> → Ph <sub>2</sub> AsC <sub>6</sub> H <sub>4</sub> <sup>+</sup> + H		304.0	304.0
m/e 306	m/e 305		
Ph <sub>3</sub> As <sup>+</sup> → PhAs <sup>+</sup> + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>		75.5	75.5
m/e 306	m/e 152		
Ph <sub>2</sub> As <sup>+</sup> → (C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> As <sup>+</sup> + H <sub>2</sub>		225.0	225.0
m/e 229	m/e 227		
(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> As <sup>+</sup> → (C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> <sup>+</sup> + As		101.8	101.9
m/e 227	m/e 152		
Ph <sup>+</sup> → C <sub>4</sub> H <sub>3</sub> <sup>+</sup> + C <sub>2</sub> H <sub>2</sub>		33.8	33.8
m/e 77	m/e 51		

Ph<sub>3</sub>Sb

		<u>calc.</u>	<u>found</u>
$\text{Ph}_3\text{Sb}^+ \longrightarrow \text{Ph}_2\text{SbC}_6\text{H}_4^+ + \text{H}$		352.0 )	
m/e 354, 352	m/e 353, 351	350.0 )	350-352
$\text{Ph}_3\text{Sb}^+ \longrightarrow \text{PhSb}^+ + (\text{C}_6\text{F}_5)_2$		113.0 )	
m/e 354, 352	m/e 200, 198	111.4 )	111-113
$\text{Ph}_2\text{Sb}^+ \longrightarrow (\text{C}_6\text{H}_4)_2\text{Sb}^+ + \text{H}_2$		273.0 )	
m/e 277, 275	m/e 275, 273	271.0 )	271-273
$(\text{C}_6\text{H}_4)_2\text{Sb}^+ \longrightarrow (\text{C}_6\text{H}_4)_2^+ + \text{Sb}$		84.6 )	
m/e 275, 273	m/e 152	84.0 )	84-85
$\text{PhSb}^+ \longrightarrow \text{Ph}^+ + \text{Sb}$		29.9 )	
m/e 200, 198	m/e 77	29.6 )	29.8
$\text{Ph}^+ \longrightarrow \text{C}_4\text{H}_3^+ + \text{C}_2\text{H}_2$		33.8	33.7
m/e 77	m/e 51		

(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>P

		<u>calc.</u>	<u>found</u>
$(\text{C}_6\text{F}_5)_3\text{P}^+ \longrightarrow (\text{C}_6\text{F}_5)_2\text{PC}_6\text{F}_4^+ + \text{F}$		494.6	494.5
m/e 532	m/e 513		
$(\text{C}_6\text{F}_5)_3\text{P}^+ \longrightarrow (\text{C}_6\text{F}_5)_2\text{P}^+ + \text{C}_6\text{F}_5$		250.4	250.4
m/e 532	m/e 365		
$(\text{C}_6\text{F}_5)_3\text{P}^+ \longrightarrow \text{C}_6\text{F}_5\text{P}^+ + (\text{C}_6\text{F}_5)_2$		73.7	73.8
m/e 532	m/e 198		
$(\text{C}_6\text{F}_5)_2\text{PC}_6\text{F}_4 \longrightarrow (\text{C}_6\text{F}_5)_2\text{P}^+ + \text{C}_6\text{F}_4$		259.7	259.4
m/e 513	m/e 365		

(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>P (continued)

		<u>calc.</u>	<u>found</u>
$(C_6F_4)_2^+$ m/e 296	$\longrightarrow C_{12}F_7^+ + F$ m/e 277	259.2	259.4
$(C_6F_5)_2P^+$ m/e 365	$\longrightarrow C_{12}F_9^+ + PF$ m/e 315	272.0	272.0
$(C_6F_5)_2P^+$ m/e 365	$\longrightarrow (C_6F_4)_2^+ + PF_2$ m/e 296	240.4	240.6
$(C_6F_5)_2P^+$ m/e 365	$\longrightarrow C_{12}F_7^+ + PF_3$ m/e 277	210.2	210.3
$(C_6F_5)_2P^+$ m/e 365	$\longrightarrow C_6F_5PF^+ + C_6F_4$ m/e 217	129.0	128.9
$(C_6F_5)_2P^+$ m/e 365	$\longrightarrow C_6F_5^+ + C_6F_5P$ m/e 167	76.4	76.5
$C_6F_5PF^+$ m/e 217	$\longrightarrow C_6F_5^+ + PF$ m/e 167	128.5	128.8
$C_6F_5P^+$ m/e 198	$\longrightarrow C_6F_5^+ + P$ m/e 167	140.9	141.2
$C_6F_5P^+$ m/e 198	$\longrightarrow C_6F_2^+ + PF_3$ m/e 110	61.1	61.1
$C_{12}F_7^+$ m/e 277	$\longrightarrow C_4F_5^+ + CF_2$ m/e 227	186.0	180.0

(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>P (continued)

		<u>calc.</u>	<u>found</u>
$C_9F_7^+$ m/e 241	$\longrightarrow C_6F_5^+ + C_3F_2$ m/e 167	115.7	116.0
$C_6F_4^+$ m/e 148	$\longrightarrow C_6F_2^+ + F_2$ m/e 110	81.8	82.0
$C_6F_5^+$ m/e 167	$\longrightarrow C_5F_3^+ + CF_2$ m/e 117	82.0	82.0
$(C_6F_4)_2^+$ m/e 296	$\longrightarrow C_6F_4^+ + C_6F_4$ m/e 148	74.0	74.0
$C_6F_3^+$ m/e 129	$\longrightarrow C_5F^+ + CF_2$ m/e 79	48.4	48.4

<u>(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>As</u>		<u>calc.</u>	<u>found</u>
(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> As <sup>+</sup> m/e 576	→ (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> As <sup>+</sup> + C <sub>6</sub> F <sub>5</sub> m/e 409	290.4	290.5
(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> As <sup>+</sup> m/e 576	→ C <sub>6</sub> F <sub>5</sub> As <sup>+</sup> + (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> m/e 242	101.7	101.7
(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> As <sup>+</sup> m/e 409	→ C <sub>12</sub> F <sub>9</sub> <sup>+</sup> + AsF m/e 315	242.6	242.6
(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> As <sup>+</sup> m/e 409	→ (C <sub>6</sub> F <sub>4</sub> ) <sub>2</sub> <sup>+</sup> + AsF <sub>2</sub> m/e 296	214.2	214.2
(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> As <sup>+</sup> m/e 409	→ C <sub>12</sub> F <sub>7</sub> <sup>+</sup> + AsF <sub>3</sub> m/e 277	187.6	187.5
(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> As <sup>+</sup> m/e 409	→ C <sub>6</sub> F <sub>5</sub> AsF <sup>+</sup> + C <sub>6</sub> F <sub>4</sub> m/e 261	166.6	166.5
C <sub>6</sub> F <sub>5</sub> As <sup>+</sup> m/e 242	→ C <sub>6</sub> F <sub>3</sub> <sup>+</sup> + AsF <sub>2</sub> m/e 129	68.7	69.0
C <sub>6</sub> F <sub>5</sub> As <sup>+</sup> m/e 242	→ C <sub>6</sub> F <sub>4</sub> As <sup>+</sup> + F m/e 223	205.5	205.0
(C <sub>6</sub> F <sub>4</sub> ) <sub>2</sub> <sup>+</sup> m/e 296	→ C <sub>11</sub> F <sub>6</sub> <sup>+</sup> + CF <sub>2</sub> m/e 246	204.5	205.0
C <sub>6</sub> F <sub>3</sub> <sup>+</sup> m/e 129	→ C <sub>5</sub> F <sup>+</sup> + CF <sub>2</sub> m/e 79	48.4	48.6

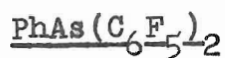


<u>(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Sb</u>		<u>calc.</u>	<u>found</u>
(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Sb <sup>+</sup> m/e 624, 622	→ (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Sb <sup>+</sup> + C <sub>6</sub> F <sub>5</sub> m/e 457, 455 167	334.7 332.8	332-335
(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Sb <sup>+</sup> m/e 624, 622	→ C <sub>6</sub> F <sub>5</sub> Sb <sup>+</sup> + (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> m/e 290, 288	134.8 133.4	133-135
(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Sb <sup>+</sup> m/e 457, 455	→ (C <sub>6</sub> F <sub>4</sub> ) <sub>2</sub> <sup>+</sup> + SbF <sub>2</sub> m/e 296	192.6 191.7	191-193
(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Sb <sup>+</sup> m/e 457, 455	→ C <sub>12</sub> F <sub>7</sub> <sup>+</sup> + SbF <sub>3</sub> m/e 277	168.6 167.9	167-169
C <sub>12</sub> F <sub>7</sub> <sup>+</sup> m/e 277	→ C <sub>12</sub> F <sub>6</sub> <sup>+</sup> + F m/e 258	240.3	240.5
C <sub>5</sub> F <sub>3</sub> <sup>+</sup> m/e 117	→ C <sub>5</sub> F <sub>2</sub> <sup>+</sup> + F m/e 98	82.1	82.0
C <sub>6</sub> F <sub>4</sub> <sup>+</sup> m/e 148	→ C <sub>6</sub> F <sub>2</sub> <sup>+</sup> + F <sub>2</sub> m/e 110	81.8	82.0
C <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 167	→ C <sub>5</sub> F <sub>3</sub> <sup>+</sup> + CF <sub>2</sub> m/e 117	82.0	82.0

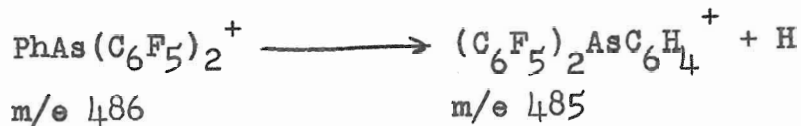
<u>Ph<sub>2</sub>PC<sub>6</sub>F<sub>5</sub></u>		<u>calc.</u>	<u>found</u>
Ph <sub>2</sub> PC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 352	→ Ph <sub>2</sub> PC <sub>6</sub> F <sub>4</sub> <sup>+</sup> + F m/e 333	315.0	314.6
Ph <sub>2</sub> PC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 352	→ PhPC <sub>6</sub> F <sub>5</sub> <sup>+</sup> + Ph m/e 275	214.8	215.0
Ph <sub>2</sub> PC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 352	→ PhPC <sub>6</sub> H <sub>4</sub> <sup>+</sup> + C <sub>6</sub> F <sub>5</sub> H m/e 184	96.2	96.0
Ph <sub>2</sub> PC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 352	→ Ph <sub>2</sub> <sup>+</sup> + C <sub>6</sub> F <sub>5</sub> P m/e 154	67.4	67.4
Ph <sub>2</sub> PC <sub>6</sub> F <sub>4</sub> <sup>+</sup> m/e 333	→ C <sub>6</sub> F <sub>4</sub> PC <sub>6</sub> H <sub>4</sub> <sup>+</sup> + C <sub>6</sub> H <sub>6</sub> m/e 255	195.3	195.5
PhPC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 275	→ C <sub>6</sub> H <sub>4</sub> PC <sub>6</sub> F <sub>4</sub> <sup>+</sup> + HF m/e 255	236.5	236.7
PhPC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 275	→ C <sub>6</sub> F <sub>4</sub> C <sub>6</sub> H <sub>4</sub> <sup>+</sup> + 51 m/e 224      P and HF	182.4	182.1
C <sub>6</sub> F <sub>4</sub> PC <sub>6</sub> H <sub>4</sub> <sup>+</sup> m/e 255	→ C <sub>6</sub> F <sub>4</sub> C <sub>6</sub> H <sub>4</sub> <sup>+</sup> + P m/e 224	196.8	197.5
Ph <sub>2</sub> P <sup>+</sup> m/e 185	→ (C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P <sup>+</sup> + H <sub>2</sub> m/e 183	181.0	181.0
Ph <sup>+</sup> m/e 77	→ C <sub>4</sub> H <sub>3</sub> <sup>+</sup> + C <sub>2</sub> H <sub>2</sub> m/e 51	33.8	33.8

<u>PhP(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub></u>		<u>calc.</u>	<u>found</u>
PhP(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> <sup>+</sup> m/e 442	→ C <sub>6</sub> H <sub>4</sub> P(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> <sup>+</sup> + H m/e 441	440.0	440.0
PhP(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> <sup>+</sup> m/e 442	→ PhPC <sub>6</sub> F <sub>5</sub> ·C <sub>6</sub> F <sub>4</sub> <sup>+</sup> + F m/e 423	404.8	404.8
PhP(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> <sup>+</sup> m/e 442	→ C <sub>6</sub> F <sub>5</sub> PPh <sup>+</sup> + C <sub>6</sub> F <sub>5</sub> m/e 275	171.1	170.0
PhP(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> <sup>+</sup> m/e 442	→ C <sub>6</sub> F <sub>5</sub> P <sup>+</sup> + C <sub>6</sub> F <sub>5</sub> Ph m/e 198	88.7	88.7
PhPC <sub>6</sub> F <sub>5</sub> ·C <sub>6</sub> F <sub>4</sub> <sup>+</sup> m/e 423	→ PhPC <sub>6</sub> F <sub>4</sub> <sup>+</sup> + C <sub>6</sub> F <sub>5</sub> m/e 256	154.9	154.8
PhPC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 275	→ C <sub>6</sub> H <sub>4</sub> ·PC <sub>6</sub> F <sub>4</sub> <sup>+</sup> + HF m/e 255	236.5	236.5
C <sub>6</sub> H <sub>4</sub> PC <sub>6</sub> F <sub>4</sub> <sup>+</sup> m/e 255	→ C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> F <sub>4</sub> <sup>+</sup> + P m/e 224	196.8	197.3
Ph <sup>+</sup> m/e 77	→ C <sub>4</sub> H <sub>3</sub> <sup>+</sup> + C <sub>2</sub> H <sub>2</sub> m/e 51	33.8	33.7

<u>Ph<sub>2</sub>AsC<sub>6</sub>F<sub>5</sub></u>		<u>calc.</u>	<u>found</u>
Ph <sub>2</sub> AsC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 396	→ C <sub>6</sub> H <sub>4</sub> AsC <sub>6</sub> F <sub>4</sub> <sup>+</sup> + 97 m/e 299 Ph and HF	225.8	226.0
Ph <sub>2</sub> AsC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 396	→ Ph <sub>2</sub> <sup>+</sup> + C <sub>6</sub> F <sub>5</sub> As m/e 154	59.9	59.9
PhAsC <sub>6</sub> F <sub>5</sub> <sup>+</sup> m/e 319	→ C <sub>6</sub> F <sub>4</sub> AsC <sub>6</sub> H <sub>4</sub> <sup>+</sup> + HF m/e 299	280.3	280.1
Ph <sub>2</sub> As <sup>+</sup> m/e 229	→ (C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> As <sup>+</sup> + H <sub>2</sub> m/e 227	225.0	225.0
Ph <sub>2</sub> As <sup>+</sup> m/e 229	→ Ph <sub>2</sub> <sup>+</sup> + As m/e 154	103.6	103.3
Ph <sub>2</sub> As <sup>+</sup> m/e 229	→ PhAs <sup>+</sup> + Ph m/e 152	100.9	100.8
(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> As <sup>+</sup> m/e 227	→ (C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> <sup>+</sup> + As m/e 152	101.8	102.0
(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> As <sup>+</sup> m/e 227	→ C <sub>6</sub> H <sub>4</sub> As <sup>+</sup> + C <sub>6</sub> H <sub>4</sub> m/e 151	100.4	100.5
PhAsF <sup>+</sup> m/e 171	→ C <sub>6</sub> H <sub>4</sub> As <sup>+</sup> + HF m/e 151	133.3	133.0
Ph <sup>+</sup> m/e 77	→ C <sub>4</sub> H <sub>3</sub> <sup>+</sup> + C <sub>2</sub> H <sub>2</sub> m/e 51	33.8	33.8



calc.   found



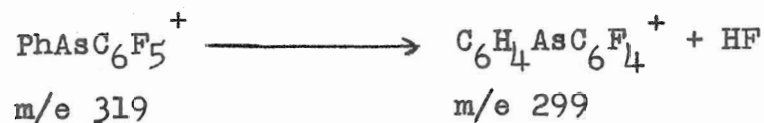
485.0   485.0



120.5   120.5



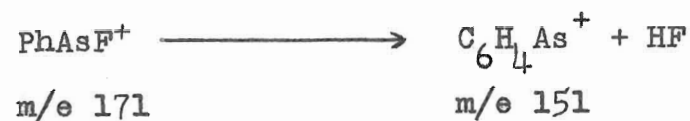
69.0   69.0



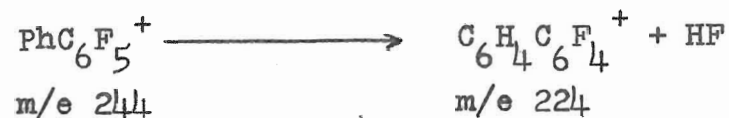
280.3   280.3



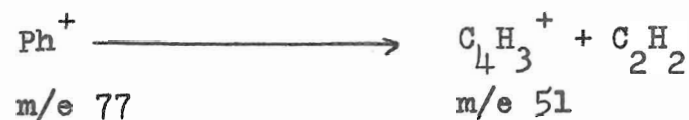
167.8   168.0



133.3   133.5



205.6   205.9



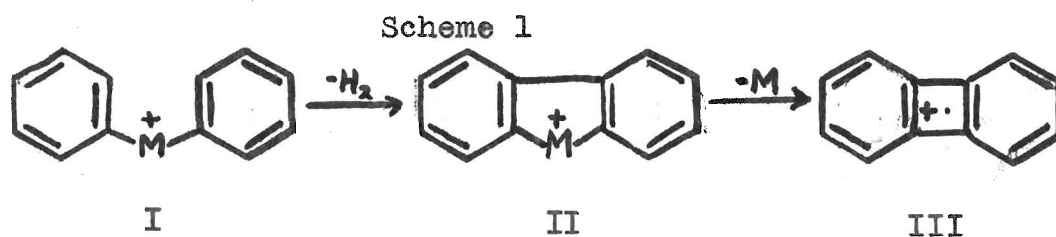
33.8   33.8

PhSb(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>

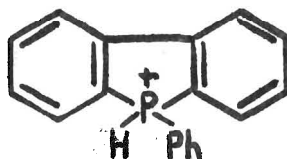
		<u>calc.</u>	<u>found</u>
PhSb(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> <sup>+</sup> →	C <sub>6</sub> F <sub>5</sub> Sb <sup>+</sup> + PhC <sub>6</sub> F <sub>5</sub>	157.5	156-158
m/e 532, 534	m/e 288, 290	156.0	
PhSbC <sub>6</sub> F <sub>5</sub> <sup>+</sup> →	C <sub>6</sub> F <sub>4</sub> SbC <sub>6</sub> H <sub>4</sub> <sup>+</sup> + HF	328.1	328-326
m/e 367, 365	m/e 347, 345	326.1	
C <sub>6</sub> F <sub>5</sub> SbF <sup>+</sup> →	SbF <sub>2</sub> <sup>+</sup> + C <sub>6</sub> F <sub>4</sub>	83.9	82-86
m/e 309, 307	m/e 161, 159	82.3	
C <sub>6</sub> F <sub>5</sub> Sb <sup>+</sup> →	SbF <sup>+</sup> + C <sub>6</sub> F <sub>4</sub>	69.5	68-70
m/e 290, 288	m/e 142, 140	68.0	
PhSbF <sup>+</sup> →	C <sub>6</sub> H <sub>4</sub> Sb <sup>+</sup> + HF	179.8	179-180
m/e 217, 219	m/e 199, 197	179.7	
Ph <sup>+</sup> →	C <sub>4</sub> H <sub>3</sub> <sup>+</sup> + C <sub>2</sub> H <sub>2</sub>	33.8	33.8
m/e 77	m/e 51		

Tris Phenyl Compounds  $\text{Ph}_3\text{M}$

All three spectra (Figures 1-3) were found to be identical in their fragmentation patterns and similar to that previously reported for triphenyl phosphine (9) (67). The proposed fragmentation schemes are shown in Figure 12 and the observed metastable transitions in Table 7. A unique feature of these compounds is the formation of the ion II from the diphenyl metal ion I shown below. In the case of phosphorus, ion II has been named the phosphofluorenylium cation



Hydrogen loss from the parent ion is also observed and supported by the appropriate metastable ion in all three derivatives. This is prominent transition for the phosphorus derivative where the <sup>intensity of the</sup> molecular ion is some six times that of the corresponding arsenic and antimony derivatives (Table 4). Williams has formulated this ion as:



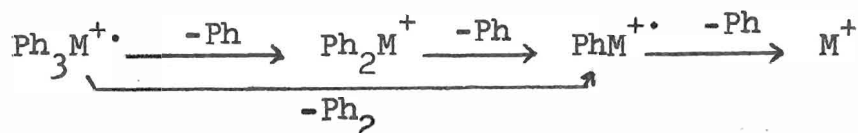
and has shown by the appropriate metastable ion that this could lead to an ion of type II by loss of benzene. It seems likely that other parent-H ions could have an analogous structure to this although due to their small abundance, the

corresponding loss of benzene from these ions was not observed.

The other main fragmentation pattern in these compounds is the loss of biphenyl from the parent ion which from the rapid rise in the abundance of the  $\text{PhM}^+$  peak (Table 4) plays a more important role in the cases of arsenic and antimony. However, it seems curious that the abundance of  $\text{C}_6\text{H}_4\text{M}^+$  shows no great variation along the series in spite of the evidence provided in the case of phosphorus, by metastable peaks that show that this ion comes predominantly from  $\text{PhM}^+$  (67).

Although there is a rapid fall in the abundance of the ion  $(\text{C}_6\text{H}_4)_2\text{M}^+$  in going from phosphorus to antimony there is no analagous decrease in the abundances of the  $\text{Ph}_2\text{M}^+$  ions. This suggests that the scheme outlined above now plays a less dominant role than does the scheme below:

Scheme II



which is observed for the heavier elements. Further evidence is provided by the increase in the aromatic hydrocarbon fragments  $\text{Ph}_2^+$ ,  $\text{Ph}^+$ , and  $\text{C}_4\text{H}_3^+$  in going from phosphorus to antimony and the presence in the mass spectrum of  $(\text{C}_6\text{H}_5)_3\text{Sb}$  of a metastable peak describing the reaction:





which can be attributed to the relatively weak carbon-antimony bond.

In a recent note Zeeh and Thompson (72) reported the formation of ions of the type  $(C_6H_4)_2M^+$  ( $M = As$  and  $Sb$ ) in the mass spectra of  $Ph_3As$  and  $Ph_3Sb$  but not in  $Ph_3Bi$ , although ions of the type  $PhM^+$  ( $M = As, Sb$  and  $Bi$ ) are found in all three cases. Except in the case of  $PhBi^+$  they then lose a hydrogen atom to give ions of the type  $C_6H_4M^+$ . From this evidence it is concluded here that for  $(C_6H_5)_3Bi$  scheme II is now the solely important mode and nicely supports the hypothesis outlined above.

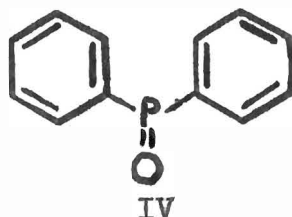
It is of interest to note that triphenylamines do not give the ion  $PhN^+$ , because the predominant mode of fragmentation in these is the loss of  $HCN$  and  $H_2CN$ . The analogous loss of  $HCM$  and  $H_2CM$  is not observed in other phenyl Group V derivatives.

The fragment ion  $C_4H_3^+$  arises by the metastable supported loss of acetylene from the phenyl ion  $Ph^+$  and has approximately the same abundance as the latter ion. This is a common process in all compounds which fragment to give a phenyl ion, but by contrast pentafluorophenyl compounds do not show loss of perfluoroacetylene from  $C_6F_5^+$  to give the analogous perfluoro ion  $C_4F_3^+$ .

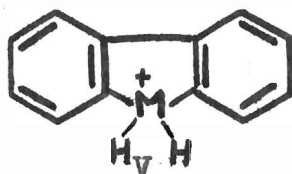
The abundance of the biphenylene ion III tends to show a slight increase in the order  $P < As < Sb$  and could arise from the scheme I in the case of phosphorus or from biphenyl produced in scheme II, for in the mass spectra of biphenyl itself, the biphenylene ion is the third most abundant peak (68). If scheme II is now the dominant process for the arsenic and antimony derivatives this could in part explain the observed trends in the abundances of the ions  $Ph_2M^+$  and  $(C_6H_5)_2^+$  since the two processes leading to the formation of  $(C_6H_4)_2^+$  can be considered to be equally energetically favourable.

The mass spectrum of  $(C_6H_5)_3P$  has been studied in detail by Williams et al (6,7 69) by the effects of deuterating various key positions on the aromatic ring. The formation of the phosphafluorenyl ion II has been shown to proceed by the loss of one hydrogen from each ring and not by formation and subsequent rearrangement of a benzene intermediate on one ring. They showed by Deuterium labelling experiments that the hydrogens on each ring are randomised prior to the formation of ion II from I and are postulated to take place via the formation of excited states since it is known that certain benzene derivatives show 1 to 2 and 1 to 3 shifts on photochemical excitation. These are thought to be due to the formation of isomeric structures in the excited state (70). The formation of the biphenylene ion III also takes place via hydrogen randomisation, which is in contrast to the formation of the M-1 peak and its subsequent loss of benzene to

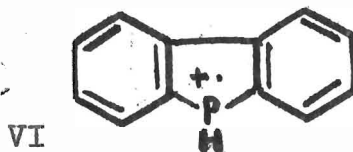
give the ion II, for which Williams has shown that randomisation of hydrogen does not occur and that it is almost certainly an ortho hydrogen that is lost in the formation of the M-1 ion. Formation of phosphafluorenyl ions are common in the mass spectra of some phosphoric acids where the most common ion has the structure IV.



This leads to a suggestion by Haake et al (71) that the  $\text{Ph}_2\text{M}^+$  ion may not be as shown in I above but is in the form



The perfluoro derivative of V perhaps can more readily explain the observed loss of  $\text{MF}_2$  species in the mass spectra of  $(\text{C}_6\text{F}_5)_3\text{M}$  compounds. In the case of triphenyl phosphine Williams has formulated the ion at  $m/e$  186 as



and has shown that this arises from  $\text{Ph}_3\text{P}^+$  by loss of benzene (67). This process is not important for  $\text{Ph}_3\text{As}$  and  $\text{Ph}_3\text{Sb}$  as analagous ions to VI are of very small abundance, and metastable transitions corresponding to the loss of benzene were not observed from the parent ions.

The mass spectra of the Group V derivatives are very different from those of Group IV (20-22) in which the loss of benzene and acetylene from metal containing ions are common phenomena. In these compounds nearly all of the ion current is carried by metal containing ions, the abundances of the aromatic fragments being negligible. The most favoured process is one leading to even electron ions from the very abundant even electron ion  $R_3M^+$  ( $M$  = Group IV elements). Some similarities to Group V derivatives are however evident in that the ion  $R_3M^+$  loses benzene to give an ion which could have a structure analogous to VI above, and also biphenyl to form the ion  $RM^+$ . Except in the case of lead, loss of biphenyl is also noted from the ions  $R_4M^+$  and  $R_2M^+$  to give  $R_2M^+$  and  $M^+$  respectively. Group V derivatives show that 70-86% of the total ion current is carried by metal containing ions (Table 6) and that the fragmentation patterns leading to an even or odd electron ion is equally likely. It is also interesting to note that while Group V derivatives have strong molecular ions, the Group IV derivatives show exceedingly weak parent ions but by contrast give very strong  $R_3M^+$  ions. There seems to be some evidence that one or three coordination is preferred in these compounds. In the tetraphenyl derivatives of Group IV the electron removed on the initial ionisation of the parent ion must almost necessarily come from a bonding orbital, but in Group V compounds this could equally come from the non bonding pair on the central atom. This could account for the above observation in the relative abundances of the parent ions in these molecules and the relative abun-

dances of the ions formed by loss of one phenyl group.

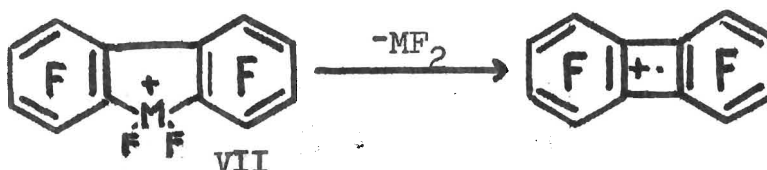
### Tris(Pentafluorophenyl) Compounds

In contrast to the tetrakis pentafluorophenyl derivatives of Group IV reported recently by Miller (9) and the tris phenyl derivatives of Group V described above, there are few trends observable in the mass spectra of tris pentafluorophenyl derivatives of Group V. Their mass spectra and fragmentation patterns are shown in Figure 4-6 and 13-15 respectively. The molecular ion is the greatest for the phosphorus derivative (42%), falls to 9.4% at arsenic and rises to 19% in the case of antimony (Table 4). The  $(C_6F_5)_2M^+$  peak also shows a similar but smaller variation. On the other hand the abundance of  $C_6F_5M^+$  rises rapidly from phosphorus (1.8%) to arsenic (15.2%) and then falls in the case of antimony (10.9%), the peak due to  $C_6F_4M^+$  staying roughly constant. There is a strong constant rise in the metal fluoride species  $MF_2^+$  on descending the series which is indicative of the weaker carbon-metal bond and a relatively stronger metal-fluorine bond forming on proceeding to heavier elements. The loss of decafluorobiphenyl from the parent ion is supported by the appropriate metastable peaks for all the members of the series (Table 7) but unlike the hydrogenic analogues, the  $(C_6F_5)_2^+$  ion is only of very small abundance.

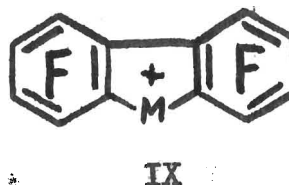
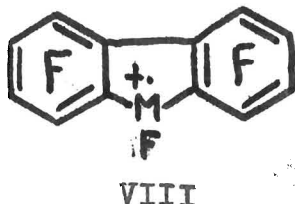
Loss of a fluorine atom from the parent ion was supported by a metastable transition only in the case of phos-

phorus but can be considered to be equally probable in the other two members of the series. The structure of this can be considered to be analogous to that proposed for the parent-H ion in the triphenyl derivatives of Group V.

The elimination of metal fluoride species in the mass spectra of pentafluorophenyl compounds is now a well established feature and has been described for many various systems (9-11). In the case of the pentafluorophenyl derivatives of Group V loss of  $\text{MF}$ ,  $\text{MF}_2$  and  $\text{MF}_3$  radicals from the ion  $(\text{C}_6\text{F}_5)_2\text{M}^+$  gives rise to the fluorocarbon ions  $\text{C}_{12}\text{F}_9^+$ ,  $(\text{C}_6\text{F}_4)_2^+$ , and  $\text{C}_{12}\text{F}_7^+$  respectively. Although the reaction scheme:

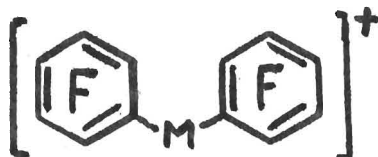


explains the loss of  $\text{MF}_2$  from  $(\text{C}_6\text{F}_5)_2\text{M}^+$  to give  $(\text{C}_6\text{F}_4)_2^+$ , the structure VII is perhaps less suitable for explaining the loss of  $\text{MF}$  and  $\text{MF}_3$  radicals. There was no evidence that ions of the types VIII and IX.



play an important role in the fragmentation routes of these compounds, even if they are formed at all. Their hydrogenic analogues however are very important in the mass spectra of the trisphenyl derivatives of Group V. No metastable

transition corresponding to the loss of hexafluorobenzene was found, although the ion  $C_6F_6^+$  was observed, and is again in marked contrast to the phenyl derivatives of Group V, where the loss of benzene is observed in the mass spectrum of  $Ph_3P$  (67). The ~~alternative~~ formulation of ion VII as



is more suitable in explaining the formation of  $C_6F_5MF^+$  species although this is perhaps less suitable in explaining the loss of metal fluoride radicals.

The other fluorocarbon peaks are due to the further fragmentation of the fluoroaromatic ions  $C_{12}F_9^+$ ,  $(C_6F_4)_2^+$ , and  $C_{12}F_7^+$  by typical loss of  $C_6F_4$ ,  $C_5F_3$ ,  $CF_2$ ,  $CF$ , and  $F$  radicals.

The loss of  $CF_3$  is not observed in these compounds and appears to be generally quite a rare phenomenon, although it has been shown to be eliminated from  $C_6F_6^+$  by the appropriate metastable ion (99). The similarity of the fragmentation patterns leading to the fluorocarbons accounts for the great similarity in the abundances of the latter in all three compounds. However, the abundance of the peak due to  $(C_6F_4)_2^+$  shows a maximum at arsenic (10.5%) while that due to  $C_{12}F_7^+$  shows a gradual rise on descending the series. This may be due to the preferential splitting out of  $AsF_2$  by ar-



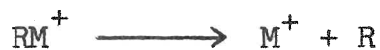
senic instead of  $\text{AsF}_3$ , because as noted above the abundances of the  $(\text{C}_6\text{F}_5)_2\text{M}^+$  peaks do not show a similar maximum. It is noticed that the abundance of the peak due to  $\text{C}_{12}\text{F}_7^+$  which arises from the loss of  $\text{MF}_3$  from  $(\text{C}_6\text{F}_5)_2\text{M}^+$  increases in a regular fashion and may be due to the tendency of the heavier metals to form the neutral metal trifluoride rather than the metal difluoride radical. The lower molecular weight fluorocarbon ions  $\text{C}_x\text{F}_y^+$  ( $x = 1-6$   $y = 3-5$ ) also show a maximum at arsenic and therefore must arise from the fragmentation of the  $\text{C}_6\text{F}_5\text{MX}^+$  and  $\text{C}_6\text{F}_5\text{M}^+$  ( $\text{M} = \text{As}$  or  $\text{Sb}$ ) by loss of the radicals of  $\text{MF}_2$  and  $\text{MF}$ . The loss of a  $\text{C}_6\text{F}_3$  radical from the ion  $\text{C}_6\text{F}_5\text{M}^+$  to give the ion  $\text{MF}_2^+$  is observed in the arsenic derivative. Phosphorus on the other hand shows only a small amount of  $\text{PF}_2^+$  (about 0.2% abundance) and is shown by the appropriate metastable (Table 7) to lose a phosphorus atom from  $\text{C}_6\text{F}_5\text{P}^+$  to give  $\text{C}_6\text{F}_5^+$  which then fragments further by loss of  $\text{CF}_2$ ,  $\text{F}$  and  $\text{F}_2$  to give lower molecular weight fluorocarbons. The total percentage of the ion current carried by fluorocarbon fragments also shows a rise at arsenic and a corresponding fall in the total percentage of the ion current carried by metal-containing ions (Table 6). Miller (10) found that the sum of the metal fluorocarbon containing ions in Group IV tetrakis (pentafluorophenyl) compounds show a maximum at germanium, but the total metal-containing ions peaked at lead. Again there are few similarities between the pentafluorophenyl derivatives of Group V and Group IV besides the loss of a metal fluoride species.

In Group IV the spectra become progressively simpler as one descends the group, the intensities of the ions falling in a regular fashion, except those due to  $C_6F_5M^+$ ,  $(C_6F_5)_3M^+$ , and  $MF_2^+$  which show a rise. The spectrum of  $(C_6F_5)_4Si$  shows peaks that are due to partial fragmentation of the aromatic ring and which contain a metal atom. Comparable peaks were not observed for the Group V derivatives although the rise in the abundance of the peak due to  $C_6F_5M^+$  is in a way similar to Group IV where it is absent for Si and Ge derivatives and is some 15 times stronger for lead than for tin.

As for the tris(phenyl) derivatives of Group V fragmentation occurs from both even and odd electron ions to an equal extent but there appears to be a change of the type of reaction:



found in the phosphine to the reaction:



found in the case of arsenic and antimony derivatives as shown by the appearance of a bare metal ion in the  $(C_6F_5)_3Sb$  spectrum.

A mechanism has been proposed by Cavell and Dobbie (73) to explain the observed fluorine migration in some trifluoromethyl derivatives of arsenic and phosphorus, these not being observed in the analogous nitrogen compounds. The explanation is that during the migration of the fluorine, the non bonding

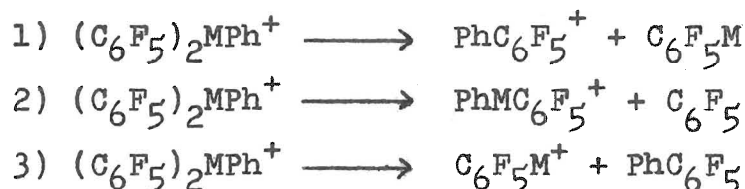
p orbitals on the fluorine interact with the vacant d orbitals on the central metal atom. Nitrogen lacks these orbitals, so fluorine migration is rendered difficult. This is also applicable to Group IV derivatives, for it has been shown (10) that the compounds  $(C_6F_5)_3COH$  and  $(C_6F_5)_2CO$  give no evidence of fluorine transfer to the central carbon atom, although transfer of one to three fluorine atoms observed for the other tetrakis(pentafluorophenyl) derivatives of Group IV (10). Simultaneous migration of up to two or three fluorines has also been observed (9, 73, 74) in many of the other compounds studied. Similar explanations involving d orbitals thus seem applicable for the pentafluorophenyl derivatives of Group V. Hawthorne Simpson and Mays (75, 76) have suggested that where there are unsaturated or  $\pi$ -bonded organic ligands present, these become  $\pi$ -bonded to the metal during fragmentation. This is perhaps preferable in explaining fluorine migration in aryl transition metal complexes. Studies on ortho meta and para fluorophenyl derivatives of transition metals show that ortho migration is the most preferred. Reactions of this type will give rise to  $C_6F_5MF_2^+$  and  $(C_6F_5)_2MF^+$  species as observed for Group IV derivatives and to the species  $C_6F_5MF^+$  observed in Group V but is less satisfactory in explaining the formation of metal fluorides and perfluorophenylenes.

It is of interest to note that in all three compounds there is a significant peak at m/e 168 due to  $C_6F_5H$ . The intensity of this can vary up to over three times the inten-

sity of the peak at  $m/e$  167 due to  $C_6F_5^+$ . Similar peaks have been found in other non hydrogen containing compounds (7) and are presumed to arise from an ion molecule reaction between  $C_6F_5^+$  and some hydrogen containing species present in the mass spectrometer, most probably water vapour.

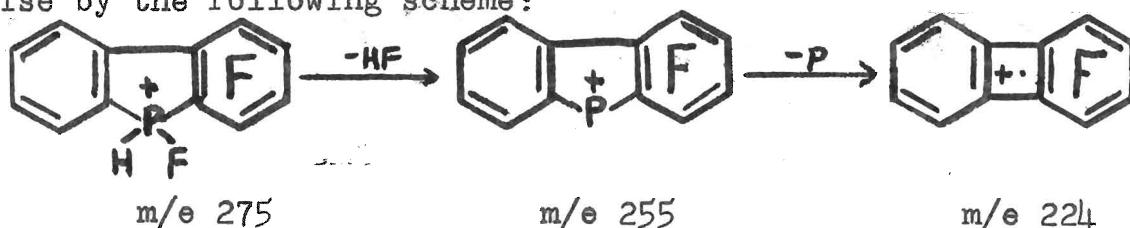
# Bis(pentafluorophenyl) phenyl Derivatives

In these compounds there is now a competition between the fragmentation modes



although the appropriate metastables were not always observed. The fragmentation patterns are presented in Figures 18, 19, and 20 and the spectra in Figures 9, 10, and 11.

For the phosphorus compound all three modes are shown to be equally likely, there being some slight preference on examination of the ion intensities for routes 2 and 3. Tetrafluorobiphenylene ions  $\text{C}_6\text{F}_4\text{C}_6\text{H}_4^+$  are also observed and could arise by the following scheme:



and also by the loss of HF from  $\text{PhC}_6\text{F}_5^+$ . The relevant metastable transitions are shown in Table 7 and processes similar to this can be postulated for the arsenic and antimony derivatives. The ion  $\text{PhPC}_6\text{F}_5^+$  can also fragment as shown in Figure 18 to give the ions  $\text{Ph}^+$ ,  $\text{PhP}^+$ , and  $\text{PhPF}^+$  the latter two ions losing H and HF respectively to give  $\text{C}_6\text{H}_4\text{P}^+$ . The arsenic and antimony derivatives are presumed to give analogous fragmentation patterns to this.

The production of the purely aromatic fluorocarbon species is via loss of phenyl from the parent ion to give  $(C_6F_5)_2M^+$  or in the case of phosphorus and arsenic by the metastable supported loss of  $PhC_6F_5$  from the parent ion to give  $C_6F_5M^+$ . These species then fragment according to that described above for the tris(pentafluorophenyl) derivatives by loss of  $C_6F_4$ ,  $MF_2$ , and  $MF_3$  etc. The fragments formed thus are generally of low intensity and show no metastable by which one can determine the unambiguous fragmentation pattern. There are no major peaks due to a fluorocarbon species containing more than six carbon atoms except for the octa-fluorobiphenylene ion and  $C_{12}F_7^+$  which only appears in the case of the antimony derivative. The absence of higher molecular weight fluorocarbon ions is explained by noting that route 3) is the dominant pathway, that leading to the formation of  $(C_6F_5)_2M^+$  playing a minor role.

The effect of the central atom in these compounds is slight but noted characteristics are the uniform decrease in the molecular ion intensity from phosphorus to antimony and a similar increase in  $C_6F_5M^+$  species. The phosphorus compound shows loss of a proton or fluorine, to be important modes while the arsenic derivatives only shows loss of a proton, and the antimony derivative shows neither. However, this may be due to the weakening in intensity of the molecular ion. The M - F ion for the phosphorus derivative also showed loss of a  $C_6F_5$  radical to give the ion  $C_6F_4PPh^+$ .

The increase in the abundance of the  $C_6F_5M^+$  species and the weakening of the carbon-metal bond in preference for a metal fluorine bond is shown by the appearance of  $MF_2^+$  in the arsine and of  $MF_2^+$ ,  $MF^+$  and  $M^+$  species for the stibine.

Appropriate metastable transitions show that in this case they are formed by loss of a  $C_6F_4$  radical from the ions  $C_6F_5SbF^+$  and  $C_6F_5Sb^+$ . These transitions were not observed in the mass spectrum of  $(C_6F_5)_3Sb$ . There is no metastable evidence for the formation of tetrafluorobiphenylene in the stibine as was found for the phosphorus and arsenic derivatives but the loss of HF from  $PhSbC_6F_5^+$  was noted to give  $C_6F_4SbC_6H_4^+$  which then presumably further loses Sb to give  $C_6F_4C_6H_4^+$ .

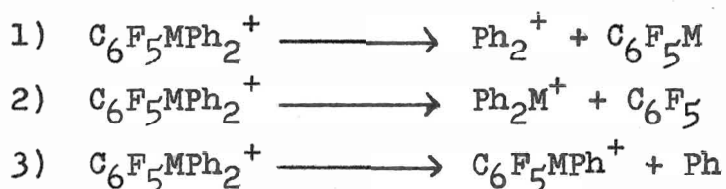
In addition there are small peaks at m/e 186 and m/e 206 present in all these compounds, the peak at m/e 186 being due to presumably  $C_6F_6^+$  ion. However, only the mass spectrum of  $(C_6F_5)_3Sb$  shows a significant peak at m/e 186, these being almost completely absent in the case of tris(pentafluorophenyl) arsenic and phosphorus. Since the abundance of  $C_6F_5^+$  is in all pentafluorophenyl compounds studied extremely low, it would seem that the abundances of  $C_6F_5^+$  and  $C_6F_6^+$  are not related to each other and that  $C_6F_6^+$  could possibly arise from the scavenging of a fluorine atom by the pentafluorophenyl ion by a mechanism that is enhanced by the presence of a phenyl group in the molecular ion.

The ion at  $m/e$  206 which is quite abundant in  $(C_6F_5)_2PPh$  could be formulated as  $C_6F_7H^+$  in which it is possible that a molecule of HF is added across the double bonds in hexafluorobenzene.



Diphenyl Pentafluorophenyl Phosphine and Arisine

The major routes of fragmentation shown in Figures 16 and 17 are comparable in both compounds and can be classed into the three reactions:



although not all the appropriate metastable transitions were observed. The mass spectra are shown in Figures 7 and 8. Only the phosphorus derivative shows the metastable supported loss of a proton and a fluorine atom. The M-F ion then shows further loss of benzene to give the tetrafluorophosphafluor-enyl ion  $\text{C}_6\text{F}_4\text{PC}_6\text{H}_4^+$ . The parent ion  $\text{Ph}_2\text{PC}_6\text{F}_5^+$  also loses pentafluorobenzene to give the ion  $\text{PhPC}_6\text{H}_4^+$ , (structure VI p83) while that of the arsenic derivative shows the simultaneous loss of Ph and HF to give the ion  $\text{C}_6\text{F}_4\text{AsC}_6\text{H}_4^+$ . Ions of the type  $\text{C}_6\text{F}_4\text{MC}_6\text{H}_4^+$  arise by loss of HF from  $\text{C}_6\text{F}_5\text{MPh}^+$  which then further fragment by loss of M to give the tetrafluoro-biphenylene ion  $\text{C}_6\text{F}_4\text{C}_6\text{H}_4^+$ . This is supported by the appropriate metastable transitions for both compounds, the phosphorus derivative also showing that these reactions can also occur in a single step. The formation of  $\text{Ph}_2^+$  by route 1 is the predominant pathway and this in turn can lose  $\text{H}_2$  to give the biphenylene ion  $(\text{C}_6\text{H}_4)_2^+$  which is also formed by loss of M from  $(\text{C}_6\text{H}_4)_2\text{M}^+$ . This reaction is metastable supported as is

the loss of  $H_2$  from the ion  $Ph_2M^+$  to give an ion of the type  $(C_6H_4)_2M^+$ . The metastable peaks in the spectra of the arsenic derivatives also showed that the ion  $Ph_2As^+$  could lose As and Ph directly to form the ions  $Ph_2^+$  and  $PhAs^+$ . The loss of  $C_6H_4$  from  $(C_6H_4)_2As^+$  was also supported by the appropriate metastable. These transitions were not observed in the spectrum of  $Ph_3As$  nor were they found for the phosphorus derivative.

Small amounts of the fluorocarbon ions  $C_6F_2^+$  and  $C_6F_3^+$  were found and are presumed to arise by the loss of  $MF_3$  and  $MF_2$  species from the ion  $C_6F_5M^+$ , which in turn is formed by the loss of biphenyl from the parent ion, although these transitions were not metastable supported. The ion  $PhMC_6F_5^+$  also fragments by loss of  $C_6F_5M$ ,  $C_6F_5$  and  $C_6F_4$  to give the ions  $Ph^+$ ,  $PhM^+$  and  $PhMF^+$ , the latter losing HF to give  $C_6H_4M^+$ , which also arises by loss of H from  $PhM^+$ .

The major mode of fragmentation is by route 1 and in the case of the arsenic derivative comes almost a third of the total ion current. This compound gives an unusually large amount of the ion  $PhC_6F_5^+$ , presumably by loss of PhAs from the parent ion. The spectra of these two compounds are otherwise very comparable, the only large increase is in the abundance of  $Ph_2^+$  ion and in the ions derived from this.

The spectra of these mixed compounds appears to be

dominated mainly by the nature of the central atom and not by the substituent groups. The increasingly electropositive nature of the central atom is shown by an accompanying increase in the amount of fluorine migration observed as one descends the group and also by the preference of the heavier central atoms to remain attached to the pentafluorophenyl group than to the phenyl group due to the greater electronegativity of the former.

Thus, for the bis(pentafluorophenyl) phenyl derivatives the main fragmentation mode is by the metastable supported loss of  $\text{PhC}_6\text{F}_5$  to give  $\text{C}_6\text{F}_5\text{M}^+$  the abundance of which rises rapidly from the phosphorus to arsenic. The diphenyl pentafluorophenyl compounds show that loss of the radical  $\text{C}_6\text{F}_5\text{M}$  is now the important mode to give  $\text{Ph}_2^+$ . Even though the mass spectrum of  $\text{Ph}_2\text{SbC}_6\text{F}_5$  was not obtained it is probable that this would be very similar to that of the arsenic derivative and show a very large abundance of  $\text{Ph}_2^+$ , indicating that the pentafluorophenyl group prefers to remain attached to the more electropositive antimony than to arsenic or phosphorus. This may also be reflected in the abundances of the molecular ions which show a regular decrease on descending the group and hence a greater increase in the probability of fragmentation.

### Low Voltage Spectra

The spectra of some of the above compounds were obtained at 16 to 20 ev. in order to observe the major mode of fragmentations and to obtain an indication of the order of magnitude of the appearance potential of some of the ions.

Although the spectra were only counted in an approximate fashion by comparison with those obtained at 70 ev. and the ion intensities were not accurately measured, they showed that for the tris compounds  $R_3M^+$  ( $R = Ph, C_6F_5, M = P, As, or Sb$ ) the molecular ion was in all cases the strongest. Other peaks were due to  $R_2M^+$  and  $RM^+$ . There were no other significant peaks, for even in the case of  $(C_6F_5)_3As$  and  $(C_6F_5)_3Sb$  the very strong peaks due to  $MF_2^+$ ,  $(C_6F_4)_2^+$  and  $C_6F_5MF^+$  observed at 70 ev. had but almost disappeared, but are just evident in the mass spectra of  $(C_6F_5)_3Sb$  at 20 ev.

The mixed derivatives also showed their base peak to be the molecular ion except in the case of  $Ph_2AsC_6F_5$  where the peak due to  $Ph_2^+$  is the base peak. The other significant peaks all contain the central atom and for the compounds  $(C_6F_5)_2MPh$  show the characteristic peaks due to  $PhMC_6F_5^+$  and  $C_6F_5M^+$  and those for  $C_6F_5MPh_2$  showed peaks due to  $Ph_2^+$  and  $PhM^+$ . Other than the peak due to  $Ph_2^+$  there are no significant non-metal containing ions in these spectra. Also although there were very small peaks due to  $C_6H_6^+$  and  $C_6F_5H^+$ .

Some clastograms of percentage ion current plotted against voltage were initially obtained at the start of this work. The spectra of each compound was recorded in decreasing steps of 5 ev. from 70 ev. until 10 ev. or until no further peaks were seen. The plotted curves showed from their shapes a fragmentation pattern that was judged to be too complex for further investigation by this method and was not further pursued. In addition, the errors were quite large and not even a good indication of the appearance potential of any ion could be obtained. Such clastograms have, however, been used to yield information regarding the probability and rates of various fragmentations in a number of simpler molecules. (40)

Appearance Potentials: Some Methods of Determination

The first true or adiabatic ionisation potential of a molecule is by definition the energy difference between the ground vibrational level of the lowest electronic state of the molecule and the ground vibrational level of the molecular ion. If, however, the potential energy curves for the molecule and molecule ion have minimums at appreciable different internuclear distances the turning point for the v=0 level of the molecule may be outside the effective Franck-Condon region for the molecule, in which case the 0-0 transition and consequently the adiabatic ionisation would in general not be observed by electron impact methods. Only relatively small displacements are necessary to prevent one from observing the adiabatic ionisation potential, and as a consequence of this, ionisation potentials as determined by electron impact methods are higher than those determined spectroscopically and can be considered to constitute an upper limit to the adiabatic values.

The experimental determination of ionisation and appearance potentials compares the ionisation efficiency curve of the ion under consideration with that of some reference molecule. Most commonly the reference molecule is a noble gas where ionisation potential can be accurately found by other methods and is of nearly the same magnitude as that of the species under study. Some methods of determining the ionisa-

tion potential from the ionisation efficiency curves are discussed.

#### Linear Extrapolation Method

The method of linear extrapolation was introduced by Vought (77) in which the linear portion of the ionisation efficiency curves is extrapolated back to zero ion current, the value of the intercept on the energy axis is the ionisation potential and the comparison of this value to the extrapolated value some standard gives the true ionisation potential of the unknown. For nearly all of the ions whose appearance potential has been measured by this method, the value obtained is higher than those obtained by other means but it does have the advantage of providing an upper limit and is rather simple in its interpretation. Svec and Junk (78) have used the method of ratio extrapolation in which the ionisation efficiency curves for the sample and the calibration gas are simultaneously extrapolated at a constant ratio to the energy axis. The difference between the extrapolated values is then taken as the difference in ionisation potential for the calibrant and sample. This method can only be used where the ionisation efficiency curves are of similar shape.

### Initial Break Method

In this method, the ionisation efficiency curve is extrapolated back to its intersection with the energy axis at which point the ion current is zero. This is not a very satisfactory method for at the foot of the ionisation efficiency curve, the signal to noise ratio is poor and also the ionisation efficiency curve at this point approaches the energy axis nearly asymptotically. This makes the determination of the initial break quite difficult since there is no sharp break actually observed. In addition Wood and Waldron (57) showed that by this method the appearance potential observed is inversely proportional to the pressure in the ion source. However, Field and Franklin (79) and Svec et al (78) have used this method to obtain results that are in close agreement with those found by more elaborate methods.

### Extrapolated Voltage Differences Method

Originally put forward by Warren (79) this method is quite popular and has been found by several workers to give reliable results. In this method the sample and a calibrating gas are admitted to the ion source as an intimate mixture and the ionisation efficiency curves drawn. The ion current scale of either of these two is now arbitrarily adjusted so that the linear portions of the two curves are parallel and the voltage differences  $\Delta V$  for various values



of  $i_t$  determined and plotted on a separate graph. The curve thus obtained is extrapolated to  $V = 0$  and the value of  $\Delta V$  thus obtained is taken as the difference between the appearance potential of the calibrant ion and the sample under study. This has been found to give reliable results for the determination of ionisation and appearance potentials if the peak under study is greater than 3% of the base peak for the extrapolations are made over the range of 0.05 to 2.0% of the 00ev. ion current. As in the vanishing current method this method also gives values of ionisation potentials close to those obtained for true adiabatic processes.

#### Semi Logarithmic Plot Method

Lossing et al (80) found that plots of the logarithm of the ion current versus electron energy of many substances were parallel in the region of 1% of the 50 ev. ion current. Reproducible values of 0.05-0.10 ev. have been obtained and the curves are parallel in the region 2 or 3% to 0.1% of the 50 ev. ion current. By using an intimate mixture of sample and calibrant gas and adjusting the pressure of each so that the ion current of each at 70 ev. is the same, good values can be obtained providing that the ionisation potentials are not too high or the ion intensities and hence the ion currents, too low. In the parallel region the voltage difference between the calibrant gas and the sample gives the value of the ionisation potential.

### Critical Slope Method

From a mathematical treatment by Honig (81) the ionisation potential is found by determining at what voltage a line of slope  $1/2 RT$  or  $2/3 RT$  becomes a tangent to the curve obtained on a semi-logarithmic plot.  $R$  is the Boltzmann constant and  $T$  the absolute temperature. This is not as satisfactory as the Warren method but gives fairly reproducible results for the determination of many different appearance potentials.

### Energy Compensation Technique

Developed by Kiser and Gallegos (82) the technique is based on the concept of the logarithmic plot method described above and being instrumental in nature eliminates the necessity of obtaining a complete ionisation curve in the determination of ionisation and appearance potentials. The ion currents of the calibrating gas and the gas being studied are measured at 50 ev. and recorded on separate channels of a dual channel recorder. The sensitivities of each channel are now increased to some convenient factor between 100 and 1000 and the electron energy decreased until the apparent recorded ion intensity is the same for each ion as it was at 50 ev. The difference in voltage required to accomplish this for the standard and unknown is taken as the difference in the appearance potentials of the calibrating gas and the sample.

### Retarding Potential Difference Method

Fox et al (83) have devised a very accurate method of determining appearance potentials using retarding potential differences and a modified ion source. By a suitable arrangement of grids and by applying the current voltages the energy spread in the electron beam is kept to an absolute minimum. An additional spread in energy caused by the ion source not being an equipotential volume is removed by a pulsing voltage so that ions are formed in a field free region. Using this method the errors are to within  $\pm 0.05$  v, and although it was originally applied to a magnetic mass spectrometer, Melton and Hamil (84) have successfully applied it to a pulsed linear time-of-flight spectrometer.

### Recording of Data

The determination of appearance potentials by manual readout from a conventional ion source is a tedious process, and has lead to some modifications of mass spectrometers such that fast determinations of ionisation efficiency curves can be made. The first of these (85) is for use with an M.S.9 mass spectrometer with just a peak switching facility normally used for precise mass measurements. This enables two peaks of different  $m/e$  to be displayed alternately in the oscilloscope by automatic switching of the ion accelerating voltage at constant magnetic field. The circuit is devised

so that after a display of the sample and calibrant gas the electron beam energy is reduced by 0.05 ev. and the trace recorded on the mass spectrometer recorder. The stepping motor is activated every 4 seconds so that rapid recording of ionisation curves can be made. The monitored peaks are made equal at approximately 30 ev., and it assumed that this equality persists down to the threshold voltage. Sample pressures are adjusted so that the linear portions of the ionisation efficiency curves are parallel and the multiplier gain adjusted so that these are as vertical as possible. Values of the appearance potential may be obtained from methods described above.

Davidson et al (50) have found this method to be rapid and simple although it violates the condition that the electrostatic fields in the ion source should be held constant during appearance potential measurements. However, good results can be obtained if the mass ratio of the two peaks is less than 1.7 and differ in appearance potential by less than 1.3 v. The other type of modification is for use with a pulsed time-of-flight mass spectrometer (86) which takes advantage of the multiple analogue output system. The chart drive of a two pen recorder can be synchronised with the continuously decreasing electron energy. A start-stop timer is used to simultaneously energise the chart drive and electron energy control, whose potentiometer was rotated by a synchronous motor mechanically coupled to the potentiometer

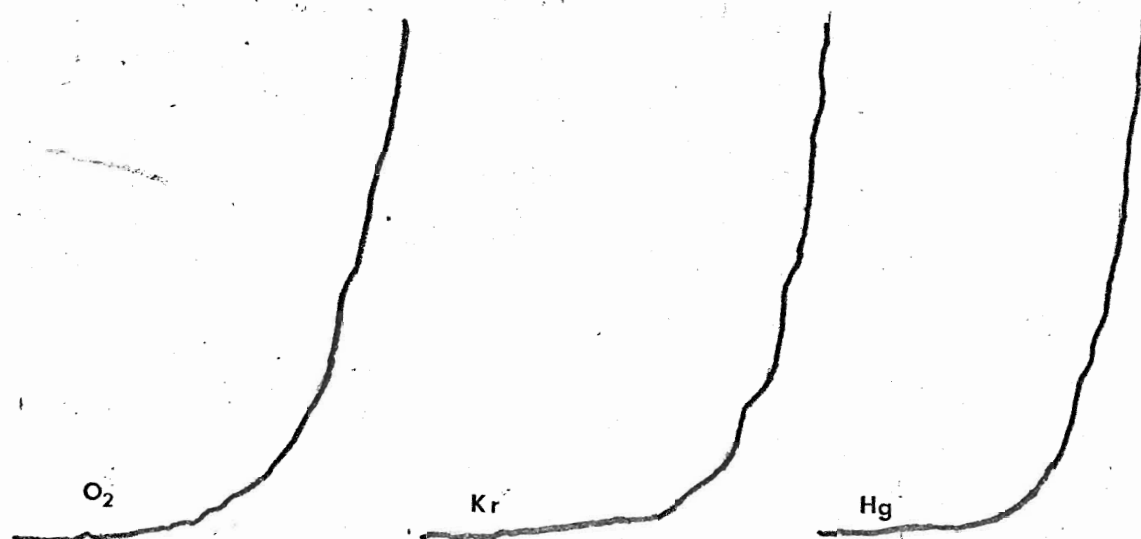
through a gear rack. The ionisation efficiency curves of the sample and standard can then be obtained simultaneously in less than 2 minutes.

### Discussion of Appearance Potential Results

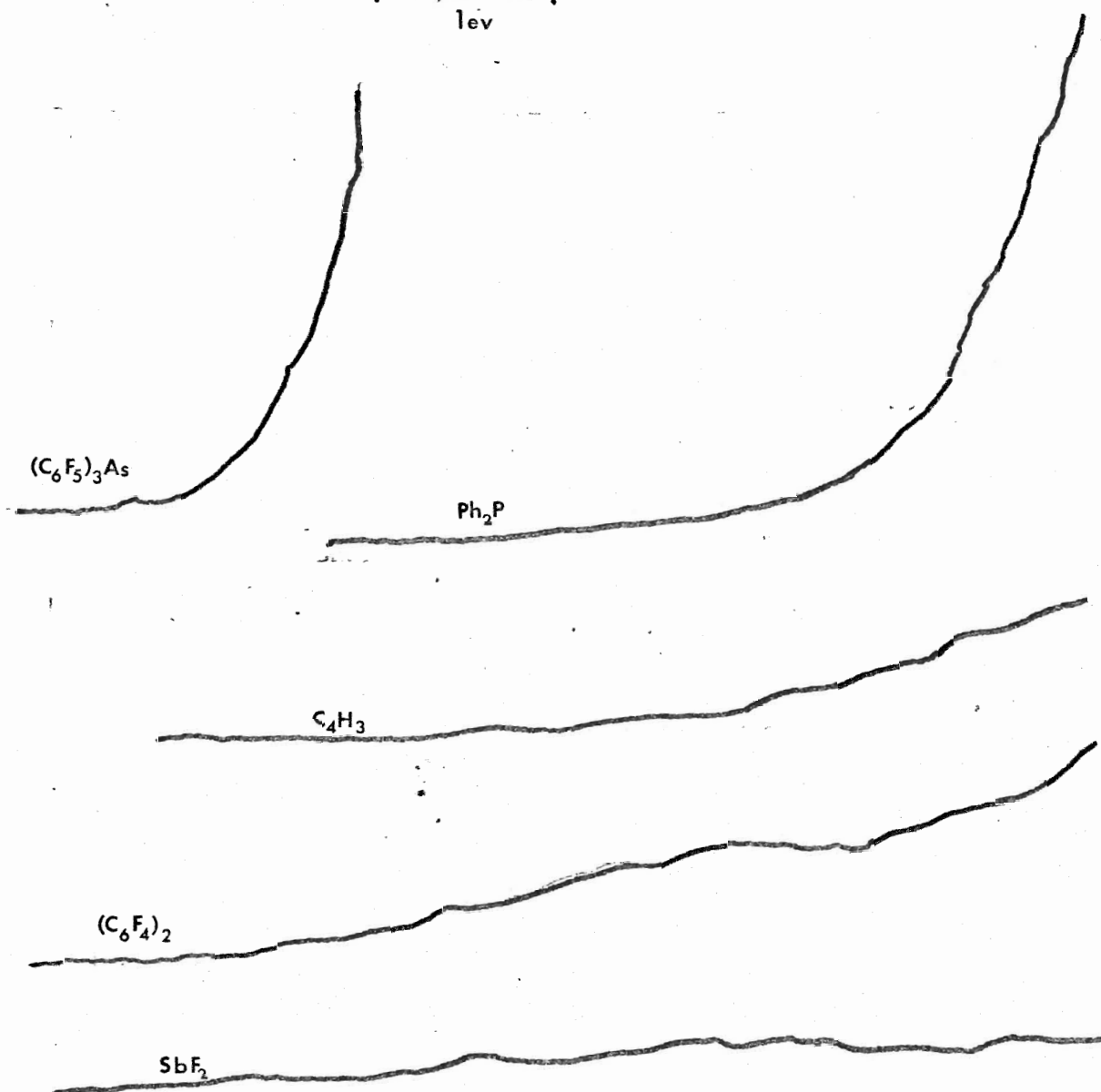
Due to the method of determination and some of the difficulties encountered in determining the appearance potentials of some of the ions, the values quoted are not to be taken as absolute, and could be in error by up to one to two volts. Ions that gave similar curves to that obtained for the standards are shown in Table 8 (A). The values in Tables 8 (B) and (C) are for those ions that gave poor ionisation efficiency curves due to either low abundance or as was usually the case from a mode of fragmentation that could involve several pathways.

Some typical ionisation efficiency curves are shown in Figure 21. It can be seen that the standards and the molecular ions gave curves that become nearly vertical at 2 volts above the value taken the initial break. The major ions  $R_2M^+$  and  $RM^+$  showed a tailing effect of 1-2 volts after the appearance of the ion and before the curve rose rapidly upward. Fragment ions that could possibly arise from several pathways showed shallow curves with no indication of where the true initial break was actually occurring. In addition, for meaningful results to be obtained in these studies it is necessary to assume that there is no excess energy involved in the fragmentation. Morrison (87) has shown that extensive tailing of the ionisation efficiency curve shows evidence for the presence of excess energies.

Figure 21: Some Typical Ionisation Efficiency Curves



1ev





1ev

$C_6F_5PF$

$C_6F_5Sb$

$C_{12}F_7$

$(C_6F_5)_2PPh$

$PhSb$

$Ph_3Sb$

$(C_6H_4)_2Sb$

$C_6H_4As$

$(C_6F_5)_2AsPh$

Table 8. Appearance Potentials in e.v.

(A) Parent Ions and ions  $R_2M^+$  and  $RM^+$  ( $R = C_6F_5, Ph$ )

Compound	Parent <sup>+</sup>	$Ph_2M^+$	$PhM^+$	$(C_6F_5)_2M^+$	$C_6F_5M^+$
$Ph_3P$	8.4±0.1	12.9±0.1	12.8±0.3		
$Ph_3As$	8.7±0.1	13.1±0.2	12.8±0.2		
$Ph_3Sb$	8.5±0.2	13.0±0.2	9.6±0.2		
$(C_6F_5)_3P$	9.9±0.1			13.9±0.2	11.7±0.3
$(C_6F_5)_3As$	9.9±0.1			14.7±0.1	14.0±0.2
$(C_6F_5)_3Sb$	10.6±0.1			15.0±0.2	13.3±0.2
$Ph_2PC_6F_5$	8.9±0.1	~ 15.3	~ 14.0		
$Ph_2AsC_6F_5$	7.9±0.1	10.7±0.1	10.2±0.2		11.5±0.2
$PhP(C_6F_5)_2$	9.5±0.1				12.3±0.2
$PhAs(C_6F_5)_2$	8.8±0.2				11.4±0.1
$PhSb(C_6F_5)_2$					12.0±0.3
$(C_6F_5)_4P_2$	9.4±0.1			10.8±0.2	12.7±0.2

Compound	$PhMC_6F_5$
$Ph_2PC_6F_5$	~ 13.3
$Ph_2AsC_6F_5$	13.0±0.1
$PhP(C_6F_5)_2$	15.1±0.2
$PhAs(C_6F_5)_2$	13.5±0.2

~ no standard deviation assigned as curve showed no initial break

(B) Metal Containing Fragment Ions

Compound	Parent $F^+$	$(C_6H_5)_2M^+$	$C_6H_5M^+$	$C_6F_5MF^+$	$PhMF^+$
$Ph_3P$		$14.0 \pm 0.2$	$16.3 \pm 0.9$		
$Ph_3As$		$12.8 \pm 0.2$			
$Ph_3Sb$		$13.2 \pm 0.2$			
$(C_6F_5)_3P$	$10.3 \pm 0.2$			$16.2 \pm 0.2$	
$(C_6F_5)_3As$	$11.1 \pm 0.1$			$14.1 \pm 0.2$	
$(C_6F_5)_3Sb$	$12.5 \pm 0.2$			$13.9 \pm 0.3$	
$Ph_2PC_6F_5$	$11.6 \pm 0.2$	$\sim 14.0$			$\sim 14.3$
$Ph_2AsC_6F_5$		$\sim 13.0$			$\sim 11.9$
$PhP(C_6F_5)_2$			$20.0 \pm 0.2$		$18.0 \pm 0.3$
$PhAs(C_6F_5)_2$			$13.7 \pm 0.3$	$12.7 \pm 0.2$	$20.3$

Compound	$C_6F_5MC_6H_5^+$	$MF_2^+$
$(C_6F_5)_3As$		$\sim 16.0$
$(C_6F_5)_3Sb$		$\sim 17.5$
$Ph_2PC_6F_5$	$\sim 13.7$	
$Ph_2AsC_6F_5$	$\sim 10.9$	
$PhP(C_6F_5)_2$	$17.4 \pm 0.2$	
$PhAs(C_6F_5)_2$	$12.3 \pm 0.2$	

(C) Non-metal Containing Fragment Ions

Compound	$\text{PhC}_6\text{F}_5^+$	$\text{C}_6\text{F}_4\text{C}_6\text{H}_4^+$	$(\text{C}_6\text{F}_4)_2^+$	$\text{Ph}_2^+$
$\text{Ph}_3\text{P}$				
$\text{Ph}_3\text{As}$				$11.7 \pm 0.4$
$\text{Ph}_3\text{Sb}$				$11.9 \pm 0.2$
$(\text{C}_6\text{F}_5)_3\text{P}$			$12.0 \pm 0.3$	
$(\text{C}_6\text{F}_5)_3\text{As}$			$14.6 \pm 0.3$	
$(\text{C}_6\text{F}_5)_3\text{Sb}$			$12.9 \pm 0.3$	
$\text{Ph}_2\text{PC}_6\text{F}_5$				$12.6 \pm 0.2$
$\text{Ph}_2\text{AsC}_6\text{F}_5$	$11.4 \pm 0.2$			$9.5 \pm 0.1$
$\text{PhP}(\text{C}_6\text{F}_5)_2$	$13.9 \pm 0.3$	$18.3 \pm 0.2$	$12.0 \pm 0.2$	
$\text{PhAs}(\text{C}_6\text{F}_5)_2$	$11.7 \pm 0.2$	$\sim 21.3$		
$\text{PhSb}(\text{C}_6\text{F}_5)_2$				

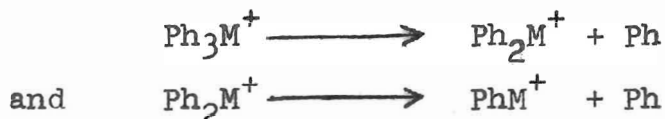
  

Compound	$\text{Ph}^+$	$\text{C}_4\text{H}_3^+$	$(\text{C}_6\text{H}_4)_2^+$	$\text{C}_{12}\text{F}_7^+$	$\text{C}_6\text{F}_3^+$
$\text{Ph}_3\text{Sb}$	$\sim 18.0$	$\sim 21.5$	$\sim 16.0$		
$(\text{C}_6\text{F}_5)_3\text{P}$					$16.6 \pm 0.5$
$(\text{C}_6\text{F}_5)_3\text{As}$				$14.8 \pm 0.3$	$16.2 \pm 0.3$
$(\text{C}_6\text{F}_5)_3\text{Sb}$				$17.8 \pm 0.3$	
$\text{Ph}_2\text{AsC}_6\text{F}_5$	$14.4 \pm 0.2$	$21.0 \pm 0.3$			
$\text{PhP}(\text{C}_6\text{F}_5)_2$	$15.6 \pm 0.3$	$20.2 \pm 0.3$			$19.1 \pm 0.3$
$\text{PhAs}(\text{C}_6\text{F}_5)_2$	$15.7 \pm 0.2$	$\sim 22.7$			
$\text{PhSb}(\text{C}_6\text{F}_5)_2$	$15.4 \pm 0.3$	$\sim 20.5$			

Stevenson (88) in a study of some alkyl compounds showed that if in the fragmentation scheme



the ionisation potential of  $R_1^+$  is less than that of  $R_2$ , then no excess energy is involved. This has also been found to hold for some organo stannanes (22) but in the compounds studied here, the appearance potentials of the  $R_2M^+$  species are of the order of 5 ev greater those found for  $R_3Sn^+$  species. Assuming a value of the mean bond dissociation energy for Ph-P to be 3.0 ev, Ph-As and Ph-Sb to be 2.6 ev (8,9) the ionisation potential of the  $Ph_2M^+$  species is found to be about 10 ev which is greater than the most reliable value for the ionisation potential of the phenyl radical (9.4 ev) (4). Thus it appears that there is excess energy involved in the dissociation



The ionisation efficiency curves of  $Ph_2M^+$  and  $PhM^+$  species tended to show extensive tailing and the high abundance of  $R^+$  and  $R_2^+$  species when compared to similar Group IV derivative supports the above hypothesis. Similarly although the bond dissociation energies of  $(C_6F_5)_3M$  compounds are not known, they can be assumed to be almost equal to those of  $Ph_3M$ . The ionisation potential of the pentafluorophenyl radical has been found to be equal to that of the phenyl radical (5) and since  $AP(Ph_2M) < AP(\text{[}C_6F_5\text{]}_2M)$  one would expect that

excess energy is involved here on successive loss of a  $C_6F_5$  group.

The heats of formation of the pentafluorophenyl derivatives are not known, nor can they be reliably calculated since recent experimental determinations on some simple pentafluorobenzene derivatives (90) show that the values obtained are lower than those calculated by as much as 40 Kcal/mole. This is thought to be caused by an unknown variation of the C-F bond strengths around the aromatic ring.

From the known heats of formation of  $Ph_3P$  and  $Ph_3As$  in the gas phase for which the most reliable values are + 72.4 Kcal/mole for  $Ph_3P$  (91) and + 92 Kcal/mole for  $Ph_3As$  (92) the heat of formation of the ion  $R_3M^+$  is found to be  $11.5 \pm 0.2$  ev for  $Ph_3P^+$  and  $12.7 \pm 0.2$  for  $Ph_3As^+$ . These values in themselves are not significant and they cannot be used to derive the heat of formation for the ions  $R_2M^+$  and  $RM^+$  since there is no way of estimating the excess energy involved. Thus the results are thus only discussed in a relative way and are not judged to be conclusive.

The appearance potentials which equal the ionisation potentials of the molecular ions shown in Table 8 A demonstrate a gentle increase with the number of pentafluorophenyl groups in the molecule. This is a similar trend to that observed by Cullen and Frost (55) and is shown quite clearly in

the case of phosphorus, but not so well in the case of arsenic, the value obtained for  $\text{Ph}_2\text{AsC}_6\text{F}_5$  being lower than that for  $\text{Ph}_3\text{As}$ . Only the values for the antimony species  $\text{Ph}_3\text{Sb}$  and  $(\text{C}_6\text{F}_5)_3\text{Sb}$  were obtained, the molecular ion for  $\text{PhSb}(\text{C}_6\text{F}_5)_2$  being of such low abundance (4.5% relative intensity) that no measurement of its appearance potential could be made. The ionisation potential of  $(\text{C}_6\text{F}_5)_4\text{P}_2$  (9.4 eV) is slightly lower than that of  $(\text{C}_6\text{F}_5)_3\text{P}$ . Its mass spectrum was in agreement with that reported by Miller (9).

The explanation for the trend is that in these cases the primary ionisation is by removal of the electron from the substituent group and not from the metal as there is no large variation on changing the central atom. The ionisation potential of these central atoms (P 10.5, As 9.8 and Sb 8.6 (93) ) show a quite appreciable variation and if the electron was removed from the p-orbital on the metal this should be evident in the ionisation potential of these molecules regardless of the substituent groups.

The photoionisation potentials of the series  $\text{Ph}_3\text{M}$  (M = N, P, As, Sb and Bi) have been measured by Vilesov and Zaitsev (94). The ionisation potential for triphenylamine is the lowest value in the series despite the fact that the ionisation potential of nitrogen is the greatest. There is however a correlation between the observed ionisation potential and the absorption spectra for these molecules and they can

be explained by assuming that the measured adiabatic ionisation potentials will correspond to transitions from non planar molecules to planar ions. The ion  $\text{NR}_3^+$  is known to be planar, as distinct from the pyramidal structure of the unionised species. In the other Group V derivatives the presence of d orbitals on the central atom may undergo p-d hybridisation and cause the pyramidal structure to be evident still for the ion  $\text{R}_3\text{M}^+$ . These authors conclude that in Group V derivatives other than nitrogen the electron removed by ionisation is from the central atom since the photoionisation curves indicate an indirect transition is occurring and is more in keeping with the ion still retaining its pyramidal structure.

However, it is suggested in this work that the removal of the electron from the lone pair on the metal would decrease repulsion effect of this lone pair and cause the ion to become more planar. The errors given by the Russians are not small enough to confidently support the trend reported and although the values reported here are 1 eV greater than theirs, and can be considered approximately constant (within possible error of 0.3 eV). The variation between the values reported by the two methods is not uncommon since photoionisation potentials on some metal carbonyls show that the latter values are lower to by about 0.5 eV.

It is considered in this work that there is still no evidence that the first ionisation potential is the removal



of an electron from the metal lone pair.

The higher appearance potentials observed for the tris-pentafluorophenyl derivatives also support the hypothesis that the electron is removed from a substituent group. If it was removed from the atom, the appearance potentials would not remain constant since it has been shown that the pentafluorophenyl group is essentially the same as the phenyl group in its bonding properties and behaviour to ionising radiation. (5)

However, an alternative explanation involving electronic interactions may be possible since the electronic spectra of some aryl arsines show an excitation of a non bonding electron from the lone pair to an antibonding  $\pi$  orbital of a phenyl group (95). In two compounds where the configuration around the central atom is the same, the energy difference in the charge transfer bands should be approximately equal to the difference in ionisation potential of the arsenic lone pairs. Aryl compounds containing fluorocarbons show a lower value than that theoretically derived and is attributed to an interaction of the fluorocarbon with the aryl group. This interaction may also be evident in the trends we observe for  $C_6F_5$  derivatives.

It is also seen that for the compounds which give the ions  $Ph_2M^+$  and  $PhM^+$  in abundances high enough to permit a determination of their appearance potential and assuming the

the absence of excess kinetic energy, in no case is the appearance potential of  $\text{PhM}^+$  greater than that of  $\text{Ph}_2\text{M}^+$ . In the compounds  $\text{Ph}_3\text{M}$  the difference between the appearance potential of  $\text{PhM}^+$  minus that of the molecular ion shows a regular decrease in the order  $\text{P} > \text{As} > \text{Sb}$ . The order  $(\text{C}_6\text{F}_5)\text{M}^+ < (\text{C}_6\text{F}_5)_2\text{M}^+ < (\text{C}_6\text{F}_5)_3\text{M}^+$  is also observed for the compounds  $(\text{C}_6\text{F}_5)_3\text{M}$  but no trend is seen. In contrast however the appearance potential of the ions  $(\text{C}_6\text{F}_5)_4\text{P}_2^+$ ,  $(\text{C}_6\text{F}_5)_3\text{P}^+$  and  $(\text{C}_6\text{F}_5)_2\text{P}^+$  derived from tetrakis (pentafluorophenyl) diphosphine are in the order  $(\text{C}_6\text{F}_5)_4\text{P}_2^+ < (\text{C}_6\text{F}_5)_3\text{P}^+ < (\text{C}_6\text{F}_5)_2\text{P}^+$  and demonstrates that the P-P bond, estimated at 50 kcal/mole (96) is much weaker than that of carbon-phosphorus, which has been found to vary between 60-70 kcal/mole (97). Thus in this compound one would expect that the first fragmentation step after initial ionisation would be the symmetrical cleavage of the P-P bond and is accounted for in the observation that for  $(\text{C}_6\text{F}_5)_4\text{P}_2$  the base peak is due to the ion  $(\text{C}_6\text{F}_5)_2\text{P}^+$  (9).

If fragmentation of these compounds is by successive loss of a phenyl group one would expect that the appearance potentials of each ion in turn would show a successive rise. has been observed with the fragment ions derived from  $\text{Mo}(\text{CO})_6$  (98) by successive loss of a neutral CO species. The inference is that the fragmentation modes of these species do not involve a successive loss of a phenyl radical but occur mainly by a loss of neutral biphenyl. This in part explains the observed trend of appearance potentials  $\text{Ph}_3\text{M}^+ < \text{PhM}^+ < \text{Ph}_2\text{M}^+$  and is

further supported by the rapid increase in the abundance of the ion due to  $\text{PhM}^+$  in the compounds  $\text{Ph}_3\text{M}$  on going from phosphorus to antimony. The observed trend in the differences between the appearance potential of  $\text{PhM}^+$  and the parent gives an indication that this process is becoming energetically more favourable in descending the group. The ions  $(\text{C}_6\text{H}_4)_2\text{M}^+$   $\text{C}_6\text{H}_4\text{M}^+$  however have higher appearance potentials than  $\text{Ph}_3\text{M}^+$   $\text{Ph}_2\text{M}^+$  and  $\text{PhM}^+$  and, although no trends are observable, they show that the formation of these species is energetically less favourable as it requires the breaking and reforming of certain bonds. The difference between the appearance potential of the ion  $\text{Ph}_2\text{M}^+$  and the parent ion is constant at 4.4-4.5 eV and that between  $\text{PhMC}_6\text{F}_5^+$  and the parent ion  $\text{Ph}_2\text{MC}_6\text{F}_5^+$  is 4.4 eV. for  $\text{Ph}_2\text{PC}_6\text{F}_5$  and 5.1 for  $\text{Ph}_2\text{AsC}_6\text{F}_5$ . This difference is the bond dissociation energy of the metal-phenyl carbon bond in the ion and, assuming that the value obtained for  $\text{Ph}_2\text{AsC}_6\text{F}_5$  is in error, can be computed to be of the order 101-104 kcal/mole. This value is a little high for a carbon-metal bond, since in the ground state they are normally in the range 40-60 kcal/mole (93) but ionisation may cause an increase in bond order. Values of a similar order of magnitude are obtained from considering the differences in appearance potentials between the ions  $\text{PhMC}_6\text{F}_5^+$  and the parent ion in the compounds  $\text{PhM}(\text{C}_6\text{F}_5)_2$ . The ions  $\text{C}_6\text{F}_5\text{MF}$  show a general decrease from phosphorus to antimony which again might be indicative of a decrease in the metal carbon bond strength of these compounds; lower values showing increasingly favourable energetic dissocia-

tion of  $\text{PhC}_6\text{F}_5$  for the migration of one of the fluorine atom to the central atom. On the other hand the appearance potentials of  $\text{PhMF}^+$  show no regular trend except that those ions observed from  $\text{Ph}_2\text{MC}_6\text{F}_5$  species have lower appearance potentials than those derived from  $\text{PhM}(\text{C}_6\text{F}_5)_2$ , so that the observations on  $\text{C}_6\text{F}_5\text{MF}^+$  ions may be entirely fortuitous.

The ions  $\text{Ph}_2^+$ ,  $\text{Ph}^+$  and  $\text{C}_4\text{H}_3^+$  show a very approximate consistency in the order  $\text{Ph}_2^+ < \text{Ph}^+ < \text{C}_4\text{H}_3^+$  and can be thought to arise by an energetically similar process to each other. The appearance potential of  $\text{Ph}^+$  from benzene has been found to be  $14.5 \pm 0.3$  eV by Dibeler (5) which is of the same order as the values reported here.

In summary, one can say that ions which arise by rearrangement processes such as  $\text{C}_6\text{F}_4\text{C}_6\text{H}_4^+$ ,  $\text{C}_6\text{F}_4\text{MC}_6\text{H}_4^+$  and  $\text{PhMF}^+$  and which require bond formation as well as bond breaking have higher appearance potentials than those which are formed by bond destruction above. The exception is in the case of the formation of  $(\text{C}_6\text{F}_4)_2^+$  which must be particularly favourable energetically.

APPENDIX

Mass Spectra: Tables of Relative Ion Abundances

I	$\text{Ph}_3\text{P}$
II	$\text{Ph}_3\text{As}$
III	$\text{Ph}_3\text{Sb}$
IV	$(\text{C}_6\text{F}_5)_3\text{P}$
V	$(\text{C}_6\text{F}_5)_3\text{As}$
VI	$(\text{C}_6\text{F}_5)_3\text{Sb}$
VII	$(\text{C}_6\text{F}_5)_2\text{PPh}$
VIII	$(\text{C}_6\text{F}_5)_2\text{AsPh}$
IX	$(\text{C}_6\text{F}_5)_2\text{SbPh}$
X	$\text{C}_6\text{F}_5\text{PPh}_2$
XI	$\text{C}_6\text{F}_5\text{AsPh}_2$

Mass Spectrum of  $\text{Ph}_3\text{P}$

TABLE I

Mass/e	Rel. Int.%	Ion <sup>+</sup>	Mass/e	Rel. Int.%	Ion <sup>+</sup>
51	5.0	$\text{C}_4\text{H}_3$	154	2.1	$\text{Ph}_2$
57	2.1		157	3.3	
63	2.1	$\text{C}_5\text{H}_3$	170	2.5	
65	1.6	$\text{C}_5\text{H}_5$	187	1.5	
77	3.2	$\text{C}_6\text{H}_5$	182	1.0	
78	11.3	$\text{C}_6\text{H}_6$	183	61.0	$(\text{C}_6\text{H}_4)_2\text{P}$
91	2.4		184	13.0	$\text{PhPC}_6\text{H}_4$
107	11.6	$\text{C}_6\text{H}_4\text{P}$	185	10.0	) $\text{Ph}_2\text{P}$
108	32.0	) $\text{PhP}$	186	1.3	
109	2.9		260	1.5	$\text{PhP}(\text{C}_6\text{H}_4)_2$
115	2.7		261	12.2	$\text{Ph}_2\text{PC}_6\text{H}_4$
131	2.2	$\text{Ph}_3\text{P}^{2+}$	262	100.0	) $\text{Ph}_3\text{P}$
133	2.5		263	20.0	
			264	2.0	
152	7.1	$(\text{C}_6\text{H}_4)_2$			
153	1.9	$\text{C}_{12}\text{H}_9$			

Mass Spectrum of  $\text{Ph}_3\text{As}$

TABLE II

Mass/e	Rel. Int. %	Ion <sup>+</sup>	Mass/e	Rel. Int. %	Ion <sup>+</sup>
39	1.7	$\text{C}_3\text{H}_3$	150	1.3	
50	1.2	$\text{C}_4\text{H}_2$	151	14.3	$\text{C}_6\text{H}_4\text{As}$
51	6.3	$\text{C}_4\text{H}_3$	152	100.0	$\text{PhAs}$ and $(\text{C}_6\text{H}_4)_2$
52	1.0	$\text{C}_4\text{H}_4$	153	14.9	$\text{PhC}_6\text{H}_4$
77	6.0	$\text{C}_6\text{H}_5$	156	13.9	) $\text{Ph}_2$
78	4.6	$\text{C}_6\text{H}_6$	155	2.0	
101	1.9		216	1.0	
102	1.4		227	28.0	$(\text{C}_6\text{H}_4)_2\text{As}$
115	2.3		228	4.9	$\text{PhAs}(\text{C}_6\text{H}_4)$
125	1.4		229	6.3	) $\text{Ph}_2\text{As}$
126	1.7		230	1.3	
127	1.3		306	28.5	) $\text{Ph}_3\text{As}$
128	2.2		307	5.9	

Mass Spectrum of  $\text{Ph}_3\text{Sb}$

TABLE III

Mass/e	Rel. Int.%	Ion <sup>+</sup>	Mass/e	Rel. Int.%	Ion <sup>+</sup>
39	1.1	$\text{C}_3\text{H}_3$	154	17.6	$\text{Ph}_2$
50	1.6	$\text{C}_4\text{H}_2$	155	9.7	$\text{C}_{12}\text{H}_{11}$
51	9.0	$\text{C}_4\text{H}_3$	197	8.2	$\text{C}_6\text{H}_4\text{Sb}^{+121}$
52	1.1	$\text{C}_4\text{H}_4$	198	100.0	$\text{PhSb}^{+121}$
76	1.4	$\text{C}_6\text{H}_4$	199	13.1	$\text{C}_6\text{H}_6\text{Sb}^{+123}$
77	8.4	$\text{C}_6\text{H}_5$	200	75.5 )	$\text{PhSb}^{+123}$
78	5.2	$\text{C}_6\text{H}_6$	201	5.5 )	
			273	5.9 )	$(\text{C}_6\text{H}_4)_2\text{Sb}^{+121}$
			276	1.1 )	
102	1.4				
			277	6.5	$\text{Ph}_2\text{Sb}^{+123}$
115	2.0				
			352	11.1 )	
121	2.5 )	Sb	353	2.3 )	$\text{Ph}_3\text{Sb}^{+121}$
123	1.9 )				
			354	8.2 )	
126	1.1		355	1.6 )	$\text{Ph}_3\text{Sb}^{+121}$
127	1.2				
128	2.4				
151	3.2	$\text{C}_{12}\text{H}_7$			
152	16.4	$(\text{C}_6\text{H}_4)_2$			
153	21.2	$\text{PhC}_6\text{H}_4$			



Mass Spectrum of  $(C_6F_5)_3P$

TABLE IV

Mass/e	Rel. Int. %	Ion <sup>+</sup>	Mass/e	Rel. Int. %	Ion <sup>+</sup>
69	21.0	$CF_3(\sim 18)$ $PF_2(\sim 2)$	258	2.7	$C_{12}F_6$
79	11.5	$C_5F$	265	1.6	$C_{11}F_7$
93	1.6	$C_3F_3$	266	4.0	$(C_6F_5)_3P^{2+}$
98	1.2	$C_5F_2$	277	5.0 )	$C_{12}F_7$
110	3.3	$C_6F_2$	278	1.1 )	
117	2.7	$C_5F_3$	296	17.0 )	$(C_6F_6)_2$
129	14.0 )	$C_6F_3$	297	2.4 )	
130	1.0 )		315	1.4	$C_{12}F_9$
148	1.0	$C_6F_4$	346	1.5	$C_6F_5PC_6F_4$
168	1.8	$C_6F_5H$	365	43.0 )	$(C_6F_5)_2P$
179	1.0	$C_6F_4P$	366	6.2 )	
198	5.3	$C_6F_5P$	513	5.2	$(C_6F_5)_2PC_6F_4$
217	14.0 )	$C_6F_5PF$	514	3.8	$(C_6F_5)_3P$
218	1.0 )		532	100.0 )	
227	4.9	$C_{11}F_5$	533	20.0 )	
241	4.5	$C_9F_7$	534	2.0 )	
246	1.7	$C_{11}F_6$			

Mass Spectrum of  $(C_6F_5)_3As$

TABLE V

Mass/e	Rel. Int. %	Ion <sup>+</sup>	Mass/e	Rel. Int. %	Ion <sup>+</sup>
31	5.0	CF	165	2.0	
69	1.2	CF <sub>3</sub>	167	2.8	C <sub>6</sub> F <sub>5</sub>
74	1.1	C <sub>3</sub> F <sub>2</sub>	168	1.5	C <sub>6</sub> F <sub>5</sub> H
79	8.0	C <sub>5</sub> F	173	1.0	
85	5.9		177	1.2	
86	1.5	C <sub>4</sub> F <sub>2</sub>	185	1.0	
91	2.1	C <sub>6</sub> F	189	1.5	C <sub>11</sub> F <sub>3</sub>
93	6.2	C <sub>3</sub> F <sub>3</sub>	192	1.8	
94	8.5	AsF	196	2.0	C <sub>10</sub> F <sub>4</sub>
98	8.1 )		203	1.1	
99	1.6 )	C <sub>5</sub> F <sub>2</sub>	208	1.1	C <sub>11</sub> F <sub>4</sub>
110	8.6 )		215	1.0	
111	1.5 )	C <sub>6</sub> F <sub>2</sub>	223	4.9	
113	82.1	AsF <sub>2</sub>	224	1.0	
117	14.3 )		227	11.6 )	
118	1.5 )	C <sub>5</sub> F <sub>3</sub>	228	1.6 )	C <sub>11</sub> F <sub>5</sub>
129	33.0 )		236	1.0	
130	3.5 )	C <sub>6</sub> F <sub>3</sub>	242	100.0 )	
132	0.9	AsF <sub>3</sub>	243	9.2 )	C <sub>6</sub> F <sub>5</sub> As
137	1.2		246	6.5 )	
141	1.5		247	1.1 )	C <sub>11</sub> F <sub>5</sub>
142	1.4		258	7.0 )	
148	6.8	C <sub>6</sub> F <sub>4</sub>	259	1.4 )	C <sub>12</sub> F <sub>6</sub>
156	1.1		261	61.9 )	
158	1.0		262	5.5 )	C <sub>6</sub> F <sub>5</sub> AsF
161	1.0		265	5.5	C <sub>11</sub> F <sub>7</sub>

Mass Spectrum of $(C_6F_5)_3As$			(continued)			V
Mass/e	Rel. Int.%	Ion <sup>+</sup>	Mass/e	Rel. Int.%	Ion <sup>+</sup>	
277	18.1 )	$C_{12}F_7$	391	1.0	$(C_6F_5)_2As$	
278	3.5 )		409	54.7 )		
296	63.5 )	$(C_6F_4)_2$	410	9.6 )		
297	11.1 )		413	1.1		
298	1.0 )					
315	2.1	$C_{12}F_4$	444	1.8		
334	3.4	$(C_6F_5)_2$	557	1.9	$(C_6F_5)_2AsC_6F_4$	
340	2.5		576	51.8 )	$(C_6F_5)_3As$	
359	2.5		577	14.5 )		
			578	1.6 )		
371	1.1					
390	2.1					

Mass Spectrum of  $(C_6F_5)_3Sb$

TABLE VI

Mass/e	Rel. Int. %	Ion <sup>+</sup>	Mass/e	Rel. Int. %	Ion <sup>+</sup>
31	3.8	CF	159	100.0 )	SbF <sub>2</sub>
50	2.6	CF <sub>2</sub>	161	71.1 )	
69	1.0	CF <sub>3</sub>	165	1.5	
74	1.2	C <sub>3</sub> F <sub>2</sub>	167	2.5	C <sub>6</sub> F <sub>5</sub>
79	8.9 )	C <sub>5</sub> F	168	9.1	C <sub>6</sub> F <sub>5</sub> H
80	1.0 )		177	1.0	C <sub>10</sub> F <sub>3</sub>
86	2.1	C <sub>4</sub> F <sub>2</sub>	186	2.4	
91	1.8	C <sub>6</sub> F	189	2.0	C <sub>11</sub> F <sub>3</sub>
93	5.0	C <sub>3</sub> F <sub>3</sub>	196	1.3	C <sub>10</sub> F <sub>4</sub>
98	7.8 )	C <sub>5</sub> F <sub>2</sub>	208	1.9	C <sub>11</sub> F <sub>4</sub>
99	4.0 )		227	11.6 )	C <sub>11</sub> F <sub>5</sub>
110	5.6 )	C <sub>6</sub> F <sub>2</sub>	228	2.1 )	
111	1.0 )		241	1.0	C <sub>9</sub> F <sub>7</sub>
117	11.0 )	C <sub>5</sub> F <sub>3</sub>	246	3.1	C <sub>11</sub> F <sub>6</sub>
118	1.1 )		258	8.6 )	C <sub>12</sub> F <sub>6</sub>
121	2.1 )	Sb	259	3.0 )	
123	2.0 )		265	3.0	C <sub>11</sub> F <sub>7</sub>
129	12.4 )	C <sub>6</sub> F <sub>3</sub>	277	54.3 )	C <sub>12</sub> F <sub>7</sub>
130	1.6 )		278	11.0 )	
137	1.9		288	56.4 )	C <sub>6</sub> F <sub>5</sub> Sb <sup>+121</sup>
140	18.1	SbF <sup>+121</sup>	289	5.7 )	
141	2.0		290	43.6 )	C <sub>6</sub> F <sub>5</sub> Sb <sup>+123</sup>
142	13.5	SbF <sup>+123</sup>	291	4.5 )	
148	5.4 )	C <sub>6</sub> F <sub>4</sub>	296	43.6 )	(C <sub>6</sub> F <sub>4</sub> ) <sub>2</sub>
149	1.0 )		297	8.0 )	
158	1.0	C <sub>10</sub> F <sub>2</sub>			

Mass Spectrum of $(C_6F_5)_3Sb$			(continued)			VI
Mass/e	Rel. Int.%	Ion <sup>+</sup>	Mass/e	Rel. Int.%	Ion <sup>+</sup>	
307	44.3 )	$C_6F_5Sb^{121}F$	457	37.6 )	$(C_6F_5)_2Sb^{+123}$	
308	4.5 )		458	7.1 )		
309	37.6 )	$C_6F_5Sb^{123}F$	603	2.1	$(C_6F_5)_2Sb^{121}C_6F_4$	
310	4.0 )		604	2.9		
311	4.1		605	2.5	$(C_6F_5)_2Sb^{123}C_6F_4$	
312	3.1		606	2.2		
315	1.5	$C_{12}F_9$	622	83.2 )	$(C_6F_5)_3Sb^{121}$	
334	2.7	$(C_6F_5)_2$	623	23.7 )		
			624	65.1 )	$(C_6F_5)_3Sb^{123}$	
444	1.1		625	17.1 )		
			626	2.9 )		
455	47.0 )	$(C_6F_5)_2Sb^{121}$				
456	9.4 )					

Mass Spectra of PhP(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>

TABLE VII

Mass/e	Rel. Int.%	Ion <sup>+</sup>	Mass/e	Rel. Int.%	Ion <sup>+</sup>
50	9.5	C <sub>4</sub> H <sub>2</sub> <sup>+</sup> and CF <sub>2</sub> <sup>+</sup>	111	4.1	
51	52.0	C <sub>4</sub> H <sub>3</sub> <sup>+</sup>	117	2.5	C <sub>5</sub> F <sub>3</sub> <sup>+</sup>
52	3.3	C <sub>4</sub> H <sub>4</sub> <sup>+</sup>	127	48.7)	PhPF <sup>+</sup>
			128	3.9)	
57	4.1		129	12.1)	
			130	1.2)	C <sub>6</sub> F <sub>3</sub> <sup>+</sup>
63	1.9	C <sub>5</sub> H <sub>3</sub> <sup>+</sup>	135	1.5	
65	1.9	C <sub>5</sub> H <sub>5</sub> <sup>+</sup>	137	1.4	
69	40.7	CF <sub>3</sub> <sup>+</sup>	141	1.0	
74	2.2	C <sub>3</sub> F <sub>2</sub> <sup>+</sup>	148	1.0	C <sub>6</sub> F <sub>4</sub> <sup>+</sup>
75	6.2	C <sub>6</sub> H <sub>3</sub> <sup>+</sup>	149	1.6	C <sub>6</sub> F <sub>4</sub> H <sup>+</sup>
76	3.0	C <sub>6</sub> H <sub>4</sub> <sup>+</sup>	155	1.0	
77	56.5	C <sub>6</sub> F <sub>5</sub> <sup>+</sup>	156	2.0	
78	5.2	C <sub>6</sub> H <sub>6</sub> <sup>+</sup>	161	1.2	
79	1.5	C <sub>5</sub> F <sup>+</sup>	167	3.0	C <sub>6</sub> F <sub>5</sub> <sup>+</sup>
80	1.7	C <sub>5</sub> FH <sup>+</sup>	168	2.9	C <sub>6</sub> F <sub>5</sub> H <sup>+</sup>
81	3.4		174	1.0	
82	1.5		175	1.5	
83	2.1		179	2.3	C <sub>6</sub> F <sub>4</sub> P <sup>+</sup>
85	1.8		180	2.0	C <sub>6</sub> F <sub>4</sub> Ph <sup>+</sup>
88	2.1		181	1.2	
93	2.1	C <sub>3</sub> F <sub>3</sub> <sup>+</sup>	185	1.3	
98	1.3	C <sub>5</sub> F <sub>2</sub> <sup>+</sup>	186	10.0	C <sub>6</sub> F <sub>6</sub> <sup>+</sup>
99	3.0	C <sub>6</sub> F <sub>2</sub> H <sup>+</sup>	187	3.2	
101	2.0		193	1.0	
107	12.2	C <sub>6</sub> H <sub>4</sub> P <sup>+</sup>	196	2.5	
108	2.7	PhP <sup>+</sup>			

Mass Spectra of $\text{PhP}(\text{C}_6\text{F}_5)_2$			(continued)			VII
Mass/e	Rel. Int. %	Ion <sup>+</sup>	Mass/e	Rel. Int. %	Ion <sup>+</sup>	
110	28.2	$\text{C}_6\text{F}_2$	255	40.0 )	$\text{C}_6\text{H}_4\text{P} \cdot \text{C}_6\text{F}_4$	
198	97.5 )	$\text{C}_6\text{F}_5\text{P}$	256	6.5 )		
199	7.4 )		258	1.5		
204	2.9		273	1.5		
205	4.8		274	4.8	$\text{C}_6\text{H}_4\text{PC}_6\text{F}_5$	
206	21.2 )	$\text{C}_6\text{F}_7\text{H}$	275	28.3 )	$\text{PhPC}_6\text{F}_5$	
207	2.8 )		276	4.2 )		
211	1.0		277	1.8		
217	4.7	$\text{C}_6\text{F}_5\text{PF}$	296	4.0	$(\text{C}_6\text{F}_4)_2$	
221	5.2 )	$\text{PhP}(\text{C}_6\text{F}_5)_2$	323	1.8		
221.5	1.2 )					
223	1.3		334	1.2	$(\text{C}_6\text{F}_5)_2$	
224	11.0 )	$\text{C}_6\text{F}_4\text{C}_6\text{H}_4$	365	2.5	$(\text{C}_6\text{F}_5)_2\text{P}$	
225	3.1 )					
227	2.6		372	1.3		
229	1.2		423	5.9 )	$\text{PhPC}_6\text{F}_5\text{C}_6\text{F}_4$	
			424	1.8 )		
244	9.5 )	$\text{PhC}_6\text{F}_5$	441	14.2	$\text{C}_6\text{H}_4\text{P}(\text{C}_6\text{F}_5)_2$	
245	1.6 )					
246	1.2		442	100.0 )	$\text{PhP}(\text{C}_6\text{F}_5)_2$	
			443	21.5 )		
			444	2.9 )		

Mass Spectrum of  $(C_6F_5)_2AsPh$

TABLE VIII

Mass/e	Rel. Int. %	Ion <sup>+</sup>	Mass/e	Rel. Int. %	Ion <sup>+</sup>
20	1.9	HF	206	2.1	
39	1.8	C <sub>3</sub> H <sub>3</sub>	223	1.7	C <sub>6</sub> F <sub>4</sub> As
50	4.3	C <sub>4</sub> H <sub>2</sub>	224	6.6	C <sub>6</sub> F <sub>4</sub> C <sub>6</sub> H <sub>4</sub>
51	23.2	C <sub>4</sub> H <sub>3</sub>	225	2.0	C <sub>6</sub> F <sub>4</sub> Ph
52	1.4	C <sub>4</sub> H <sub>4</sub>	227	1.2	
74	1.0	C <sub>6</sub> H <sub>2</sub>	242	100.0 )	C <sub>6</sub> F <sub>5</sub> As
75	1.3	C <sub>6</sub> H <sub>3</sub>	243	8.5 )	
76	1.1	C <sub>6</sub> H <sub>4</sub>	244	16.3 )	PhC <sub>6</sub> F <sub>5</sub>
77	20.4	C <sub>6</sub> H <sub>5</sub>	245	2.3 )	
78	2.4	C <sub>6</sub> H <sub>6</sub>	261	6.1 )	C <sub>6</sub> F <sub>5</sub> AsF
94	1.1	AsF	277	1.0 )	
99	1.0		296	3.8	(C <sub>6</sub> F <sub>4</sub> ) <sub>2</sub>
110	2.1	C <sub>6</sub> F <sub>2</sub>	299	13.9 )	C <sub>6</sub> F <sub>4</sub> AsC <sub>6</sub> H <sub>4</sub>
113	10.1	AsF <sub>2</sub>	300	2.3 )	
117	1.1	C <sub>5</sub> F <sub>3</sub>	319	5.9 )	PhAsC <sub>6</sub> F <sub>5</sub>
129	4.4	C <sub>6</sub> F <sub>3</sub>	320	1.1 )	
151	7.0	C <sub>6</sub> H <sub>4</sub> As	409	2.3	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> As
152	3.7	PhAs	486	14.8 )	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> AsPh
153	1.2	PhC <sub>6</sub> H <sub>4</sub>	487	3.1 )	
154	1.8	Ph <sub>2</sub>			
168	2.0	C <sub>6</sub> F <sub>5</sub> H			
171	13.6 )				
172	1.2 )	PhAsF			
186	1.8	C <sub>6</sub> F <sub>6</sub>			
192	1.0				
205	1.3				



Mass Spectrum of  $(C_6F_5)_2SbPh$

TABLE IX

Mass/e	Rel. Int.%	Ion <sup>+</sup>	Mass/e	Rel. Int.%	Ion <sup>+</sup>
27	7.0	$C_2H_3$	154	7.0 )	$Ph_2$
31	1.0	CF	155	1.8 )	
38	1.0	$C_3H_2$	156	1.1	
39	4.0	$C_3H_3$	159	31.5 )	$SbF_2$
50	15.0	$C_4H_2$	161	23.4 )	
51	85.7	$C_4H_3$	165	1.0	
52	4.6	$C_4H_4$	167	2.4	$C_6F_5$
74	3.0	$C_6H_2$	168	2.4	$C_6F_5H$
75	4.1	$C_6H_3$	174	1.0	$C_6F_6$
76	4.1	$C_6H_4$	175	1.2	
77	78.7	$C_6H_5$	186	4.1	
78	6.1	$C_6H_6$	187	1.5	$C_6H_4Sb^{121}$
79	1.7	$C_5F$	192	1.0	
93	1.1	$C_3F_3$	193	1.1	
98	1.5	$C_5F_2$	197	11.9	$PhSb^{121}$
99	1.8		198	4.4	$C_6H_4Sb^{123}$
110	1.8	$C_6F_2$	199	9.1	$PhSb^{123}$
111	1.0		200	3.0	
117	2.4	$C_5F_3$	204	1.5	
121	6.0 )	Sb	205	1.9	
123	4.7 )		206	2.9	
129	3.2	$C_6F_3$	217	22.5 )	$PhSbF$
140	17.7 )	SbF	218	2.2 )	
142	13.1 )		219	16.7 )	
147	1.0		220	1.3 )	
153	1.0	$C_{12}H_9$			

Mass Spectrum of PhSb(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (continued)						IX
Mass/e	Rel. Int.%	Ion <sup>+</sup>	Mass/e	Rel. Int.%	Ion <sup>+</sup>	
224	9.0	C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> F <sub>4</sub>	345	9.0 )	C <sub>6</sub> F <sub>4</sub> SbC <sub>6</sub> H <sub>4</sub>	
225	2.4	PhC <sub>6</sub> F <sub>4</sub>	346	1.4 )		
			347	6.8 )		
			348	1.1 )		
227	3.0	C <sub>4</sub> F <sub>5</sub>	365	7.0 )	PhSbC <sub>6</sub> F <sub>5</sub>	
244	7.9 )	PhC <sub>6</sub> F <sub>5</sub>	366	1.1 )		
245	1.2 )		367	5.3 )		
			368	0.9 )		
246	1.0	C <sub>11</sub> F <sub>6</sub>	455	1.9 )	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Sb	
258	2.2	C <sub>12</sub> F <sub>6</sub>	456	0.5 )		
			457	1.5 )		
277	7.0 )	C <sub>12</sub> F <sub>7</sub>	458	0.5 )		
278	1.2 )		532	4.5 )	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> SbPh	
288	100.0 )		533	1.2 )		
289	7.5 )		534	3.5 )		
		C <sub>6</sub> F <sub>5</sub> Sb <sup>121</sup>	535	0.9 )		
290	75.6 )	C <sub>6</sub> F <sub>5</sub> Sb <sup>123</sup>				
291	5.6 )					
296	5.8 )	(C <sub>6</sub> F <sub>4</sub> ) <sub>2</sub>				
297	1.0 )					
307	7.0 )	C <sub>6</sub> F <sub>5</sub> Sb <sup>121</sup> F				
308	0.9 )					
309	5.4 )	C <sub>6</sub> F <sub>5</sub> Sb <sup>123</sup> F				
310	0.5 )					

Mass Spectrum of  $\text{Ph}_2\text{PCF}_5$

TABLE X

Mass/e	Rel. Int.%	Ion <sup>+</sup>	Mass/e	Rel. Int.%	Ion <sup>+</sup>
39	4.3	$\text{C}_3\text{H}_3$	92	3.9	
45	1.4		93	1.5	
50	5.1	$\text{C}_4\text{H}_2$ or $\text{CF}_2$	98	1.1	$\text{C}_5\text{F}_2$
51	16.1	$\text{C}_4\text{H}_3$	99	2.0	$\text{C}_5\text{F}_2\text{H}$
52	2.0	$\text{C}_4\text{H}_4$	101	1.6	
56	1.7		102	1.5	
57	3.6		104	1.0	$\text{C}_6\text{HP}$
62	1.2	$\text{C}_5\text{H}_2$	105	1.0	$\text{C}_6\text{H}_2\text{P}$
63	3.0	$\text{C}_5\text{H}_3$	106	1.1	$\text{C}_6\text{H}_3\text{F}$
65	2.0	$\text{C}_5\text{H}_5$	107	12.0	$\text{C}_6\text{H}_4\text{P}$
68	1.1		108	21.3 )	
69	5.9	$\text{CF}_3$	109	2.6 )	$\text{PhP}$
74	2.0	$\text{C}_6\text{H}_2$	110	2.4	$\text{C}_6\text{F}_2$
75	3.4	$\text{C}_6\text{H}_3$	111	1.6	
76	2.2	$\text{C}_6\text{H}_4$	115	2.7	
77	10.5	$\text{C}_6\text{H}_5$	117	1.1	$\text{C}_5\text{F}_3$
78	3.2	$\text{C}_6\text{H}_6$	123	1.1	$\text{C}_6\text{HPF}$
79	1.2	$\text{C}_5\text{F}$	124	1.0	$\text{C}_6\text{H}_2\text{PF}$
80	1.8		125	1.1	$\text{C}_6\text{H}_3\text{PF}$
81	3.5		126	1.3	$\text{C}_6\text{H}_4\text{PF}$
82	1.6		127	16.6 )	
83	2.0		128	2.8 )	$\text{PhPF}$
88	1.1		129	1.3	$\text{C}_6\text{F}_3$
89	1.5		131	1.2	
90	1.2		133	2.1	
91	1.8		135	1.2	

Mass Spectrum of $\text{Ph}_2\text{PC}_6\text{F}_5$			(continued)			X
Mass/e	Rel. Int.%	Ion <sup>+</sup>	Mass/e	Rel. Int.%	Ion <sup>+</sup>	
139	1.2		187	1.9		
140	1.2		198	3.9	$\text{C}_6\text{F}_5\text{P}$	
141	2.0		204	1.1		
150	2.0		205	2.7		
151	1.3		206	6.6	$\text{C}_6\text{F}_7\text{H}?$	
152	1.5	$(\text{C}_6\text{H}_4)_2$	207	1.3		
153	7.7	$\text{PhC}_6\text{H}_6$	224	3.7 )		
154	39.5 )		225	1.2 )	$\text{C}_6\text{F}_4\text{C}_6\text{H}_4$	
155	7.9 )	$\text{Ph}_2$	255	14.2 )		
156	1.9		256	3.7 )	$\text{C}_6\text{F}_4\text{PC}_6\text{H}_4$	
157	2.4		273	1.0	$\text{C}_6\text{F}_5\text{PC}_6\text{H}_3$	
159	1.1		274	2.5	$\text{C}_6\text{F}_5\text{PC}_6\text{H}_4$	
165	7.2		275	5.8 )		
167	2.8	$\text{C}_6\text{F}_5$	276	1.6 )	$\text{C}_6\text{F}_5\text{PPh}$	
168	2.4	$\text{C}_6\text{F}_5\text{H}$	333	3.8	$\text{Ph}_2\text{PC}_6\text{F}_4$	
170	2.5		334	2.1	$\text{Ph}_2\text{PC}_6\text{F}_4\text{H}$	
176	4.2 )		350	3.8	$\text{C}_6\text{F}_5\text{P}(\text{C}_6\text{H}_4)_2$	
176.5	1.0 )	$\text{Ph}_2\text{PC}_6\text{F}_5^{2+}$	351	16.4	$\text{PhPC}_6\text{F}_5\text{C}_6\text{H}_4$	
179	1.3		352	100.0 )		
180	1.4		353	21.2 )	$\text{Ph}_2\text{PC}_6\text{F}_5$	
181	2.2		354	3.8 )		
182	2.4					
183	32.7	$(\text{C}_6\text{H}_4)_2\text{P}$				
184	6.8	$\text{PhPC}_6\text{H}_4$				
185	10.9	$\text{Ph}_2\text{P}$				
186	4.9	$\text{C}_6\text{F}_6$				

Mass Spectrum of  $\text{Ph}_2\text{AsC}_6\text{F}_5$

TABLE XI

Mass/e	Rel. Int.%	Ion	Mass/e	Rel. Int.%	Ion
20	1.9	HF	156	1.2	
39	3.7	$\text{C}_3\text{H}_3$	168	1.2	$\text{C}_6\text{F}_5\text{H}$
41	1.1	$\text{C}_3\text{H}_5$	171	11.3	PhAsF
50	5.3	$\text{C}_4\text{H}_2$	186	1.4	$\text{C}_6\text{F}_6$
51	21.5	$\text{C}_4\text{H}_3$	198	1.2	
52	2.8	$\text{C}_4\text{H}_4$	206	1.3	
63	1.2		224	3.9	
74	1.1	$\text{C}_6\text{H}_2$	225	1.3	
75	1.7	$\text{C}_6\text{H}_3$	227	11.5	$(\text{C}_6\text{H}_4)_2\text{As}$
76	1.8	$\text{C}_6\text{H}_4$	228	2.0	PhAs $\text{C}_6\text{H}_4$
77	20.6	$\text{C}_6\text{H}_5$	229	4.8 )	Ph <sub>2</sub> As
78	6.9	$\text{C}_6\text{H}_6$	230	1.1 )	
101	1.8		242	3.6	$\text{C}_6\text{F}_5\text{As}$
102	1.1		244	3.3	Ph $\text{C}_6\text{F}_5$
113	1.5	AsF <sub>2</sub>	286	1.2	
115	1.6		299	6.3	$\text{C}_6\text{H}_4\text{AsC}_6\text{F}_4$
126	1.4		300	1.1	PhAs $\text{C}_6\text{F}_4$
127	1.1		319	2.4	PhAs $\text{C}_6\text{F}_5$
128	1.6		396	13.1 )	Ph <sub>2</sub> As $\text{C}_6\text{F}_5$
149	1.1		397	2.8 )	
150	1.3				
151	13.7	$\text{C}_6\text{H}_4\text{As}$			
152	34.7	PhAs and			
153	10.6	$(\text{C}_6\text{H}_4)_2$			
154	100.0 )	Ph $\text{C}_6\text{H}_4$			
155	14.8 )	Ph <sub>2</sub>			

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