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A FAST ATOM BOMBARDMENT MASS SPECTROMETRY STUDY OF THE HEXAMETHYLPHOSPHORAMIDE ADDUCTS OF PHENYLTIN(IV) AND PHENYLLEAD(IV) HALIDES

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Summary

The fast atom bombardment (FAB) mass spectra of a series of hexamethylphosphoramide (HMPA) adducts of phenyltin(IV) halides [Ph₃SnX \cdot HMPA (X = Cl, Br, I); Ph₂SnX₂ \cdot HMPA (X = Br, I); Ph₂SnX₂ \cdot 2HMPA (X = Br, I)] and phenyllead(IV) halides [Ph₃PbX \cdot HMPA (X = Cl, Br, I); Ph₂PbX₂ \cdot HMPA (X = Br, I) and Ph₂PbX₂ \cdot 2HMPA (X = Cl, Br, I)] in a glycerol/HMPA matrix have been investigated, and compared with their electron impact (EI) spectra. No parent ions are observed in either FAB or EI, but in the FAB spectra there is a much higher proportion of metal-containing ions which also have an HMPA molecule attached. This is the case even in a HMPA-free matrix such as *p*-nitrophenyloctyl ether (NPOE). The main difference in the FAB spectra is the preferential loss of halide compared to phenyl, the reverse of that observed in the EI spectra. The same trend is observed for the EI and FAB spectra of the uncomplexed organometallics. Diphenyltin dihalide \cdot HMPA adducts in the glycerol/HMPA matrix form Ph₃Sn species which are absent when NPOE is used as the matrix liquid.

Introduction

The application of FAB mass spectrometry to the study of organometallic compounds is expanding rapidly and has been extensively reviewed [1]. Recently, the use of various matrix liquids to study a series of phenyl derivatives of Group IV halides and related compounds was investigated [2,3]. For the simple organometallic

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halides, the FAB spectra, just as the EI spectra, do not show parent ions. The FAB data show a preferential loss of halide compared to phenyl, on fragmentation, i.e. the opposite of that observed for the EI spectra. Sulpholane, crown ethers and most recently NPOE have proven to be particularly effective matrix liquids for these compounds. Halide loss is most prominent in the polar protic matrix liquids such as glycerol, but is still prevalent over phenyl loss even with the aprotic matrices. Previously, we used EI mass spectrometry to study the HMPA adducts of phenyltin(IV) and -lead(IV) [5] halides. We now report the results of a FAB mass spectrometric study of the same compounds using a glycerol/HMPA matrix. This study was completed before the advantages of NPOE as a matrix were realized. However, the results in NPOE are similar to those with glycerol/HMPA in most cases. An even higher fraction of the total ion current is carried by HMPA-containing ions. Hence, the conclusions based on the HMPA-containing matrix are not determined by having excess ligand present in the matrix. Comparisons between the two FAB matrix systems are given for the tin compounds.

Experimental

The mass spectra were obtained with a modified Kratos MS-30 mass spectrometer interfaced with a DS-55 data system as described previously [3]. A resolving power of 1000 was used with an accelerating voltage of 4 kV. EI samples were inserted with a heated direct probe into a source held at 180°C. FAB spectra were obtained with Xenon bombardment ($\sim 7 \text{ kV}$). Ions were identified by pattern matching of isotope clusters, using deconvolution when necessary. In this study the usual matrix liquids such as glycerol, thioglycerol, sulpholane, and 18-crown-6 were not successful, though they worked with varying degrees of success for the free uncomplexed organometallic [3]. For the HMPA adducts, we found that HMPA itself was a suitable matrix, which was improved by the addition of a small amount of glycerol to reduce the volatility of the HMPA. Saturated solutions of the adducts in the matrix liquid were used, leading to good reproducibility of the FAB spectra. In all the FAB spectra the data system was used for the background subtraction of the matrix peaks. To compare the effect of using an HMPA-free matrix with the data from the HMPA/glycerol matrix, several of the tin systems were repeated using NPOE.

The adducts used in the study were those described earlier [4,5].

Results and discussion

The role of HMPA and glycerol as matrix

HMPA, as a matrix, plays a major role by dissolving the organometallic adducts. However, excess HMPA would be expected to increase the amount of the HMPA \cdot organometallic adduct present. Thus the observation of stable HMPA-containing metal ions in FAB could be an artifact of the matrix liquid. However, in another study [6], in which the use of NPOE as a matrix liquid was further explored, we found that the fraction of total ion current carried by metal/HMPA-containing ions is greater in NPOE than in HMPA as the matrix. In the latter case, the metal/HMPA species typically account for 30–60% of the ion current, whereas the NPOE matrix, i.e. with no excess HMPA, usually leads to 70–80% metal/HMPA ions. Therefore we feel justified in reporting metal/HMPA species as being characteristic of the adducts and not the matrix liquid, even when the matrix liquid contains HMPA. To confirm this we also examined several of these adducts using NPOE as a matrix liquid. The same behaviour was observed, i.e. the fraction of the ion current carried by species containing both tin and HMPA was greater with NPOE than with glycerol/HMPA as the matrix. There are also distinct shifts in the abundances of at least one species in each case, as discussed below. Perhaps NPOE is a sufficiently weak O-donor that it does not effectively displace HMPA from its adducts, while the dielectric constant of the NPOE is sufficiently less than that of HMPA/glycerol so that any ionic dissociation is suppressed.

Comparison of the EI and positive ion FAB mass spectra of some phenyltin(IV) halide adducts with hexamethylphosphoramide

Previously reported EI data [4] are listed in parentheses beside the positive ion FAB data in Table 1 for (i) $Ph_3SnX \cdot HMPA$, (ii) $Ph_2SnX_2 \cdot HMPA$ and (iii) $Ph_2SnX_2 \cdot 2HMPA$. The data are listed only for the metal-containing ions and expressed as a percentage of the total metal-containing ion current.

(i) $Ph_3SnX \cdot HMPA$ (X = Cl, Br, I)

In both EI and FAB over 50% of the ion current is carried by HMPA and its fragmentation products. The only difference in FAB is that (HMPA)H⁺ ions are observed instead of molecular ions. Even the dimers of HMPA give prominent peaks in most of the spectra taken. However, metal-containing ions are the species of interest and only these are reported. For the $Ph_3Sn \cdot HMPA^+$ ion, the intensity decreases from X = Cl to X = Br and then increases for X = I in both EI and FAB. The EI spectra show a decrease in intensity for the $Ph_2SnX \cdot HMPA^+$ in the order of I < Br < Cl whereas only the $Ph_2SnBr \cdot HMPA^+$ cluster is observed in FAB. The same trend is observed for the $SnX \cdot HMPA^+$ species. While the stability of PhSn $\cdot HMPA^+$ decreases in EI, it increases in FAB as the halide changes from Cl to I.

 $Sn \cdot HMPA$ ion clusters are observed in almost all EI and FAB spectra. HMPA bonds strongly to tin even after the subsequent loss of all phenyls and halogens from the parent ion. Most of the high mass ions observed in both EI and FAB have one HMPA coordinated. This may be due to the loss of phenyl or halogen from the parent ions being favoured over HMPA loss. Ions having one HMPA coordinated are not due to the HMPA matrix since they are also observed in the EI spectra and in the NPOE FAB spectra. The mass spectra of alkyls and aryls of Group IV elements are dominated by even-electron ions [7]. The dominance of even-electron ions is evident over the odd-electron ions in both EI and FAB, although in FAB, free tin ion intensities are much more prominent.

The existence of tin \cdot HMPA ions in the EI spectra and the fragmentation patterns differing from those of the parent halides was previously taken [4] to show that the molecular complex ions Ph₃SnX \cdot HMPA⁺⁺ were formed and then they rapidly dissociated. The much larger quantities of organotin \cdot HMPA ions in the FAB spectra are consistent with ions having lower internal energy on formation, and hence fragment less. When the FAB spectra are repeated in NPOE, the most apparent change is the doubling of the intensity of the Ph₃Sn \cdot HMPA⁺ ion. Difference between the chloride and bromide compounds are markedly less in

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lon +	(Ph ₃ SnX·H	(MPA)	And and a second se		Nation	(Ph_2SnX_2)	(MPA)			(Ph ₂ SnX ₂ .2	(NAMPA)	and a second	
	X = Cl		X = Br		X = 1	X = Br		l = X		X = Br		X = I	and the system may be with the summary of
	HMPA	NPOE	HMPA	NPOE		HMPA	NPOE	HMPA	NPOE	HMPA	NPOE	HMPA	NPOE
Ph ₂ MX·2HMPA	(-) -	-	(-) -		(-) -	1.0 (-)	4.1	(-) -	3.3				And a second
Ph ₃ M 2HMPA	2.7 (-)	trace	0.8 (-)	0.4	(-) -	(-) -	ł	(-)	t				
Ph ₃ M·HMPA	24.8 (.2)	45.0	17.4 (.1)	42.0	31.0 (.3)	34.5 (-)	ł	11.1 (-)					
Ph ₂ M·HMPA	- (2.9)	6.2	16.0 (1.0)	ŧ	- (.4)	7.0 (-)	56.2	16.6 (-)	61.3	12.6 (.5)	64.8	32.5 (2.9)	55.7
PhMX ₂ HMPA	(-) -	1	(-) -		(-) -	(-) -	7.1	-	I	9.6 (.1)	ł	- (.1)	ŧ
Ph ₂ M·HMPA	(-) -	1.5	(-) -	2.9	2.7 (-)	(-)	ł	(-) -	I	(-) -			
PhM-HMPA	5.0 (0.9)	6.1	(2) 1.7	7.8	13.2 (-)	12.7 (-)	2.0	11.2 (-)	4.0	(10.9 (.7)	15.4	11.3 (-)	7.6
MX·HMPA	- (6.8)	1	4.6 (1.7)	Ę	- (.8)	(-) -	11.0	13.0 (-)	10.3	7.7 (.1)	I	6.2 (1.8)	5.9
Ph ₂ N·2HMPA	(-) -	1	(-) -	ł	(-)	1.0 (-)	***	(-) -	ł	(-) -	ł	(-) ~	ł
M-HMPA	4.3 (2.1)	i	2.9 (.4)	ł	(-) -	(-) -	1	4.9 (-)	I	3.4 (-)		3.3 (1.1)	ŧ
Ph ₃ MX	- (2.3)	I	- (1.3)	ł	(-) -	(-) -	1	(-) [*] -	ł	(-) -	ł	(-) -	-
PH_2SnX_2	(-) -	1	(-) -	í	(-) -	- (6.9)	1	- (21.7)	ł	- (2.6)	ł	9.1 (-)	1
Ph ₂ MX	(-) -	**	9.0 (52.1)	i	1.7 (-)	2.6 (19.5)	ł	3.9 (25.9)	ł	-) -	ţ	(-) -	*
PhSnX ₂	(-) -	ļ	(-) -	1	(-) -	- (10.4)	I	- (11.9)	ı	6.1 (28.3)	5.5	2.4 (26.0)	11.6
Ph ₃ M	26.7 (31.7)	15.3	11.6 (-)	22.0	25.2 (39.5)	12.1 (-)	I	1.4 (-)	ŧ	(-) -	1	(-) -	ł
PhMX	- (27.8)	1	2.3 (6.1)	J	(-) -	- (26.3)	+	1.2 (4.1)	1.2	- (6.2)	I	- (.8)	1
Ph ₂ M	(-) -	i	1.4 (1.4)	ł	(-) -	(-) -	1	2.5 (1.7)	ł	(9.) -	ł	(-) -	ł
MX_2	(-) -	ţ	(-) -	404	(-) -	(-) -	ł	- (2.1)	i	- (.3)	400	10.0 (2.3)	ł
MX	- (13.0)	ļ	5.5 (24.8)	ł	- (8.2)	- (22.1)	1	6.4 (20.6)	1.4	9.2 (42.7)	ł	- (19.2)	ţ
РһМ	23.0 (6.1)	7.6	10.5 (6.2)	10.8	14.3 (25.4)	19.2 (6.4)	2,2	17.3 (7.9)	3.2	17.0 (3.6)	3.3	11.0 (25.9)	7.3
M	13.6 (4.2)	12.3	10.8 (4.5)	11.2	11.8 (21.0)	9.8 (6.3)	11.7	9.8 (4.0)	10.0	21.4 (12.9)	11.0	14.2 (18.3)	9.0
PbX · ZHMPA													

COMPARISON OF POSITIVE ION FAB (AND EI) DATA FOR METAL-CONTAINING IONS a

TABLE 1

	(Ph ₃ PbX·HM	(PA)		(Ph ₂ PbX ₂ ·H	MPA)	(Ph ₂ PbX ₂ ·2H	IMPA)	
	X = Cl	X = Br	I = X	X = Br	X = 1	X = CI	$\mathbf{X} = \mathbf{Br}$	X = I
MX · 2HMPA								
0 ₃ M·∠HMPA	6.0 (0.5)	13.0 (.1)	2.0 (.2)	5.9 (-)	(-) -	6.7 (-)	(-) -	(-) -
M HMPA	- (1.4)	(f) -		4.8 (.4)	- (5)	17.1 (.6)	- (.)	- (.4)
MX, HMPA	6.4 (.5)	10.6 (.1)	5.8 (-)	9.3 (-)	3.0 (-)	15.7 (-)	13.3 (-)) - -
, M . HMPA	- (1.4)	- (,4)	2.5 (-)	5.8 (.6)	6.0 (1.1)	11.4 (-)	- (.)	11.9 (1.2)
	18.4 (16.6)	14.9 (22.9)	32.5 (.9)	8.3 (.4)	25.3 (1.7)	6.9 (1.3)	23.7 (.3)	28.2 (.8)
X·HMPA	(-)	(-) -	(-) -	- (.2)	(-) -	(-) -	- (.3)	(-) -
N · 2HMPA	- (16.6)	- (22.5)	- (6)	- (17.8)	- (11.2)	2.0 (10.2)	- (15.2)	- (24.4)
·HMPA	(-) -	(-) -	(-) -	- (4.3)	- (.3)	- (2.6)	- (4.3)	- (10.2)
, XM _r	9.3 (11.4)	19.4 (6.0)	5.6 (28.)					
H ₂ SnX ₂	(-) +	- (6.)	(-) -	(9 [.]) -	(9) -	- (1.9)	- (1.1)	- (1.0)
2 MX	(-) -	(6.) -	(-) -					
ISnX ₂								
M ₆								
MX				÷				
M ₂ M	(-) -	- (9)	(-) -					
x,	(-) -	(-) -	(-) •	- (2.5)	- (5.6)	(-) -	- (8.8)	(6.7) -
×	- (23.7)	- (22.0)	(6.6)	6.7 (33.0)	- (25.4)	- (23.1)	- (4.7)	- (25.0)
W	9.9 (14.2)	17.8 (17.9)	- (36.0)	23.6 (6.4)	- (14.6)	20.1 (9.6)	14.9 (4.5)	5.0 (10.4)
	49.9 (28.9)	24.2 (26.0)	51.4 (29.0)	35.5 (33.8)	62.4 (39.0)	16.9 (50.6)	48.3 (23.3)	46.1 (21.3)
X · 2HMPA					1.4 (-)			8.7 (-)

NPOE than in glycerol/HMPA. These data suggest that theories of FAB ionization mechanisms involving the formation of large solvated gas phase ions cannot be correct in this case. The observed differences between the two matrices is most consistent with a mechanism involving preionization in solution. The presence of $Ph_3Sn \cdot 2HMPA$ in FAB spectra using the glycerol/HMPA matrix, may reflect prior ionization, i.e. $Ph_3Sn \cdot HMPA + HMPA \rightarrow Ph_3Sn \cdot 2HMPA^+ + X^-$, or reaction of ions with HMPA before ejection from the matrix.

(ii) $Ph_2SnX_2 \cdot HMPA$ (X = Cl, Br)

The EI spectra of these compounds have not previously been reported. There is a surprising difference between their EI spectra and those of the bis-HMPA adducts described below. These differences may be the result of different energetics involved in the loss of two vs. one molecule of HMPA. We are planning to explore this possibility using linked scans, metastable ions and collisional activation techniques.

In this series of compounds, HMPA-organotin ions are not observed in EI in contrast to FAB in which their intensities are significant. The stability of $Ph_2SnX \cdot HMPA^+$ in FAB is a clear indication of the preferential loss of halogen from the parent ion. This is even more striking in an NPOE matrix. Although the mechanism of the formation of the $Ph_2SnCl \cdot 2HMPA$ ions in FAB is uncertain, such ions must occur in the solution which is undergoing atom bombardment, since they are also observed in an NPOE matrix. They cannot be attributed to the excess of HMPA in the matrix liquid. Tin fragments are dominated by even electron species in both EI and FAB. The most abundant odd electron species are PhSnX⁺ and Sn⁺ itself. Ph₂Sn⁺ ions are observed for X = Br in both EI and FAB. FAB does not produce any dihalogenated tin species, in marked contrast to EI spectra.

The observation of $Ph_3Sn \cdot HMPA^+$ and Ph_3Sn^+ in the FAB spectra using the glycerol/HMPA matrix was unexpected. Since these ions are not formed using NPOE, a much less basic solvent than HMPA, as the matrix liquid, the triphenyltin species probably arise from a base-catalyzed disproportionation of diphenyltin dihalides to triphenyltin species along with SnX_2 and PhX. This reaction is well known in organolead chemistry [7].

(iii) $Ph_2SnX_2 \cdot 2HMPA$ (X = Br, I)

This series of compounds shows HMPA-containing tin ions in both EI (comparatively low intensities, i.e. only a few %) and FAB (40–50% of the total metal-containing ion current). Even electron ions $PhSnX_2^+$, Ph_2SnX^+ , SnX^+ and $PhSn^+$ dominate the EI spectra as usual. However FAB using glycerol/HMPA shows lower intensities except for the PhSn⁺ cluster. The odd-electron ions PhSnX⁺ (in EI) and Sn⁺ (in both EI and FAB) have high intensities. However, in this case tin ion intensities are increased. $Ph_2SnI_2^+$ and SnI_2^+ are more intense than their brominated counterparts, thus contradicting the general trend usually observed in mass spectra of halogenated organometallics.

The FAB spectra in an NPOE matrix again show a remarkable change, with the $Ph_2SnX \cdot HMPA^+$ ion increasing from 12.6 to 64.8% for X = Br and from 32.5 to 55.7% for the iodide between the glycerol/HMPA and NPOE matrix. There are also fewer fragment ions and the fragment intensities are weaker. In this sense, NPOE is acting as a less ionizing medium that glycerol/HMPA, but as in all other Group IV cases studied, there is a major loss of a substituent from the original Lewis acid.

This feature is seen for the tetrahedral acids, but in the EI spectra of adducts, it has usually been the donor ligand that is lost. FAB seems to be the exception to this rule. No coordinated NPOE was observed, in any of the NPOE experiments.

FAB-MS of Ph₄Sn

When an attempt was made to analyze Ph_4Sn by FAB in an HMPA matrix, only matrix ions were observed. The same type of fragmentation pattern as observed for the organotin halides was observed for Ph_4Sn in aprotic matrices such as sulfolane or NPOE, as we reported earlier [3]. Sulfolane behaved as the better matrix in this case. The FAB spectra showed Ph_3Sn coordinated to sulfolane to give a stable ion cluster of $Ph_3Sn \cdot$ sulfolane. No analogous HMPA species were observed with a HMPA matrix. This is quite surprising, since sulfolane is a strong O-donor, even though not so strong as HMPA.

Comparison of the EI and positive ion FAB mass spectra of some phenyllead halide adducts with hexamethylphosphoramide

Table 1 shows the FAB spectra of the following series of lead compounds using a HMPA/glycerol matrix; (i) $Ph_3PbX \cdot HMPA$ (X = Cl, Br, I), (ii) $Ph_2PbX_2 \cdot HMPA$ (X = Br, I), (iii) $Ph_2PbX_2 \cdot 2HMPA$ (X = Cl, Br, I). The previously reported EI data [5] are shown in Table 1 in parentheses. Again only the metal-containing ions are shown.

(i) $Ph_3PbX \cdot HMPA$ (X = Cl, Br, I)

More than 50% of the ion current is carried by HMPA⁺ and its fragments. analogous to those of the tin-containing compounds in both EI and FAB. The protonated dimers of HMPA carry over 20% of the ion current in most of the FAB spectra of these compounds. HMPA organolead fragments (without the halogens) are more intense in the FAB spectra compared to the corresponding EI data. A survey of the intensity patterns of tin- and lead-containing ions suggests that lead bonds more strongly with HMPA than tin. Although the possibility of formation of this bond by recombination in the EI mass spectra was suggested [5], the FAB data appear to rule out gas phase recombinations. All the singly-coordinated Pb · HMPA species are formed by the loss of halogens or phenyls from the parent molecular ions. The fragmentation patterns of lead-containing ions follow the general trend observed in the mass spectra of the organometallics of Group IV elements [8] by yielding highly abundant even-electron ions such as Ph₂PbX⁺, Ph₃Pb⁺, PbX⁺ and $PhPb^+$. Although Ph_3Pb^+ and $PhPb^+$ appear as prominent species, the halogenated species are not visible in FAB spectra. In FAB, the lead cation exhibits much higher abundance and the intensity relative to other ions does not change even when it is coordinated with HMPA. Similarities in the behaviour of the Lewis acid fragments with their HMPA-coordinated counterparts leads us to suspect that the former ions are most probably formed from the corresponding HMPA-organolead ions by the loss of HMPA.

(ii) $Ph_2PbX_2 \cdot HMPA$ (X = Br, I)

HMPA-organolead ions are again more prominent in FAB than in EI. In addition to other ions of higher masses common to both techniques, the ions $PbX \cdot 2HMPA^+$, $PhPb \cdot HMPA^+$ and $Ph_3Pb \cdot HMPA^+$ appear in FAB spectra,

analogous to the tin compounds. Halogenated lead species for this series of compounds are more dominant than those for the $Ph_3PbX \cdot HMPA$ series. This is probably indicative of purely statistical factors, the halide/phenyl ratio being 1/1 rather than 1/3 in the parent compounds. FAB as well as EI produces highly intense lead ion abundances which are greatest when X = I. The same trend is also evident for the Pb \cdot HMPA⁺ ions, which might have been formed by the preferential loss of iodine from the halogenated lead-containing ions.

(iii) $Ph_{2}PbX \cdot 2HMPA$ (X = Cl, Br, I)

In EI, unlike the case for the tin analogues, the addition of another HMPA to the series, $Ph_2PbX_2 \cdot HMPA$ makes little difference in the relative intensities and intensity patterns of the HMPA-lead ions. In FAB most of these ions behave in the same way. When these spectra are compared to those of the corresponding tin compounds, it is evident that most of the EI results agree. However, those of FAB vary. In the absence of metastable ions for this series of compounds, or for the previous five series, (metastables are observed only for the HMPA fragments), it is impossible to propose detailed fragmentation pathways.

Differences in spectra of mono- and di-HMPA adducts for both tin and lead suggest that even with samples in solution, FAB detects systems that are not just solution equilibrium phenomena. This is further confirmed by the greater abundance of Sn-HMPA species in an NPOE rather than in an HMPA matrix.

Ligand-exchange phenomenon

While most ions containing the metal in the FAB spectra as well as all those in EI spectra will be formed as a result of a gas phase fragmentation process, certain species in the FAB spectra must be formed by chemical processes in solution before or during the ionization and or sputtering process. Examples include (i) $Ph_3Sn \cdot$ 2HMPA⁺ from Ph₃Sn \cdot HMPA (X = Cl, Br, I) and PbI \cdot 2HMPA⁺ from Ph₂PbI₂ \cdot HMPA (these require HMPA-halide ion exchange) and (ii) Ph₃Sn · HMPA⁺ and Ph_3Sn^+ from $Ph_2SnX_2 \cdot HMPA$ (X = Cl, Br), and $Ph_3Pb \cdot HMPA$ from $Ph_2PbBr_2 \cdot$ HMPA or Ph₂PbCl₂·2HMPA (requiring phenyl group transfer). The phenomenon of some ionization of Ph_3SnX by HMPA even in a 1/1 ratio, in dichloromethane to form Ph₃SnHMPA₂⁺ has been observed by ¹¹⁹Sn NMR studies [9] and conductivity measurements [10]. Therefore the occurrence of some ionization in HMPA and even in NPOE matrices is not unexpected. More surprising was the formation of Ph_3M^+ species, by phenyl group transfer, with or without a coordinated HMPA, from $Ph_2MX_2 \cdot nHMPA$ (M = Sn, Pb, n = 1 or 2 (when M = Pb)). The effect was greater for the tin compounds. Although, as noted above, disproportionation of diphenyllead systems is well known, diphenyltin systems are usually considered chemically inert. However, we have found [11] that all attempts to prepare Ph_2SnY_2 (Y = imidazolate or benzimidazolate) by reaction of Ph₂SnCl₂ with NaY in ethanol gave the polymeric Ph₃SnY product. Recently the neutral base, adenine, was found to promote the disproportionation of Ph₂SnCl₂ to Ph₃SnCl and PhSnCl₃ in boiling methanol [12]. Thus chemically forcing conditions can cause phenyl group transfers and formation of the very stable triphenyltin moiety to occur. The HMPA matrix used in these FAB experients combined with the atom bombardment may provide such an environment.

In conclusion, parent ions of Group IV organohalide coordination compounds are not detected by FAB, but the very much greater ability of FAB to detect metal/ligand type ions makes the identification of such compounds by FAB much more certain than by EI mass spectral techniques. For tin and lead adducts the FAB spectra show that the loss of halide is preferred to loss of phenyl. This is the opposite to that observed in the EI spectra. Furthermore, the fragmentation of organometallic-ligand ions usually follows a similar pattern to the organometallic ions alone.

Again, we stress that in all FAB measurements careful attention must be given to the possibility of chemical reactions in or with the matrix liquid.

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