

Journal of Organometallic Chemistry, 82 (1974) 159–184
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MASS SPECTROMETRY OF SYSTEMS CONTAINING A GROUP IVB- TRANSITION METAL BOND

I. THE PHENYL- AND PENTAFLUOROPHENYL- SILICON, -GERMANIUM AND -TIN DERIVATIVES OF PENTACARBONYLMANGANESE

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(Received May 29th, 1974)

Summary

The 70 eV mass spectra of the series $\text{Ph}_{3-n}(\text{C}_6\text{F}_5)_n\text{MMn}(\text{CO})_5$ ($n = 0$ to 3 and $M = \text{Si}, \text{Ge}$ or Sn) and $\text{Ph}_3\text{PbMn}(\text{CO})_5$ have been examined and the proposed fragmentation schemes are supported by the observance of the appropriate meta-stable ions. Most of the total ion current is carried by metal-containing ions, particularly those containing just a Group IV metal. In all cases the initial fragmentation is by the loss of one or more carbonyl groups from the molecular ion, followed, except in the case of the fully fluorinated silicon derivatives, by the cleavage of the metal-metal bond. The fragmentation of the remainder of the molecule is then controlled by the nature of M and the number of pentafluorophenyl groups, the silicon derivatives showing a greater abundance of ions formed by the cleavage of the C-C, C-H or C-F bonds in the aromatic ring, in contrast to the tin and lead derivatives which fragment almost exclusively by the cleavage of the metal-carbon bond. The formation of metal fluoride species plays an important part in the fragmentation of the pentafluorophenyl derivatives and becomes more important as the Group IV metal becomes heavier, while except for $\text{Ph}_3\text{PbMn}(\text{CO})_5$ the abundances of the ions resulting from the migration of a complete aromatic ring from one metal to the other remain essentially constant. However, some of the observed changes in the fragmentation modes are not readily predicted on the basis of the expected variation in the relative metal-carbon or metal-metal bond strengths since these appear to be more dependent on the stabilities of the radical species or on the ion species formed. The tin-metal molecular bond dissociation energies in $\text{Ph}_3\text{SnMn}(\text{CO})_5$ and $\text{Ph}_3\text{SnFe}(\text{CO})_2\text{Cp}$ were found to be 61 ± 8 and 54 ± 9 kcal mol⁻¹, respectively.

Introduction

Mass spectrometry of inorganic and particularly organometallic systems is now well established [1-4], but although many organometallic molecules have been studied, there have been relatively few studies on systems containing a Group IV—transition metal bond, and even fewer studies have involved changes in only one variable, even though such approaches have been found to be particularly valuable in the understanding of relative bond strengths [5, 6]. The abundances and identities of the major ions have been tabulated for the systems $\text{Ph}_{3-n}\text{Cl}_n\text{SnFe}(\text{CO})_2\text{Cp}$ [7] ($n = 0$ to 3), and $\text{R}_3\text{GeM}'(\text{CO})_3\text{Cp}$ [8] ($\text{R} = \text{Me}, \text{Et}$ and $n\text{-Pr}$ and $\text{M}' = \text{Mo}$ or W), as well as for some tetranuclear systems containing tin—manganese [9] and tin—cobalt bonds [10]. More complete studies including attempts to measure the strengths of the metal—metal bonds have been carried out for $\text{Me}_3\text{MMn}(\text{CO})_5$ [11] ($\text{M} = \text{Si}, \text{Ge}$ or Sn), $\text{Me}_3\text{MM}'(\text{CO})_3\text{Cp}$ [12] ($\text{M} = \text{Ge}$ or Sn and $\text{M}' = \text{Cr}, \text{Mo}$ or W), $\text{RCo}(\text{CO})_4$ [13] ($\text{R} = \text{Me}_3\text{Si}, \text{Cl}_3\text{Si}, \text{F}_3\text{Si}$ or MeF_2Si) and more recently the heats of formation for the series $\text{Me}_3\text{SiMn}(\text{CO})_x(\text{PF}_3)_{5-x}$ [14] ($x = 1$ to 5) have been reported. In an attempt to better understand the nature of the metal—metal bond, we undertook the study of a system where several variables can be changed one at a time, but some difficulty was encountered in the choice of compounds since we did not wish to pick a group of compounds all with essentially the same mass spectrum. Moreover, they had to be thermally stable and of sufficient volatility that they could be easily sublimed. The phenyl(pentafluorophenyl) derivatives fit these last two criteria. Also, the introduction of the pentafluorophenyl group into the molecule introduces a characteristic aspect in the mass spectrum, involving the migration of fluorine from the aromatic ring to the metal atom. This feature has been observed in the spectra of several pentafluorophenyl derivatives of Groups IV [15-17], V [18, 19], and VI [20]. Since spectroscopic evidence suggests that the introduction of a good acceptor group such as C_6F_5 may lead to an increase in metal to metal π -bonding, this system seemed to be particularly suitable for study. This paper describes our investigations of $\text{Ph}_{3-n}(\text{C}_6\text{F}_5)_n\text{MMn}(\text{CO})_5$ ($n = 0$ to 3 and $\text{M} = \text{Si}, \text{Ge}$ or Sn) and $\text{Ph}_3\text{PbMn}(\text{CO})_5$.

Results and discussion

The $\text{Ph}_3\text{MMn}(\text{CO})_5$ derivatives

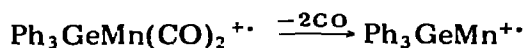
The monoisotopic abundances of the ions, expressed as a percentage of the total ion current, are given in Table 1. The molecular ions are very low in abundance and no signals, or only very weak ones are observed for ions resulting from the loss of one or more carbonyl groups. However, the silicon and germanium derivatives did show the appropriate metastable peaks* for the loss of two carbonyl groups from $\text{Ph}_3\text{SiMn}(\text{CO})_n^{+}$ ($n = 4$ or 2) and $\text{Ph}_3\text{GeMn}(\text{CO})_2^{+}$ respectively. (See next page for equations.)

* It is recognized that metastable transition data do not identify unambiguously the particular species lost, although it is reasonable to deduce the most probable species lost, as we have done in this discussion.

TABLE 1
THE 70 eV MASS SPECTRA OF $\text{Ph}_3\text{MMn}(\text{CO})_5$

Ion	Relative abundance (%) ^a				Ion	Relative abundance (%)			
	Si	Ge	Sn	Pb		Si	Ge	Sn	Pb
<i>(a) Ions containing two metals</i>									
$\text{Ph}_3\text{MMn}(\text{CO})_5^{+\bullet}$	0.3	< 0.1	0.6	0.2	$\text{Ph}_3\text{MMn}^{+\bullet}$	2.2	2.9	10.6	0.4
$\text{Ph}_3\text{MMn}(\text{CO})_4^{+\bullet}$	0.1				$\text{Ph}_2\text{MMn}^{+\bullet}$				0.7
$\text{Ph}_3\text{MMn}(\text{CO})_2^{+\bullet}$	0.3				$\text{PhMMn}^{+\bullet}$			0.1	0.4
$\text{Ph}_2\text{MMn}(\text{CO})_5^+$				0.2	$\text{C}_6\text{H}_4\text{MMn}^{+\bullet}$			0.1	
$\text{Ph}_2\text{MMn}(\text{CO})_4^+$				0.3	$\text{MMn}^{+\bullet}$			0.5	1.3
$\text{Ph}_2\text{MMn}(\text{CO})_3^+$				0.3					
<i>(b) Ions containing one metal</i>									
Ph_3M^+	56.2	58.9	32.4	21.7	$\text{C}_6\text{H}_2\text{M}^{+\bullet}$	0.8			
$\text{C}_{18}\text{H}_{13}\text{M}^+$	1.0				$\text{C}_4\text{H}_3\text{M}^+$	1.1	1.5	0.5	
$\text{C}_{18}\text{H}_{11}\text{M}^+$	0.7				C_2HM^+	1.3	1.4		
$\text{C}_{18}\text{H}_9\text{M}^+$	0.5				$\text{M}^{+\bullet}$		0.2	5.4	10.1
$\text{Ph}_2\text{M}^{+\bullet}$	0.5	1.9	0.4		$\text{Ph}_3\text{MnCO}^{+\bullet}$				0.4
$\text{C}_{12}\text{H}_9\text{M}^+$	5.4	2.8	0.9		$\text{Ph}_3\text{Mn}^{+\bullet}$				7.3
$\text{C}_{12}\text{H}_8\text{M}^+$	2.0	0.9	0.2		$\text{PhMn}^{+\bullet}$	0.4	1.6	1.3	13.7
$\text{C}_{12}\text{H}_7\text{M}^+$	1.3	0.5			$\text{Mn}(\text{CO})_5^+$	0.3	0.3	<i>b</i>	0.4
$\text{C}_{10}\text{H}_7\text{M}^+$	1.6				$\text{Mn}(\text{CO})_4^+$	0.3	0.3	0.2	0.3
$\text{C}_8\text{H}_7\text{M}^+$	0.3				$\text{Mn}(\text{CO})_3^+$	0.6	0.5	0.4	0.3
$\text{C}_8\text{H}_5\text{M}^+$	0.9	0.2			$\text{Mn}(\text{CO})_2^+$	0.6	0.5	0.4	0.6
PhM^+	4.7	10.8	24.4	7.8	MnCO^+	1.1	0.9	0.7	1.2
$\text{C}_6\text{H}_4\text{M}^{+\bullet}$	0.3				$\text{MnH}^{+\bullet}$	0.3	0.2	0.1	0.3
$\text{C}_6\text{H}_3\text{M}^+$	0.3				Mn^+	5.0	6.9	5.5	8.6
<i>(c) Hydrocarbon ions</i>									
$\text{Ph}_2^{+\bullet}$	0.3	0.4	0.6	1.3	$\text{C}_6\text{H}_6^{+\bullet}$	0.9	0.6	4.3	4.7
$\text{C}_{12}\text{H}_9^+$	0.4	0.6	0.3	0.4	Ph^+	0.6	0.5	0.9	1.8
$\text{C}_{12}\text{H}_8^{+\bullet}$	0.5	0.5	0.4	0.7	C_4H_3^+	0.4	0.6	1.1	1.7
PhCO^+				1.5	$\text{C}_4\text{H}_2^{+\bullet}$	0.2	0.3	0.7	0.3

^a In Tables 1-4, relative abundances are cited as percentages of the total positive ion current. ^b Overlapped with $\text{Ph}^{118}\text{Sn}^+$



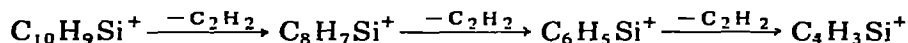
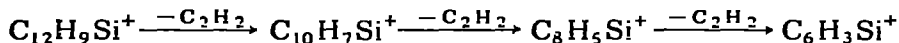
The fragmentation paths for the remainder of the spectra do not seem to be dependent upon the metal-metal bond strength, since the next step involves its cleavage giving in all cases the Ph_3M^+ ion as the base (most abundant) peak. This can arise by the loss of manganese from the ion $\text{Ph}_3\text{MMn}^{++}$ or alternatively by the loss of $\text{Mn}(\text{CO})_5$ from the molecular ion, for which the appropriate metastable ions were observed in most cases.



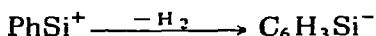
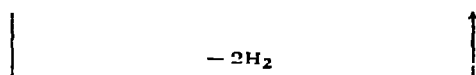
(M = Si, Ge or Sn)

(M = Si, Sn or Pb)

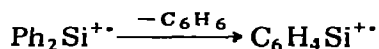
The fragmentation path of the Ph_3M^+ ion is largely governed by the strength of the M-C bond, the silicon compound showing two series of ions that arise by the consecutive loss of acetylene from the ions $\text{C}_{12}\text{H}_9\text{M}^+$ and $\text{C}_{10}\text{H}_9\text{M}^+$, although the origin of both these ions was not determined. The former could conceivably arise by the loss of benzene (or phenyl and a hydrogen radical) from Ph_3M^+ , while the latter could arise by the loss of an acetylene radical from $\text{Ph}_2\text{Si}^{++}$.



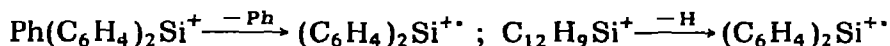
Another, but relatively minor, fragmentation path for the PhSi^+ ion by the loss of one or two molecules of hydrogen, and a similar loss of hydrogen from PhSi^{++} is also observed.



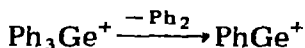
Although the loss of benzene from the Ph_3Si^+ was not supported by the appropriate metastable transition, the analogous transition was observed for the germanium derivative, and further support that such transitions are not uncommon for silicon-containing species was provided by the metastable supported loss of benzene from $\text{Ph}_2\text{Si}^{++}$.



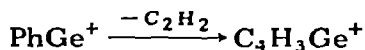
Finally, although the loss of acetylene, benzene and hydrogen molecules is the predominant fragmentation route for these and other phenylsilicon derivatives [4, 21], the loss of a hydrogen radical or a phenyl group can also occur as evidenced by the formation of the ion $(\text{C}_6\text{H}_4)_2\text{Si}^{++}$ by two separate routes.



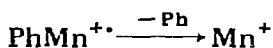
The ion Ph_3Ge^+ fragments in exactly the same way as the same ion derived from tetraphenylgermane [22]. Loss of benzene or hydrogen is observed, but the more important fragmentation mode is by the simultaneous loss of two phenyl groups, perhaps in the form of biphenyl.



The ion PhGe^+ then loses acetylene as in the case of the PhSi^+ ion.



Such a transition does not occur with the rearrangement ion $\text{PhMn}^{+\cdot}$, since there is no ion due to $\text{C}_4\text{H}_3\text{Mn}^+$ and the appropriate metastable for the process:



was found to be present in all other spectra, which showed fairly large abundances of this ion.

The mass spectrum of the tin compound has been previously reported [23, 24], but although the identities and abundances of the ions are in good agreement with those in this work, only a few metastable transitions were reported previously and a detailed examination was not made. Unlike the silicon and germanium derivatives, the tin compound gives a spectrum which shows no ions due to loss of hydrogen or benzene from the Ph_3Sn^+ ion, and the successive loss of acetylene becomes unimportant. The controlling factor in the fragmentation of this and other tin compounds [4, 17, 25] is the cleavage of the tin-carbon bond, which in this case can occur before the tin-manganese bond is broken.

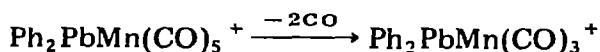


The Ph_3Sn^+ ion fragments by the loss of two phenyl groups to give PhSn^+ which then loses phenyl to give the tin ion. These are exactly the same processes as those observed in the mass spectrum of Ph_4Sn [25].



The decreasing strength of the metal-carbon bond with respect to the metal-metal or metal-carbonyl bond as M becomes heavier is further exemplified by the lead derivative, in which one of the phenyl groups is lost before all five carbonyl groups are removed, to give the series of ions $\text{Ph}_2\text{PbMn}(\text{CO})_n^+$ ($n = 0, 3, 4, \text{ or } 5$). A similar loss of a methyl group from the molecular ion in the mass spectra of the series $\text{Me}_3\text{MMn}(\text{CO})_5$ [11] is also known to occur, such that the abundance of the $\text{Me}_2\text{MMn}(\text{CO})_5^+$ species increases in the order

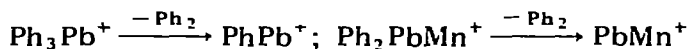
Si < Ge < Sn < Pb. Although no metastable transitions were observed for the loss of carbonyl groups from the molecular ion, the loss of two carbonyl groups from the ion $\text{Ph}_2\text{PbMn}(\text{CO})_5^+$ was observed.



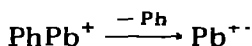
The most interesting feature of this spectrum was the fragmentation of the $\text{Ph}_3\text{PbMn}^{+\cdot}$ ion, which not only loses manganese as previously described, but also loses lead to give the rearrangement ion $\text{Ph}_3\text{Mn}^{+\cdot}$ which then loses two phenyl groups to give the very abundant $\text{PhMn}^{+\cdot}$ ion.



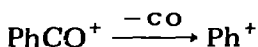
The ready loss of two phenyl groups in this compound is further exemplified by the formation of the ions PhPb^+ and PbMn^+ :



while the PhPb^+ ion then finally loses phenyl.



The occurrence of the $\text{MMn}^{+\cdot}$ ion in the spectra of the tin and lead derivatives is of course not an indication of the stronger relative strength of the metal-metal bond, but of a fragmentation process which makes their formation easier. Finally the lead derivative shows larger abundances of hydrocarbon ions than do the other three derivatives, and is the only spectrum to show the presence of the benzoyl ion, which was observed to fragment by the loss of CO.



This ion could well arise by the loss of PhCO^+ from the molecular ion or by the loss of Ph_2Mn from the ion $\text{Ph}_3\text{MnCO}^{+\cdot}$.

The $(\text{C}_6\text{F}_5)_3\text{MMn}(\text{CO})_5$ derivatives

The ion abundances for these derivatives are presented in Table 2. The molecular ion peaks are still quite weak, but are stronger than those for the above derivatives and in addition, many more metastable transitions for the loss of one to four carbonyl groups were observed even though not all the ions resulting from such processes had measurable abundances.

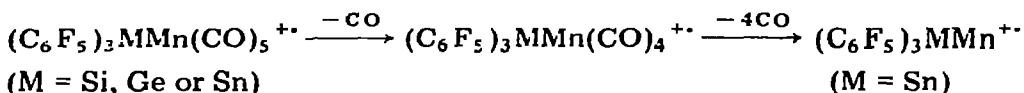


TABLE 2
THE 70 eV MASS SPECTRA OF $(C_6F_5)_3Mn(CO)_5$

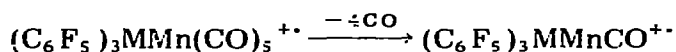
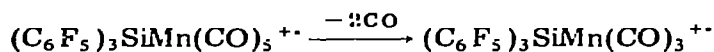
Ion	Relative abundance (%)			Ion	Relative abundance (%)		
	Si	Ge	Sn		Si	Ge	Sn
<i>(a) Ions containing two metals</i>							
$(C_6F_5)_3Mn(CO)_5^{++}$	0.9	2.2	5.7	$C_{15}F_{12}Mn(CO)_2^+$	0.5		
$(C_6F_5)_3Mn(CO)_4^{++}$	3.5	1.5	0.5	$(C_6F_5)_2Mn(CO)_5^+$		0.4	0.8
$(C_6F_5)_3Mn(CO)_2^{++}$	0.7			$(C_6F_5)_2FMMn^{++}$		0.6	0.3
$(C_6F_5)_3MnCO^{++}$	2.0	1.9	0.9	$(C_6F_5)_2MMn^+$			0.3
$(C_6F_5)_3Mn^{+-}$	16.2	11.2	5.1	$(C_6F_5)F_2MMn^{+-}$		0.7	
$C_{15}F_{13}Mn(CO)_2^{+-}$	0.3			F_3MMn^{+-}		2.4	3.1
<i>(b) Ions containing one metal</i>							
$(C_6F_5)_3MF^{+-}$		0.5					
$(C_6F_5)_3M^+$				$C_6F_5M^+$	0.8	21.0	28.5
$(C_6F_5)_2Mn(CO)_4^+$	0.4	3.1	3.0	MF_3^+	0.8		
$C_{18}F_{14}M^{++}$	0.2			MF^+	1.1	16.5	24.2
$C_{18}F_{13}M^+$	0.4			M^{+-}		0.3	1.8
$C_{18}F_{12}M^{++}$	1.8			$C_6F_5Mn^{+-}$	1.9	0.9	0.7
$C_{17}F_{13}M^+$	0.3			$Mn(CO)_5^+$	a	2.9	2.6
$C_{17}F_{11}M^+$	1.3			$Mn(CO)_4^+$	0.6	2.1	1.6
$(C_6F_5)_2MF^+$		0.5	0.9	$Mn(CO)_3^+$	0.6	0.8	b
$(C_6F_5)_2M^{+-}$	0.5			$Mn(CO)_2^+$	0.6	0.5	0.6
$C_{12}F_9M^+$	1.4	0.4		$MnCO^+$	0.9	0.9	1.3
$C_{11}F_8M^+$	0.5			MnF_3^{+-}	0.2		
$C_{12}F_8M^{+-}$	0.6			MnF_2^+	0.2		
$C_6F_5MF_2^+$	0.2	0.3	0.4	MnF^{+-}	7.5	3.4	2.6
$C_6F_5MCO^+$			0.9	Mn^+	4.0	2.8	2.8
<i>(c) Fluorocarbon ions</i>							
$C_{18}F_{13}^+$		0.1		$C_{11}F_6^{+-}$	0.2	0.6	
$C_{18}F_{12}^{+-}$	0.2	0.3	0.1	$C_{12}F_5^+$	1.5		
$C_{18}F_{11}^+$	0.1	0.1		$C_{11}F_5^+$	1.4	1.0	
$C_{17}F_{11}^+$	0.1			$C_{12}F_4^{+-}$	0.2		
$C_{18}F_{10}^{+-}$	1.9	0.7	0.1	$C_{11}F_4^{+-}$	0.4	0.2	
$C_{18}F_9^+$	0.7			$C_{11}F_3^+$	1.9	0.4	0.2
$C_{17}F_9^+$	1.1	0.4		$C_6F_5H^{+-}$	0.6	0.3	1.0
$C_{18}F_8^{+-}$	2.5			$C_6F_5^+{}^c$			
$C_{17}F_8^{+-}$	0.2			$C_6F_4^{+-}$	0.9	1.1	0.7
$C_{17}F_7^+$	2.0			$C_6F_3^+$	0.2	0.8	0.4
$C_{17}F_6^{+-}$	0.3			$C_5F_3^+$	0.9	0.5	0.4

(continued)

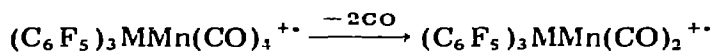
TABLE 2 (continued)

Ion	Relative abundance (%)			Ion	Relative abundance (%)		
	Si	Ge	Sn		Si	Ge	Sn
$C_{17}F_5^+$	0.3			$C_6F_2^{+*}$	0.7	0.5	0.5
$C_{12}F_9^+$		0.2		$C_5F_2H^+$	0.4	0.2	0.6
$C_{12}F_8^{+*}$	0.6	1.7	0.4	$C_5F_2^{+*}$	0.6	0.4	0.4
$C_{12}F_7^+$	2.2	0.7		C_6F^+	0.5		
$C_{11}F_7^+$	0.2	0.4	0.2	C_5F^+	1.0	0.7	0.7
$C_{12}F_6^{+*}$	1.7						

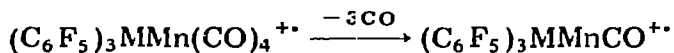
^a Overlapped with $C_6F_5Si^+$. ^b Overlapped with $F^{120}Sn^+$. ^c Overlapped with $Mn(CO)_4^+$.



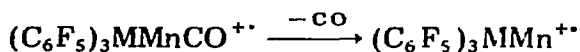
(M = Ge or Sn)



(M = Si or Ge)

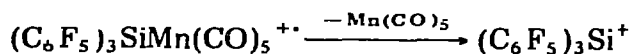


(M = Si, Ge or Sn)



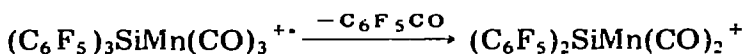
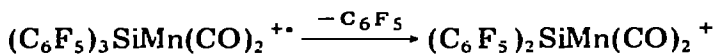
(M = Si or Ge)

In contrast to their hydrocarbon analogues, none of the spectra exhibited a metastable transition for the loss of manganese from the $(C_6F_5)_3MMn^{+*}$ ion and only the silicon derivative showed the loss of $Mn(CO)_5$ from the molecular ion.

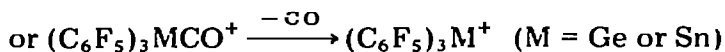
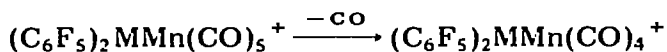


This suggests that in these derivatives the major mode of fragmentation is not by cleavage of the metal-metal bond followed by subsequent fragmentation of the $(C_6F_5)_3M^+$ ion, but rather by fragmentation of the ion $(C_6F_5)_3MMn^{+*}$. A comparison of their relative abundances tends to support this conclusion, since the abundances of the former are quite small even though they are not

particularly unstable. This can be shown from the mass spectra of the tetrakis-(pentafluorophenyl) derivatives of the Group IV metals [6], which show large abundances of the $(C_6F_5)_3M^+$ ion. Moreover, in the present case, the abundances of the ions containing two metals are considerably larger than those for the hydrocarbon analogues. The fact that the ions $C_6F_5^+$ and $Mn(CO)_3^+$ have the same nominal mass to charge ratio caused some problems in the identification of some of the ions. Thus the ions $(C_6F_5)_2MMn(CO)_5^+$ and $(C_6F_5)_2MMn(CO)_4^+$ can be alternatively formulated as $(C_6F_5)_3MCO^+$ and $(C_6F_5)_3M^+$ respectively, but since the mass spectra of the compounds $(C_6F_5)_3MFe(CO)_2Cp$ [26] exhibit peaks that can only be due to the loss of a C_6F_5 group an analogous process is assumed to have taken place in this case. This is further supported in the case of the silicon derivative by the appearance of the appropriate metastable peaks for the transitions:

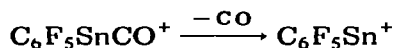


Furthermore metastable peaks corresponding to the transitions:



were observed. The former is assumed to be correct since the metastable transition for the loss of the first carbonyl group from an ion containing the $Mn(CO)_5$ group is generally very intense, even from weak precursor ions. The contribution of the $(C_6F_5)_2MMn(CO)_4^+$ ions to $(C_6F_5)_3M^+$ could not be measured by an exact mass measurement since the abundances of this ion are too low but it is assumed that the major proportion is due to the $(C_6F_5)_3M^+$ ion.

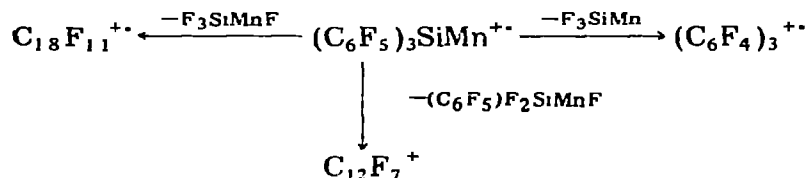
However, the tin derivative did show the transition:



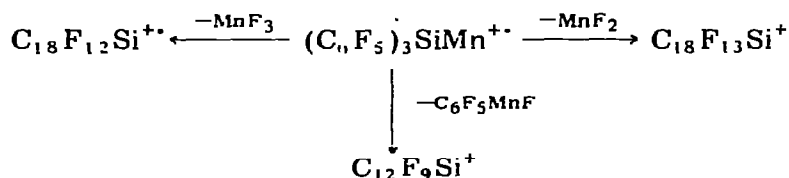
and this is assumed to be correct since its alternative formulation as $SnMn(CO)_5^+$ is rather unlikely and no ions or metastable peaks for the loss of one or more carbonyl groups were observed.

The mass spectrum of the silicon derivative is extremely complex, thus making the assignment of some of the peaks uncertain or impossible and this results in a rather low total percentage abundance (81% as opposed to over 90% for the other two derivatives). No attempts will be made to describe all of the metastable transitions as many of these first involve a fluorocarbon residue which fragments by the characteristic loss of F, CF_2 , CF_3 , C_6F_3 , C_6F_4 , C_5F etc. found in the mass spectra of other fluorocarbon derivatives [15-19]. The major fragmentation route is dominated by the very intense

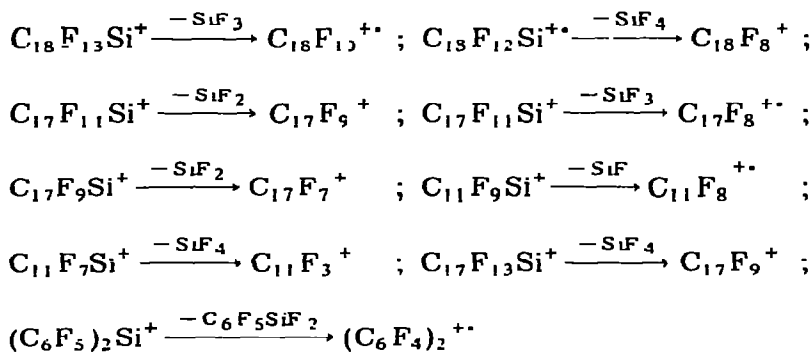
$(C_6F_5)_3SiMn^{++}$ ion, while the relatively weak $(C_6F_5)_3Si^+$ ion unlike its hydrocarbon analogue plays a negligible role. There are two main fragmentation paths for the former ion, the first of which involves the loss of a silicon and manganese fluoride species to give a fluorocarbon ion:



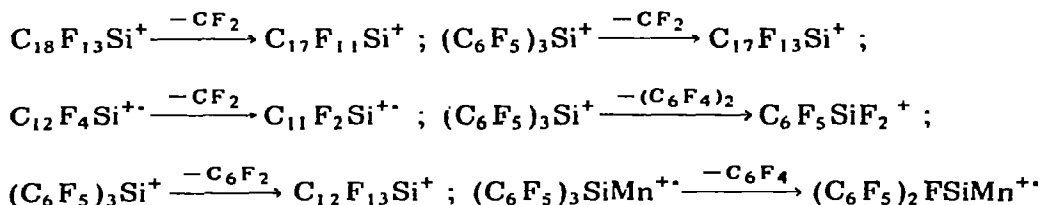
The second route is by the loss of a manganese fluoride species to give a fluorocarbon-silicon ion:



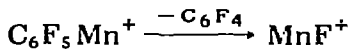
which then further fragments by the loss of a silicon fluoride species to give a fluorocarbon ion. The latter is probably responsible for the very much higher abundances of these ions compared to those of the hydrocarbon ions formed in the spectra of the triphenyl derivatives.



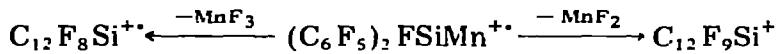
Due to the high stability of the SiF_4 and SiF_2 [27] species, this process is probably more important than the loss of a fluorocarbon radical, especially C_6F_4 , which tends to become more dominant for the heavier members of Group IV, but nevertheless such processes were observed.



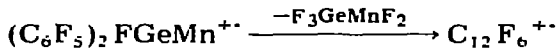
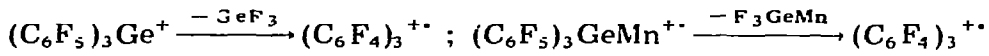
The $C_6F_5Mn^+$ ion in this as in other cases fragmented by the loss of C_6F_4 to give the MnF^+ ion:



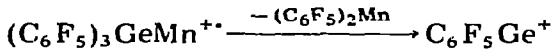
while the extremely weak $(C_6F_5)_2FSiMn^{+\bullet}$ ion was observed to lose MnF_2 and MnF_3 in a similar way to that described for $(C_6F_5)_3SiMn^{+\bullet}$.



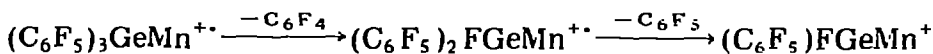
The spectrum of the germanium compound is not as complex but some of the ions have clearly arisen by the same processes as those described for the silicon compound, and in particular those involving the loss of a germanium and manganese fluoride species.



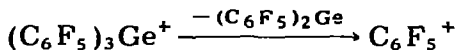
However, the high abundance of the $C_6F_5Ge^+$ ion and the observation of the appropriate metastable peak for the transition:



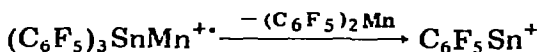
suggests that this route is determining the fragmentation. Unlike the silicon compound, there is only a small tendency for this compound to fragment by the loss of a germanium fluoride species, the major mode of fragmentation being the loss of C_6F_4 and C_6F_5 radicals, neither of which were found to be very common for the silicon derivative.



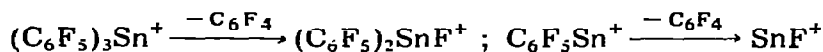
The loss of $(C_6F_5)_2Ge$ was also observed:



For the tin derivative, the spectrum is simplified even further and nearly all the ion current is carried by metal-containing ions. As for the germanium derivative the dominant fragmentation mode appears to be the loss of $(C_6F_5)_2Mn$ from the $(C_6F_5)_3SnMn^{+\bullet}$ ion



while the loss of C_6F_4 radicals appears to be the sole process for the production of $(C_6F_5)_2SnF^+$ and SnF^+ ions and is thus similar to those observed in the mass spectra of other pentafluorophenyltin compounds [16, 17].



The ratio of the abundances of the $C_6F_5M^+$ ions to those of the MF^+ ions tends to support this proposal, but although the appropriate metastable transitions for the formation of MnF^+ ions from $C_6F_5Mn^+$ were observed in the germanium and tin derivatives, the relatively large abundance of the MnF^+ ion in the spectrum of the silicon derivative suggests that some other process might be responsible in this case.

In contrast to the spectra of the hydrocarbon derivatives the abundances of the $Mn(CO)_n^+$ ($n = 0$ to 5) ion in these derivatives tended to be larger and in some spectra they fragmented by the successive loss of carbonyl groups.



Although none of the compounds contain hydrogen, there are ions present that can only be reasonably assigned as $C_6F_5H^+$ and $C_6F_2H^+$. Similar ions have been observed in the spectra of other fully fluorinated derivatives [17, 18] and probably arise by the scavenging of a hydrogen atom from the background water vapour. However, although the ions $(C_6F_5)_3GeF$ and $Ph(C_6F_5)_2SiF$ observed in the mass spectrum of $Ph_2(C_6F_5)_2SiMn(CO)_5$ could be formed by a similar scavenging of fluorine radicals, the absence of the analogous ions in the spectra of the other members of the series, suggests that these ions are formed by an ion-molecule reaction, or that some thermal pyrolysis of the sample had taken place.

The $Ph_2(C_6F_5)MMn(CO)_5$ derivatives

The relative abundances are given in Table 3. Inspection of the ion identities shows that although these derivatives bear a much greater resemblance to the triphenylmetal derivatives than to their fluorocarbon analogues, the introduction of a single pentafluorophenyl group does have a profound effect upon the fragmentation pattern. The molecular ions and those ions resulting from the loss of one or more carbonyl groups are still quite weak but the loss of the first carbonyl group and of $Mn(CO)_5$ directly from the molecular ion is consistent with the observed metastable transitions in all cases.



(M = Si, Ge or Sn)

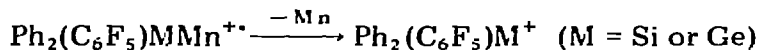
The loss of manganese from the $Ph_2(C_6F_5)MMn^{++}$ ion was observed in the spectra of the silicon and germanium derivatives and probably occurs to an equal extent in the tin derivative since the abundance of the daughter ion is higher in this case while the abundances of the parent ions remain essentially constant.

TABLE 3

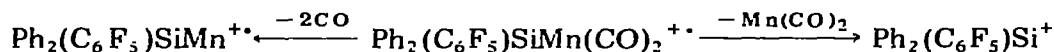
THE 70 eV MASS SPECTRA OF $\text{Pb}_2(\text{C}_6\text{F}_5)\text{MMn}(\text{CO})_5$

Ion	Relative abundance (%)			Ion	Relative abundance (%)		
	Si	Ge	Sn		Si	Ge	Sn
<i>(a) Ions containing two metals</i>							
$\text{Pb}_2(\text{C}_6\text{F}_5)\text{MMn}(\text{CO})_5^{++}$	1.5	0.4	2.0	$\text{Pb}_2(\text{F})\text{MMn}^{++}$		4.0	2.1
$\text{Pb}_2(\text{C}_6\text{F}_5)\text{MMn}(\text{CO})_4^{++}$	1.5	0.4	1.0	$\text{Pb}(\text{F})\text{MMn}^+$		0.2	
$\text{Pb}_2(\text{C}_6\text{F}_5)\text{MMn}(\text{CO})_2^{++}$	0.5	0.2		FMMn^{++}		a	b
$\text{Pb}_2(\text{C}_6\text{F}_5)\text{MMn}^{++}$	6.8	7.9	6.7				
<i>(b) Ions containing one metal</i>							
$\text{Pb}_2(\text{C}_6\text{F}_5)\text{M}^+$	12.6	17.4	20.6	$\text{C}_6\text{H}_3\text{M}^+$	0.3		
$\text{C}_{18}\text{H}_9\text{F}_5\text{M}^{++}$	0.6			$\text{C}_4\text{H}_3\text{M}^+$	0.6	2.4	0.5
$\text{C}_{18}\text{H}_8\text{F}_5\text{M}^+$	0.1			C_2HM^+			0.2
$\text{C}_{18}\text{H}_{10}\text{F}_4\text{M}^+$		0.5		MF^+	4.0	3.8	4.5
$\text{Pb}(\text{C}_6\text{F}_5)\text{MF}^+$		3.5	1.0	M^{++}			4.4
$\text{Pb}(\text{C}_6\text{F}_5)\text{M}^{++}$	0.6			$\text{C}_6\text{F}_5\text{Mn}^{++}$		0.2	0.2
$\text{C}_{12}\text{H}_5\text{F}_4\text{M}^+$	1.2			$\text{Mn}(\text{CO})_5^+$	0.1	0.2	0.4
$\text{C}_{12}\text{H}_4\text{F}_4\text{M}^{++}$			0.4	$\text{Mn}(\text{CO})_4^+$	0.4	0.2	0.3
Pb_2MF^+	16.4	5.2	1.9	$\text{Mn}(\text{CO})_3^+$	0.2	0.2	c
$\text{C}_{12}\text{H}_9\text{MF}^{++}$	0.3			$\text{Mn}(\text{CO})_2^+$	0.4	0.3	0.5
$\text{C}_{12}\text{H}_8\text{MF}^+$	1.6			MnCO^+	0.7	0.8	0.8
$\text{C}_{12}\text{H}_7\text{MF}^{++}$	0.2			PbMn^{++}	0.7	1.1	0.6
Pb_2M^{++}		0.7	0.1	MnF_2^+	0.2		
$\text{C}_{12}\text{H}_9\text{M}^+$	0.9	0.7	0.3	MnF^{++}	1.6	1.6	0.9
$\text{C}_{10}\text{H}_7\text{M}^+$	0.3			MnH^{++}	0.4	0.2	0.2
$\text{C}_8\text{H}_5\text{M}^+$	0.3			Mn^+	6.3	5.8	3.6
PbM^+	1.6	22.7	26.5				
<i>(c) Hydrocarbon/fluorocarbon ions</i>							
$\text{C}_{18}\text{F}_2\text{H}_{10}^{++}$	2.0			$\text{C}_6\text{F}_4\text{H}^+$	0.6		0.3
$\text{PbC}_6\text{F}_5^{++}$	1.9	1.0	0.2	$\text{C}_6\text{F}_4^{++}$	0.1	0.2	0.3
$(\text{C}_6\text{F}_4)(\text{C}_6\text{H}_4)^{++}$	1.0			$\text{C}_5\text{F}_2\text{H}^+$	0.7	0.6	0.9
$\text{C}_{12}\text{F}_3\text{H}_5^+$	0.4			C_5F^+	0.6	0.1	
$\text{C}_{12}\text{F}_2\text{H}_5^+$	1.2			$\text{C}_6\text{H}_6^{++}$	0.6	0.3	2.1
Pb_2^{++}	0.5	0.1	0.5	C_6H_5^+	3.1	2.4	1.7
$(\text{C}_6\text{H}_4)_2^{++}$	0.5		0.2	C_4H_3^+	1.8	1.6	1.7
$\text{C}_6\text{F}_5\text{H}^{++}$	1.0	0.7	1.0	$\text{C}_4\text{H}_2^{++}$	0.4	0.4	0.2
C_6F_5^+d							

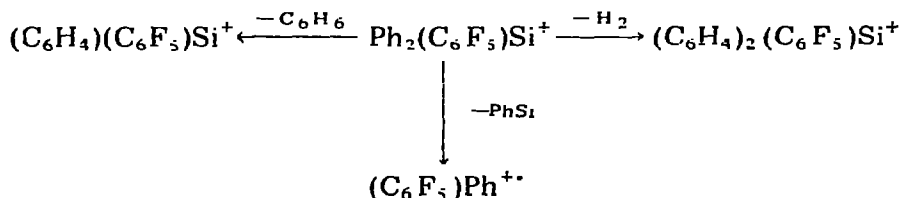
^a Overlapped with $\text{C}_6\text{F}_4^{++}$ and $\text{Pb}^{71}\text{Ge}^+$. ^b Overlapped with $\text{Pb}^{115}\text{Sn}^+$. ^c Overlapped with $\text{F}^{120}\text{Sn}^+$.
^d Overlapped with $\text{Mn}(\text{CO})_4^+$.



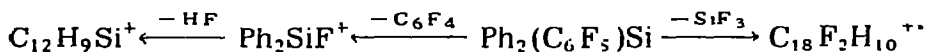
However, the spectrum of the silicon compound was the only one to show the loss of more than one carbonyl group or of a manganese carbonyl species containing less than five carbonyl groups, both these transitions occurring from the $\text{Ph}_2(\text{C}_6\text{F}_5)\text{SiMn}(\text{CO})_2^{+\bullet}$ ion.



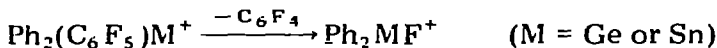
As would be expected, the silicon compound fragments in a substantially different way from either the germanium or tin analogue and, as in the case of the hydrocarbon derivative, shows the loss of benzene and PhSi , although curiously enough no ions due to the successive loss of acetylene were observed.



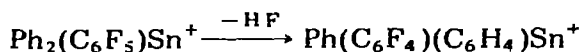
In addition several fragmentation routes characteristic of a fluorocarbon derivative were also observed, as well as the loss of HF , which is characteristic of compounds containing both hydrogen and fluorine [17, 18].



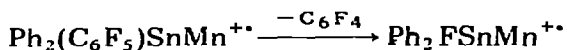
In the mass spectra of the germanium and tin derivatives the major fragmentation mode appears to be the loss of PhC_6F_5 from the $\text{Ph}_2(\text{C}_6\text{F}_5)\text{M}^+$ ion to give the PhM^+ ion as the base peak, although none of the appropriate metastable peaks were observed. However, some loss of C_6F_4 does occur, as is evident from the metastable transitions.



There is no evidence that the loss of hydrogen, benzene, PhM or a metal fluoride species occurs to any appreciable extent in either of these derivatives although the tin compound did show the loss of HF from the weak $\text{Ph}_2(\text{C}_6\text{F}_5)\text{Sn}^+$ ion.



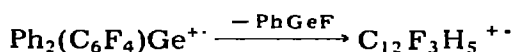
As in the case of $\text{Ph}_3\text{SnMn}(\text{CO})_5$, some fragmentation of the $\text{Ph}_2(\text{C}_6\text{F}_5)\text{MMn}^+$ ion can occur before the metal-metal bond is broken:



while the analogous germanium ion showed its subsequent fragmentation by the loss of PhMnF or Ph_2 .

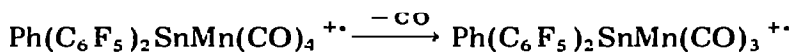
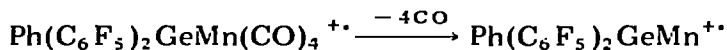
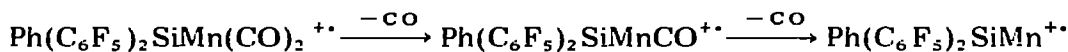
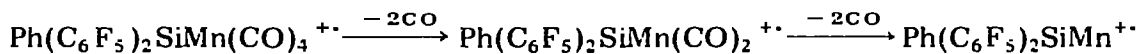
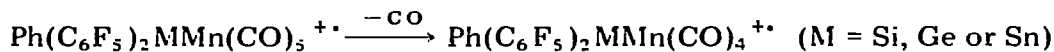


The substantial difference between the spectrum of the silicon derivative and its congeners is emphasized by noting that there are no ions of the type $\text{Ph}_2\text{FMMn}^{+\cdot}$ present in the spectrum of the silicon derivative, and this can be attributed to a higher M—C bond strength such that the Si—Mn bond will be preferentially cleaved. In both the germanium and tin derivatives the loss of a fluorine radical from the $\text{Ph}_2(\text{C}_6\text{F}_5)\text{M}^+$ ion was observed and the germanium derivative showed its subsequent fragmentation by loss of PhGeF .

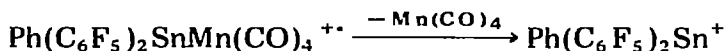


The $\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}(\text{CO})_5$ derivatives

The relative abundances for these derivatives are given in Table 4. As might be expected the spectrum of the silicon compound is characterized by a complex fragmentation pattern that gives rise to a large number of ions that contain just hydrogen and fluorine. Once again there is a distinct contrast between this spectrum and those of the germanium and tin compounds which are dominated by the very intense PhM^+ ions. As for the tris(pentafluorophenyl) derivatives the loss of the first carbonyl group from the molecular ion, as well as the loss of one or more carbonyl groups from the series $\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}(\text{CO})_n^{+\cdot}$ ($n = 0$ to 4), is observed.



The metastable supported loss of manganese from the ion $\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}^{+\cdot}$ or the loss of $\text{Mn}(\text{CO})_5$ from the molecular ion was not observed in any of the spectra, although it must occur to some extent since the $\text{Ph}(\text{C}_6\text{F}_5)_2\text{M}^+$ ions are quite abundant and the tin derivative did show the transition:

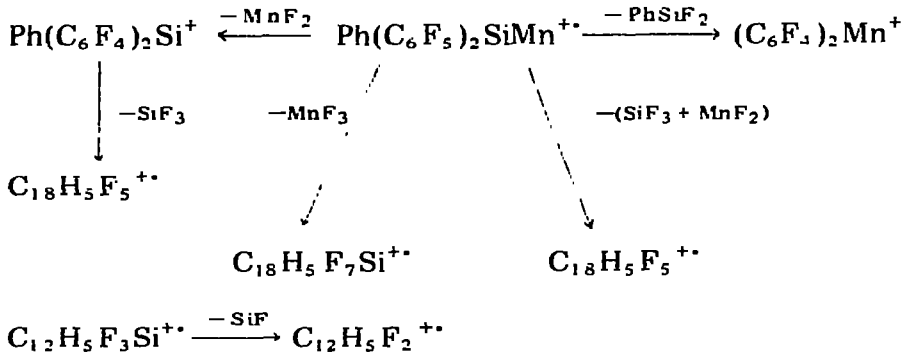


The silicon derivative showed the expected loss of silicon and manganese fluorides from the ion $\text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}^{+\cdot}$ and from its parent daughter ions:

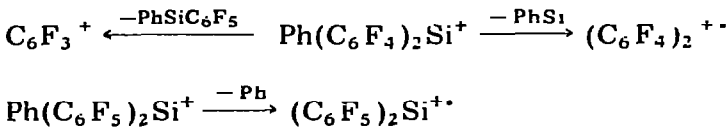
TABLE 4
THE 70 eV MASS SPECTRA OF $\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}(\text{CO})_5$

Ion	Relative abundance (%)			Ion	Relative abundance (%)		
	Si	Ge	Sn		Si	Ge	Sn
<i>(a) Ions containing two metals</i>							
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}(\text{CO})_5^{++}$	0.4	1.0	4.1	$\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMnCO}^{++}$	0.5		
$\text{Ph}(\text{C}_6\text{H}_5)_2\text{MMn}(\text{CO})_4^{++}$	3.5	2.2	1.3	$\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}^{++}$	10.6	6.2	2.9
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}(\text{CO})_3^{++}$	0.1			$\text{Ph}(\text{C}_6\text{F}_5)\text{MMn}(\text{CO})_5^+$		0.2	0.3
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}(\text{CO})_2^{++}$	1.1			$\text{F}_3\text{MMn}^{++}$			0.7
<i>(b) Ions containing one metal</i>							
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{MF}^{++}$	0.4			$(\text{C}_6\text{F}_4)_2\text{Mn}^+$	0.2		
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{M}^+$	1.6	8.2	10.6	$\text{C}_6\text{F}_5\text{Mn}^{++}$	<i>a</i>	0.1	0.4
$\text{C}_{18}\text{H}_4\text{F}_9\text{M}^+$		0.2	0.3	$\text{Mn}(\text{CO})_5^+$	0.1	0.1	0.7
$\text{C}_{18}\text{H}_5\text{F}_8\text{M}^+$	0.2			$\text{Mn}(\text{CO})_4^{+c}$			
$\text{C}_{18}\text{H}_4\text{F}_8\text{M}^{++}$	0.7			$\text{Mn}(\text{CO})_3^+$	0.2	0.2	<i>d</i>
$(\text{C}_6\text{F}_5)_2\text{MF}^+$	1.1			$\text{Mn}(\text{CO})_2^+$	0.3	0.3	0.4
$\text{Ph}(\text{C}_6\text{F}_5)\text{MF}^+$		0.9	0.8	MnCO^+	0.6	0.6	0.9
$\text{C}_6\text{F}_5\text{M}^+$	<i>a</i>	0.3	1.8	PhMn^{++}	1.8	1.1	0.7
PhMF_2^+	1.2			MnF_2^+	0.4	<i>e</i>	0.3
PhM^+	4.4	43.0	29.9	MnF^{++}	2.4	2.0	1.5
$\text{C}_4\text{H}_3\text{M}^+$	<i>b</i>	1.0	0.7	MnH^{++}	0.2	0.1	0.1
MF^+	1.0	7.3	10.0	Mn^+	3.7	4.8	4.0
M^{++}		0.5	3.2				
<i>(c) Hydrocarbon/fluorocarbon ions</i>							
$(\text{C}_6\text{F}_5)_2^{++}$	1.4			$\text{C}_6\text{F}_4\text{H}^+$	1.1		0.2
$\text{C}_{12}\text{F}_9\text{H}^{++}$	3.3			C_6F_4^+	0.3	0.4	0.2
$\text{C}_{12}\text{F}_9^+$	0.7			C_6F_3^+	0.7		
$\text{C}_{12}\text{F}_8^{++}$	2.8			$\text{C}_6\text{F}_2^{++}$	0.4		
$\text{C}_{12}\text{F}_7\text{H}^{++}$	1.0			$\text{C}_5\text{F}_2\text{H}^+$	1.3	0.6	1.1
$\text{C}_{12}\text{F}_7^+$	1.0			$\text{C}_5\text{F}_2^{++}$	0.5		
$\text{C}_{12}\text{F}_3\text{H}_5^+$	2.1	0.6		C_5F^+	0.5	0.2	0.3
$\text{C}_{12}\text{F}_2\text{H}_5^+$	2.2	0.5		$\text{C}_6\text{H}_6^{++}$	0.5	0.3	0.7
$\text{C}_{12}\text{F}_2\text{H}_4^{++}$	1.2	0.6		Ph^+	2.6	2.2	3.5
$\text{C}_6\text{F}_5\text{H}^{++}$	2.1	0.7	2.1	C_4H_3^+	1.7	1.4	2.0
C_6F_5^+	0.7	0.3	0.3	$\text{C}_4\text{H}_2^{++}$	0.4	0.4	0.4

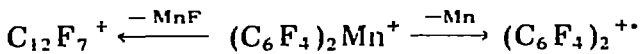
a Overlapped with $\text{Mn}(\text{CO})_5^+$. *b* Overlapped with C_5F^{++} . *c* Overlapped with C_6F_5^+ . *d* Overlapped with $\text{F}^{120}\text{Sn}^+$. *e* Overlapped with F^{73}Ge^+ .



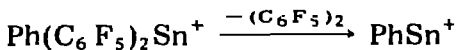
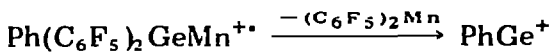
Unlike the spectra of other silicon derivatives in this work the losses of phenyl, PhSi and Ph(C₆F₅)Si were also observed and are rather unusual since these fragmentation routes are more characteristic of the heavier members of Group IV.



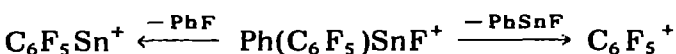
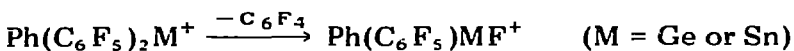
The abundance of the C₆F₅Mn⁺ ion in this spectrum was virtually zero and the only other fluorocarbon-manganese ion was observed to lose manganese or manganese fluoride.



The spectra of the germanium and tin derivatives are very comparable, and by far the most important fragmentation route appears to be the loss of (C₆F₅)₂Mn from the Ph(C₆F₅)₂MMn⁺ ion or by the loss of (C₆F₅)₂ from the Ph(C₆F₅)₂M⁺ ion to give the very intense PhM⁺ ions.



Even though only one metastable transition was observed for each derivative it is quite probable that each occurs to an equal extent since the abundances of the parent and daughter ions do not vary appreciably. As in the other pentafluorophenyl derivatives of germanium and tin, the characteristic loss of C₆F₄ and tin fluorides was observed as well as the rather unusual loss of fluorobenzene from the ion Ph(C₆F₅)SnF⁺.



The metastable transitions are listed in Table 5.

(continued on p. 179)

TABLE 5

METASTABLE TRANSITIONS (Values quoted refer to the most-abundant isotope ^{12}C , ^{28}Si , ^{74}Ge , ^{120}Sn , ^{208}Pb and ^{55}Mn)

			M^* calcd.	M^* found
<i>Ph₃MMn(CO)₅ derivatives</i>				
$\text{Ph}_3\text{SiMn}(\text{CO})_4^{++}$	$\rightarrow \text{Ph}_3\text{SiMn}(\text{CO})_2^{++} + 2\text{CO}$		321.5	322.0
$\text{Ph}_3\text{SiMn}(\text{CO})_2^{++}$	$\rightarrow \text{Ph}_3\text{SiMn}^{++} + 2\text{CO}$		266.5	266.5
$\text{Ph}_3\text{GeMn}(\text{CO})_2^{++}$	$\rightarrow \text{Ph}_3\text{GeMn}^{++} + 2\text{CO}$		311.8	312.0
$\text{Ph}_3\text{MMn}^{++}$	$\rightarrow \text{Ph}_3\text{M}^+ + \text{Mn}$	M = Si	213.6	213.5
		M = Ge	258.5	258.0
		M = Sn	303.5	303.5
$\text{Ph}_3\text{MMn}(\text{CO})_5^{++}$	$\rightarrow \text{Ph}_3\text{M}^+ + \text{Mn}(\text{CO})_5$	M = Si	147.8	148.0
		M = Sn	225.6	225.0
		M = Pb	304.0	304.0
$\text{C}_{12}\text{H}_9\text{Si}^+$	$\rightarrow \text{C}_{10}\text{H}_7\text{Si}^+ + \text{C}_2\text{H}_2$		132.7	132.8
$\text{C}_{10}\text{H}_7\text{Si}^+$	$\rightarrow \text{C}_8\text{H}_5\text{Si}^+ + \text{C}_2\text{H}_2$		107.4	107.5
$\text{C}_8\text{H}_5\text{Si}^+$	$\rightarrow \text{C}_6\text{H}_3\text{Si}^+ + \text{C}_2\text{H}_2$		82.2	82.0
$\text{C}_{10}\text{H}_9\text{Si}^+$	$\rightarrow \text{C}_8\text{H}_7\text{Si}^+ + \text{C}_2\text{H}_2$		109.3	109.3
$\text{C}_8\text{H}_7\text{Si}^+$	$\rightarrow \text{C}_6\text{H}_5\text{Si}^+ + \text{C}_2\text{H}_2$		84.2	84.3
$\text{C}_6\text{H}_5\text{Si}^+$	$\rightarrow \text{C}_4\text{H}_3\text{Si}^+ + \text{C}_2\text{H}_2$		59.4	59.3
Ph_3Si^+	$\rightarrow \text{C}_{18}\text{H}_{13}\text{Si}^+ + \text{H}_2$		255.0	255.0
$\text{C}_{18}\text{H}_{13}\text{Si}^+$	$\rightarrow \text{C}_{18}\text{H}_{11}\text{Si}^+ + \text{H}_2$		251.0	251.0
and/or Ph_3Si^+	$\rightarrow \text{C}_{18}\text{H}_{11}\text{Si}^+ + 2\text{H}_2$		251.1	251.0
PhSi^+	$\rightarrow \text{C}_6\text{H}_3\text{Si}^+ + \text{H}_2$		101.0	101.0
$\text{Ph}_2\text{Si}^{++}$	$\rightarrow \text{C}_6\text{H}_4\text{Si}^{++} + \text{C}_6\text{H}_6$		59.4	59.3
$\text{Ph}(\text{C}_6\text{H}_4)_2\text{Si}^+$	$\rightarrow (\text{C}_6\text{H}_4)_2\text{Si}^{++} + \text{Ph}$		126.0	126.0
$\text{C}_{12}\text{H}_9\text{S}^+$	$\rightarrow (\text{C}_6\text{H}_4)_2\text{Si}^{++} + \text{H}$		179.0	179.0
Ph_3Ge^+	$\rightarrow \text{C}_{18}\text{H}_{13}\text{Ge}^+ + \text{H}_2$		301.0	301.0
Ph_3Ge^+	$\rightarrow \text{C}_{12}\text{H}_9\text{Ge}^+ + \text{C}_6\text{H}_6$		168.9	159.0
Ph_3Ge^+	$\rightarrow \text{PhGe}^+ + \text{Pb}_2$		74.8	74.7
PhGe^+	$\rightarrow \text{C}_4\text{H}_3\text{Ge}^+ + \text{C}_2\text{H}_2$		103.5	104.0
PhMn^{++}	$\rightarrow \text{Mn}^+ + \text{Ph}$		22.9	22.8
$\text{Ph}_3\text{SnMn}^{++}$	$\rightarrow \text{PhSn}^+ + \text{Ph}_2\text{Mn}$		95.5	95.5
$\text{Ph}_3\text{SnMn}^{++}$	$\rightarrow \text{PhSnMn}^{++} + \text{Ph}_2$		156.4	156.3
Ph_3Sn^+	$\rightarrow \text{PhSn}^+ + \text{Ph}_2$		110.5	110.5
PhSn^+	$\rightarrow \text{Sn}^{++} + \text{Ph}$		73.0	73.0
$\text{Ph}_2\text{PbMn}(\text{CO})_5^+$	$\rightarrow \text{Ph}_2\text{PbMn}(\text{CO})_3^+ + 2\text{CO}$		450.6	451.0
$\text{Ph}_3\text{PbMn}^{++}$	$\rightarrow \text{Ph}_3\text{Mn}^{++} + \text{Pb}$		165.6	165.5
$\text{Ph}_3\text{Mn}^{++}$	$\rightarrow \text{PhMn}^{++} + \text{Ph}_2$		60.9	61.0
Ph_3Pb^+	$\rightarrow \text{PhPb}^+ + \text{Ph}_2$		185.0	184.3
Ph_2PbMn^+	$\rightarrow \text{PbMn}^+ + \text{Ph}_2$		165.9	166.0
PhPb^+	$\rightarrow \text{Pb}^+ + \text{Ph}$		101.8	152.0
PhCO^+	$\rightarrow \text{Ph}^+ + \text{CO}$		56.5	56.4

(continued)

TABLE 5 (continued)

		<i>M</i> * calcd. <i>M</i> * found		
<i>(C₆F₅)₃MMn(CO)₅ derivatives</i>				
$(C_6F_5)_3MMn(CO)_5^{+}$	$\rightarrow (C_6F_5)_3MMn(CO)_4^{+} + CO$	<i>M</i> = Si	669.0	669.0
		<i>M</i> = Ge	715.0	715.0
		<i>M</i> = Sn	760.9	761.0
$(C_6F_5)_3SnMn(CO)_4^{+}$	$\rightarrow (C_6F_5)_3SnMn^{+} + 4 CO$		607.3	607.0
$(C_6F_5)_3SiMn(CO)_5^{+}$	$\rightarrow (C_6F_5)_3SiMn(CO)_3^{+} + 2 CO$		616.3	616.0
$(C_6F_5)_3MMn(CO)_5^{+}$	$\rightarrow (C_6F_5)_3MMnCO^{+} + 4 CO$	<i>M</i> = Ge	562.3	562.0
		<i>M</i> = Sn	607.3	607.0
$(C_6F_5)_3MMn(CO)_4^{+}$	$\rightarrow (C_6F_5)_3MMn(CO)_2^{+} + 2 CO$	<i>M</i> = Si	616.3	616.0
		<i>M</i> = Ge	634.2	634.0
$(C_6F_5)_3MMn(CO)_4^{+}$	$\rightarrow (C_6F_5)_3MMnCO^{+} + 3 CO$	<i>M</i> = Si	538.1	538.0
		<i>M</i> = Ge	583.5	583.5
		<i>M</i> = Sn	628.7	629.0
$(C_6F_5)_3MMnCO^{+}$	$\rightarrow (C_6F_5)_3MMn^{+} + CO$	<i>M</i> = Si	557.3	558.0
		<i>M</i> = Ge	603.2	603.0
$(C_6F_5)_3SiMn(CO)_5^{+}$	$\rightarrow (C_6F_5)_3Si^{+} + Mn(CO)_5$		385.5	385.0
$(C_6F_5)_3SiMn(CO)_2^{+}$	$\rightarrow (C_6F_5)_2SiMn(CO)_2^{+} + C_6F_5$		349.6	300.0
$(C_6F_5)_3SiMn(CO)_3^{+}$	$\rightarrow (C_6F_5)_2SiMn(CO)_2^{+} + C_6F_5CO$		334.9	335.0
$(C_6F_5)_2MMn(CO)_5^{+}$	$\rightarrow (C_6F_5)_2MMn(CO)_4^{+} + CO$	<i>M</i> = Ge	548.3	548.0
		<i>M</i> = Sn	595.0	595.0
$C_6F_5SnCO^{+}$	$\rightarrow C_6F_5Sn^{+} + CO$		261.5	261.0
$(C_6F_5)_3SiMn^{+}$	$\rightarrow C_{18}F_{10}^{+} + F_3SiMnF$		337.5	338.0
$(C_6F_5)_3SiMn^{+}$	$\rightarrow (C_6F_4)_3^{+} + F_3SiMn$		281.5	282.0
$(C_6F_5)_3SiMn^{+}$	$\rightarrow C_{12}F_7^{+} + (C_6F_5)_2F_2SiMnF$		131.5	131.3
$(C_6F_5)_3SiMn^{+}$	$\rightarrow C_{18}F_{13}Si^{+} + MnF_2$		412.8	413.0
$(C_6F_5)_3SiMn^{+}$	$\rightarrow C_{18}F_{12}Si^{+} + MnF_3$		381.5	381.5
$(C_6F_5)_3SiMn^{+}$	$\rightarrow C_{12}F_9Si^{+} + C_6F_5MnF$		201.5	202.0
$C_{18}F_{12}Si^{+}$	$\rightarrow C_{18}F_8^{+} + SiF_4$		286.9	287.0
$C_{18}F_{13}Si^{+}$	$\rightarrow C_{18}F_9^{+} + SiF_4$		305.0	305.0
$C_{17}F_{11}Si^{+}$	$\rightarrow C_{17}F_9^{+} + SiF_2$		318.9	319.0
$C_{17}F_{11}Si^{+}$	$\rightarrow C_{17}F_8^{+} + SiF_3$		287.4	287.0
$C_{17}F_9Si^{+}$	$\rightarrow C_{17}F_7^{+} + SiF_2$		243.7	244.0
and/or $C_{11}F_9Si^{+}$	$\rightarrow C_{11}F_8^{+} + SiF$		243.7	244.0
$C_{11}F_7Si^{+}$	$\rightarrow C_{11}F_3^{+} + SiF_4$		121.9	122.0
$C_{17}F_{13}Si^{+}$	$\rightarrow C_{17}F_9^{+} + SiF_4$		293.6	293.5
$(C_6F_5)_3Si$	$\rightarrow (C_6F_4)_2^{+} + C_6F_5SiF_2$		165.5	166.0
$C_{18}F_{13}Si^{+}$	$\rightarrow C_{17}F_{11}Si^{+} + CF_2$		396.0	396.0
$(C_6F_5)_3Si^{+}$	$\rightarrow C_{17}F_{13}Si^{+} + CF_2$		433.7	434.0
$C_{12}F_9Si^{+}$	$\rightarrow C_{11}F_7Si^{+} + CF_2$		250.3	250.5
$(C_6F_5)_3Si^{+}$	$\rightarrow C_6F_6SiF_2^{+} + (C_6F_4)_2$		102.5	102.5
$(C_6F_5)_3Si^{+}$	$\rightarrow C_{12}F_{13}Si^{+} + C_6F_2$		331.9	332.0
$(C_6F_5)_3SiMn^{+}$	$\rightarrow (C_6F_5)_2FSiMn^{+} + C_6F_4$		325.5	326.0
$C_6F_5Mn^{+}$	$\rightarrow MnF^{+} + C_6F_4$		24.7	24.7

(continued)

TABLE 5 (continued)

		<i>M</i> ⁺ calcd.	<i>M</i> ⁺ found
$(C_6F_5)_2FSiMn^{++}$	$\rightarrow C_{12}F_9Si^+ + MnF_2$	269.8	270.0
$(C_6F_5)_2FSiMn^{++}$	$\rightarrow C_{12}F_8^{++} + MnF_3$	240.5	240.7
$(C_6F_5)_3Ge^+$	$\rightarrow (C_6F_4)_3^{++} + GeF_3$	342.8	343.0
$(C_6F_5)_3GeMn^{++}$	$\rightarrow (C_6F_4)_3^{++} + F_3GeMn$	312.9	313.0
$(C_6F_5)_2FGeMn^{++}$	$\rightarrow C_{12}F_6^{++} + F_3GeMnF_2$	138.1	138.0
$(C_6F_5)_3GeMn^{++}$	$\rightarrow C_6F_5Ge^+ + (C_6F_5)_2Mn$	92.2	92.0
$(C_6F_5)_3GeMn^{++}$	$\rightarrow (C_6F_5)_2FGeMn^{++} + C_6F_5$	368.7	369.0
$(C_6F_5)_2FGeMn^{++}$	$\rightarrow F(C_6F_5)GeMn^+ + C_6F_5$	317.1	317.0
$(C_6F_5)_3Ge^+$	$\rightarrow (C_6F_5)_2GeF^+ + C_6F_4$	205.9	206.0
$C_6F_5Ge^+$	$\rightarrow GeF^+ + C_6F_4$	35.9	35.9
$(C_6F_5)_3Ge^+$	$\rightarrow C_6F_5^+ + (C_6F_5)_2Ge$	48.5	48.5
$(C_6F_5)_3SnMn^{++}$	$\rightarrow C_6F_5Sn^+ + (C_6F_5)_2Mn$	121.9	122.0
$(C_6F_5)_3Sn^+$	$\rightarrow (C_6F_5)_2F_2Sn^+ + C_6F_4$	360.3	360.0
$C_6F_5Sn^+$	$\rightarrow SnF^+ + C_6F_4$	67.3	67.3
$Mn(CO)_5^+$	$\rightarrow Mn(CO)_4^+ + CO$	143.0	143.0
$Mn(CO)_4$	$\rightarrow Mn(CO)_3^+ + CO$	115.7	115.7
<i>Ph₂(C₆F₅)MMn(CO)₅ derivatives</i>			
$Ph_2(C_6F_5)MMn(CO)_5^{++}$	$\rightarrow Ph_2(C_6F_5)MMn(CO)_4^{++} + CO$	<i>M</i> = Si 489.4 <i>M</i> = Ge 535.5 <i>M</i> = Sn 581.2	489.0 536.0 581.0
$Ph_2(C_6F_5)MMn(CO)_5^{++}$	$\rightarrow Ph_2(C_6F_5)M^+ + Mn(CO)_5$	<i>M</i> = Si 223.9 <i>M</i> = Ge 264.4 <i>M</i> = Sn 305.8	224.0 264.0 306.0
$Ph_2(C_6F_5)MMn^{++}$	$\rightarrow Ph_2(C_6F_5)M^+ + Mn$	<i>M</i> = Si 301.5 <i>M</i> = Ge 354.6	302.0 355.0
$Ph_2(C_6F_5)SiMn(CO)_2^{++}$	$\rightarrow Ph_2(C_6F_5)SiMn^{++} + 2CO$	354.8	355.0
$Ph_2(C_6F_5)SiMn(CO)_2^{++}$	$\rightarrow Ph_2(C_6F_5)Si^+ + Mn(CO)_2$	264.8	265.0
$Ph_2(C_6F_5)Si^+$	$\rightarrow (C_6H_4)(C_6F_5)Si^+ + C_6H_6$	210.4	210.0
$Ph_2(C_6F_5)Si^+$	$\rightarrow (C_6H_4)_2(C_6F_5)Si^+ + H_2$	334.7	335.0
$Ph_2(C_6F_5)Si^+$	$\rightarrow C_6F_5 \cdot C_6H_5^{++} + PhSi$	170.6	170.5
$Ph_2(C_6F_5)Si^+$	$\rightarrow C_{18}F_2H_{10}^{++} + SiF_3$	199.7	200.0
$Ph_2(C_6F_5)Si^+$	$\rightarrow Ph_2SiF^+ + C_6F_6$	116.8	116.0
Ph_2SiF^+	$\rightarrow C_{12}H_9Si^+ + HF$	163.0	163.0
$Ph_2(C_6F_5)M^+$	$\rightarrow Ph_2MF^+ + C_6F_4$	<i>M</i> = Ge 154.5 <i>M</i> = Sn 194.7	154.0 195.0
$Ph_2(C_6F_5)Sn^+$	$\rightarrow Ph(C_6F_5)(C_6H_4)Sn^+ + HF$	401.9	402.0
$Ph_2(C_6F_5)SnMn^{++}$	$\rightarrow Ph_2FSnMn^{++} + C_6F_4$	244.2	244.0
Pb_2FGeMn^{++}	$\rightarrow FGeMn^{++} + Pb_2$	72.5	72.5
Pb_2FGeMn^{++}	$\rightarrow PbGe^+ + PbMnF$	75.5	75.6
$Pb_2(C_6F_4)Ge^{++}$	$\rightarrow C_{12}F_3H_5^{++} + PhGeF$	113.5	113.5

(continued)

TABLE 5 (continued)

		M^* calcd. M^* found	
<i>Ph(C₆F₅)₂MMn(CO)₅ derivatives</i>			
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}(\text{CO})_5^{++}$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_5)_2\text{MMn}(\text{CO})_6^{++} + \text{CO}$	M = Si	579.2 580.0
		M = Ge	625.2 625.0
		M = Sn	671.1 671.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}(\text{CO})_4^{++}$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}(\text{CO})_2^{++} + 2\text{CO}$		499.2 499.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}(\text{CO})_2^{++}$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}^{++} + 2\text{CO}$		443.7 444.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}(\text{CO})_2^{++}$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMnCO}^{++} + \text{CO}$		495.0 495.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMnCO}^{++}$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}^{++} + \text{CO}$		467.5 468.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{GeMn}(\text{CO})_4^{++}$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_5)_2\text{GeMn}^{++} + 4\text{CO}$		447.2 447.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SnMn}(\text{CO})_4^{++}$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_5)_2\text{SnMn}(\text{CO})_3^{++} + \text{CO}$		643.0 643.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SnMn}(\text{CO})_4^{++}$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_5)_2\text{Sn}^{++} + \text{Mn}(\text{CO})_4$		492.0 492.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}^{++}$	$\rightarrow (\text{C}_6\text{F}_4)_2\text{Mn}^+ + \text{PhSiF}_2$		249.3 249.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}^{++}$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_4)_2\text{Si}^+ + \text{MnF}_2$		295.4 295.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}^{++}$	$\rightarrow \text{C}_{18}\text{H}_5\text{F}_7\text{Si}^{++} + \text{MnF}$		202.1 202.4
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{SiMn}^{++}$	$\rightarrow \text{C}_{18}\text{H}_5\text{F}_5^{++} + \text{F}_3\text{SiMnF}_2$		325.5 326.0
$\text{Ph}(\text{C}_6\text{F}_4)_2\text{Si}^+$	$\rightarrow \text{C}_{18}\text{H}_5\text{F}_5^{++} + \text{SiF}_3$		218.6 219.0
$\text{C}_{12}\text{H}_5\text{F}_3\text{Si}^{++}$	$\rightarrow \text{C}_{12}\text{H}_5\text{F}_2^+ + \text{SiF}$		149.4 149.0
$\text{Ph}(\text{C}_6\text{F}_4)_2\text{Si}^+$	$\rightarrow \text{C}_6\text{F}_3^+ + \text{Ph}(\text{C}_6\text{F}_5)\text{Si}$		41.5 41.5
$\text{Ph}(\text{C}_6\text{F}_4)_2\text{Si}^+$	$\rightarrow (\text{C}_6\text{F}_4)_2^{++} + \text{PhSi}$		218.6 219.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{Si}^+$	$\rightarrow (\text{C}_6\text{F}_5)_2\text{Si}^{++} + \text{Ph}$		298.5 298.0
$(\text{C}_6\text{F}_4)_2\text{Mn}^+$	$\rightarrow (\text{C}_6\text{F}_4)_2^{++} + \text{Mn}$		249.6 250.0
$(\text{C}_6\text{F}_4)_2\text{Mn}^+$	$\rightarrow \text{C}_{12}\text{F}_7^+ + \text{MnF}$		218.6 219.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{GeMn}^{++}$	$\rightarrow \text{PhGe}^+ + (\text{C}_6\text{F}_5)_2\text{Mn}$		42.0 42.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{Sn}^+$	$\rightarrow \text{PhSn}^+ + (\text{C}_6\text{F}_5)_2$		73.1 73.0
$\text{Ph}(\text{C}_6\text{F}_5)_2\text{M}^+$	$\rightarrow \text{Ph}(\text{C}_6\text{F}_5)_2\text{MF}^+ + \text{C}_6\text{F}_4$	M = Ge	234.2 234.0
		M = Sn	276.2 276.3
$\text{Ph}(\text{C}_6\text{F}_5)\text{SnF}^+$	$\rightarrow \text{C}_6\text{F}_5\text{Sn}^+ + \text{PhF}$		338.5 338.4
$\text{Ph}(\text{C}_6\text{F}_5)\text{SnF}^+$	$\rightarrow \text{C}_6\text{F}_5^+ + \text{PhSnF}$		72.8 73.0

Bond strength measurements

If there is no excitational or excess kinetic energy involved in a transition of the type: $\text{Ph}_3\text{SnX}^{++} \rightarrow \text{Ph}_3\text{Sn}^+ + \text{X}^*$ where X is a transition metal carbonyl species, the molecular metal-metal bond energy $D(\text{Sn}-\text{X})$ is given by the expression:

$$D(\text{Sn}-\text{X}) = AP(\text{Ph}_3\text{Sn}^+) - IP(\text{Ph}_3\text{Sn}^*)$$

and thus by measuring the appearance potential (*AP*) of the Ph_3Sn^+ ion, the bond dissociation energy of the tin—manganese or tin—iron bond may be calculated if the ionization potential (*IP*) of the Ph_3Sn radical is known. The early value of 6.0 ± 0.4 eV reported by Glockling [28] for this ionization potential appears to be too low since it is reasonable to expect that the real value should be close to that for Me_3Sn at 6.77 eV [6, 29] and thus on this basis the more recent value of 6.9 ± 0.1 eV [30] appears to be more reliable. In this work the error weighted value between the two of 6.85 ± 0.1 eV was used. The effect of any excitational energy on the value for $D(\text{Sn}-\text{X})$ is difficult to measure but is probably less than 0.2 eV, but the absence of any excess kinetic energy can be deduced from Stevenson's rule [31] which states that if the *IP* of X is greater than that for Ph_3Sn then there is no excess kinetic energy involved. This is true in the present case since the *IP* of both $\text{Mn}(\text{CO})_5$ (8.44 ± 0.1 eV) [32] and $\text{Fe}(\text{CO})_2\text{Cp}$ (7.70 ± 0.1 eV) [33] are greater than that for Ph_3Sn . However, processes other than the cleavage of the Sn—X bond could also lead to the formation of the Ph_3Sn radical and since these processes will have different energies, these will lead to different values in the *AP* of the Ph_3Sn ion. Although the metastable supported loss of both $\text{Mn}(\text{CO})_5$ and $\text{Fe}(\text{CO})_2\text{Cp}$ [26] radicals from the molecular ions was observed it has also been shown that the Ph_3Sn ion could arise by a simultaneous or consecutive loss of all carbonyl groups and then manganese or FeCp radicals, respectively. However, studies on the similar systems $\text{Me}_3\text{SiMn}(\text{CO})_5$ [34] and $\text{Me}_3\text{GeMo}(\text{CO})_3\text{Cp}$ [6] show that the energy required for the removal of the first carbonyl group is about the same as that required for the breaking of the metal—metal bond and consequently is not likely to contribute to the formation of the trimethyl-silicon or -germanium radical at least at the threshold region where *AP*'s are measured. The Ph_3Sn ion could also arise by thermal decomposition of the sample but this again is not considered likely since studies on the system $\text{Me}_3\text{MM}'(\text{CO})_3\text{Cp}$ ($\text{M} = \text{Ge}$ or Sn and $\text{M}' = \text{Cr}$, Mo or W) show no variation in appearance potential within experimental error over a temperature range of 100 to 150°C [6], and a thermal pyrolysis study on $\text{Me}_3\text{SnMn}(\text{CO})_5$ [34] shows that thermal decomposition does not begin until a source temperature of 300°C has been reached. In view of the greater thermal stability of $\text{Ph}_3\text{SnMn}(\text{CO})_5$ or $\text{Ph}_3\text{SnFe}(\text{CO})_2\text{Cp}$ to either of these compounds, thermal decomposition of the sample can be ruled out and this assumption is further supported by an analysis of the shape of the ionization efficiency (*IE*) curve for the Ph_3Sn ion. If this ion was being produced from more than one source, either by electron impact or thermal means, then the *IE* curve would exhibit a long tail at the point of vanishing ion current [35], but in both cases the *IE* curve for this ion was nearly parallel to that for the xenon standard, for which only one process is possible, thus suggesting that only one process was responsible for its formation.

From the measured *AP*'s of the Ph_3Sn ion derived from $\text{Ph}_3\text{SnMn}(\text{CO})_5$ (9.00 ± 0.24 eV) and $\text{Ph}_3\text{SnFe}(\text{CO})_2\text{Cp}$ (9.16 ± 0.21 eV) the bond dissociation energies of the Sn—Mn and Sn—Fe bonds were calculated to be 61 ± 8 and 54 ± 9 kcal mol⁻¹, respectively, and these values are to be compared to those for some similar compounds as shown in Table 6. However, as pointed out in

TABLE 6
BOND DISSOCIATION ENERGIES FOR SOME GROUP IV—TRANSITION METAL BONDS

Compound	$D(M-M)$ (kcal mol ⁻¹)	Reference
Me ₃ SiMn(CO) ₅	57 ± 7	34
	61	11
Me ₃ GeMn(CO) ₅	62.5 ± 8	34
	55	11
Me ₃ SnMn(CO) ₅	55 ± 7	34
	58	11
Me ₃ PbMn(CO) ₅	47 ± 12	34
Me ₃ GeCr(CO) ₃ Cp	47	6
Me ₃ SnCr(CO) ₃ Cp	53.5	6
Me ₃ GeMo(CO) ₃ Cp	60	6
Me ₃ SnMo(CO) ₃ Cp	71	6
Me ₃ GeW(CO) ₃ Cp	65	6
Me ₃ SnW(CO) ₃ Cp	76	6
Ph ₃ SnMn(CO) ₅	61 ± 8	this work
Ph ₃ SnFe(CO) ₂ Cp	54 ± 9	this work

an earlier paper [36], these values are not solely responsible for the different behaviour of these compounds towards the halogens or hydrogen halides and if a realistic error in the measurement of 10 to 15% is assumed in all cases then these values are not substantially different from each other. Thus, the values of metal—metal bond energies obtained by this method are not particularly meaningful in correlations of data collected from other sources, in explaining differences in their chemical reactivities.

Mainly on the basis of infrared and crystallographic evidence the strength of the metal—metal bond in such compounds has been thought to vary according to the nature of the substituents on the Group IV atom and to a lesser extent upon the Group IV atom itself. As the latter become better electron acceptors, the amount of π -bonding in the metal—metal bond increases and this may be reflected as an increase in the overall strength of the metal—metal bond. However, thermochemical or electron impact experiments designed to probe the nature of this bond are severely limited by the availability of the data needed to calculate such bond strengths, and at the outset of this investigation it was hoped that a careful analysis of the fragmentation patterns would at least give some indications of a variation in the metal—metal bond strength as phenyl is successively replaced by pentafluorophenyl and Si is replaced by Ge or Sn. This now appears not to be the case, since although some of the fragmentation routes can be ascribed to changes in the metal—carbon or metal—metal bond strengths, some anomalies are also apparent and the spectra of the germanium and tin derivatives are very similar thus suggesting little difference in either of the two bond strengths between the

two compounds. This is not unexpected, since the data given in Table 6 show differences in Ge—M and Sn—M bond strengths which are not significant relative to an assumed minimum error of at least ± 5 kcal mol⁻¹. The effect of replacing a methyl group with a better acceptor ligand such as fluoride or chloride has only been studied for some Si—Co bonds and is reported to lead to bond strengths in the range of 70 to 100 kcal mol⁻¹ [13] thus tending to support the hypothesis for an extensive increase in π -bonding for these compounds. However, this proposal is not supported by some molecular orbital calculations which show only a small amount of π -bonding in this bond [37] and by some Mössbauer studies which give no evidence for any increase in the π -bonding in the Sn—Fe bond as phenyl is successively replaced by chlorine [38]. Thus, although the change in fragmentation of the Ph₃Si ion compared to that for the Ph₃Sn or Ph₃Pb ion can be ascribed to a relative weakening of the metal—carbon bond, the ready loss of PhC₆F₅ rather than Ph₂ from the Ph₂(C₆F₅)M ions or the loss of (C₆F₅)₂ from the Ph(C₆F₅)₂M ions (M = Ge or Sn) is not expected. It would be reasonable to suppose that the C₆F₅—M bond is stronger than the Ph—M bond since it has been shown that the latter can be selectively cleaved by chlorine [36]. The larger abundances of the ions containing two metals encountered for the tris(pentafluorophenyl) derivatives could be taken as an indication of an increase in the metal—metal bond strength, but the subsequent fragmentation by the loss of (C₆F₅)₂Mn is not consistent with this, since this requires the simultaneous breaking of three bonds, rather than of only one if the metal—metal bond was cleaved. If the metal—metal bond was indeed stronger then a more logical process would be the cleavage of the pentafluorophenyl—metal bond but the almost complete absence of ions of the type (C₆F₅)₂MMn and C₆F₅MMn does not seem to support this process to any extent. Thus we conclude that the fragmentation paths are more dependent on the stabilities of the ions formed and of the neutral species ejected rather than on the relative bond strengths in the ground state molecules.

Experimental

The preparations of the compounds Ph₃MMn(CO)₅ (M = Si, Ge or Pb), Ph_{3-n}(C₆F₅)_nMMn(CO)₅ (*n* = 0 to 3) and (C₆F₅)₃SiMn(CO)₅ were accomplished by literature procedures, and the preparation and properties of the other compounds have been published elsewhere [39]. Mass spectra were obtained on an AEI MS-12 instrument operating at 70 eV and a resolution power of about 1000. Samples were introduced directly into the ion source by a direct lock insertion probe, and possible thermal decomposition was kept to a minimum by keeping the temperature of the ion source and probe at or a little below the melting point of the sample. The ion intensities were measured in the usual way starting at *m/e* of 50 such that the largest (or base peak) was given an arbitrary figure of 100. The patterns of all polyisotopic ions were compared to those calculated for ions of known composition and where necessary, possible overlapping species were deconvoluted by use of a computer program [34]. Metastable transitions were also elucidated by the use of a computer program and where several possibilities for a given transi-

tion were found the ones that best fitted the expected or known transitions were chosen. Appearance potentials were determined on a Bendix Model 12 Time of Flight instrument fitted with a Model 14-107 ion source. Samples were introduced via the direct lock insertion probe into an ion source at a temperature of 90°C and the ionization efficiency time was produced by the semi-automatic method of Lloyd and Stafford [40]. A set of at least six ionization efficiency curves for the calibration gas (xenon) and the Ph_3Sn ion were drawn and the curves were then analyzed by a computer program based on Warrens extrapolated voltage difference method, which besides eliminating the tedious manipulation of the results also gives a more reliable assessment of possible errors.

Acknowledgements

We wish to thank the National Research Council of Canada for financial support of this work, Mr. J. Cashmore of the Department of Chemistry, Trent University, Peterborough, Ontario for obtaining the mass spectra, and the Department of Chemistry, Brock University, St. Catharines, Ontario for the use of the Time of Flight mass spectrometer.

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