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COMPLEXES OF BIDENTATE GROUP VB CHELATES

XIX *. MASS SPECTRAL STUDIES ON SOME METHYL-SUBSTITUTED BIDENTATE GROUP VB DONOR LIGANDS

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Summary

The fragmentation patterns of seven bidentate and two tridentate Group VB donor ligands are reported. For these methyl-substituted ligands the initial fragmentation is essentially loss of methyl radicals. Phenyl, but not methyl, migration occurs for the bis(phenylmethylarsino)alkanes, but methyl migration is evident in the all aliphatic bidentate chelates. The tridentate ligands $PhE(CH_2CH_2CH_2AsMe_2)_2$ (E = P, As) show similar fragmentation routes, but are more complex. The long chain diarsine, $Me_2As(CH_2)_{12}AsMe_2$, exhibits a tendency to cyclise and lose C_2H_4 fragments progressively.

Introduction

There is increasing interest in the mass spectral fragmentation patterns of bi- and multi-dentate ligands. In addition to their inherent interest, mass spectra of ligands have been recorded in an attempt to elucidate the difficulties in the synthesis of various diarsines [2], to identify the products from the attempted preparations of several ditertiary stibines [3], and to examine the possibility of a correlation beteen the electron impact fragmentation of thioether ligands and metal catalysed *S*-dealkylation reactions [4]. Previous studies have reported the mass spectra of EPh_3 [5], $Ph_2E(CH_2)_nEPh_2$ [6,7], *cis*- and *trans*-$Ph_2ECH{=}CHEPh_2$ [6] (E = P, As), and the range of *o*-phenylene ligands *o*-$C_6H_4(E'Ph_2)(E''Ph_2)$ [8]. Alkyl substituted ligands have been much less studied although the fragmentation of *o*-phenylenebis(dimethylarsine) [2,9], and *cis*-1,2-bis(dimethylarsino)ethylene [9] have been briefly discussed.

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* For Part XVIII see ref. 1.

TABLE 1

FRAGMENTATION PATTERNS OF COMPOUNDS I-IV

$Me_2PCH_2CH_2CH_2PMe_2$ (I)			$Me_2AsCH_2CH_2CH_2PMe_2$ (II)			$Me_2AsCH_2CH_2CH_2AsMe_2$ (III)			$Me_2SbCH_2CH_2CH_2SbMe_2$ (IV) [a]		
Mass	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment
149	100	$C_6H_{15}P_2$	193	100	$C_6H_{15}AsP$	237	100	$C_6H_{15}As_2$	329	49.8	$C_6H_{15}Sb_2$
134	25.0	$C_5H_{12}P_2$	178	59.2	$C_5H_{12}AsP$	222	24.2	$C_5H_{12}As_2$	314	3.4	$C_5H_{12}Sb_2$
133	3.0	$C_5H_{11}P_2$	151	9.4	C_3H_9AsP	195	19.3	$C_3H_9As_2$	302	2.0	$C_4H_{12}Sb_2$
122	6.0	$C_4H_{12}P_2$	136	9.5	C_2H_6AsP	180	3.3	$C_2H_6As_2$	287	19.5	$C_3H_9Sb_2$
119	1.7	$C_4H_9P_2$	131	10.7	C_4H_8As	165	6.0	CH_3As_2	272	4.0	$C_2H_6Sb_2$
107	10.6	$C_3H_9P_2$	121	3.2	CH_3AsP	131	14.2	C_4H_8As	257	6.3	CH_3Sb_2
104	1.4	$C_3H_6P_2$	119	5.0	C_3H_8As	120	2.1	C_3H_9As	242	1.9	Sb_2
103	2.4	$C_5H_{12}P$	105	13.6	C_2H_6As	117	3.4	C_3H_6As	117	30.3	C_4H_8Sb
89	4.8	$C_4H_{10}P$	103	19.2	$\left.\begin{matrix}C_5H_{12}P\\C_2H_4As\end{matrix}\right\}$	105	24.3	C_2H_6As	166	13.6	C_3H_9Sb
88	2.4	C_4H_9P				103	26.4	C_2H_4As	151	100.0	C_2H_6Sb
87	7.0	C_4H_8P	91	5.7	CH_4As	91	7.2	CH_4As	149	16.8	C_2H_4Sb
79	2.4	CH_5P	90	6.5	CH_3As	90	6.8	CH_3As	136	40.4	CH_3Sb
77	3.3	CH_3P_2	89	11.8	CH_2As	89	13.6	CH_2As	135	17.9	CH_2Sb
76	23.9	C_3H_9P	76	13.2	AsH	75	0.8	As	121	21.4	Sb
					C_3H_9P	41	8.4	C_3H_5	41	16.1	C_3H_5
75	17.4	C_3H_8P	75	16.9	As						
73	3.9	C_3H_6P	61	13.0	C_2H_6P						
62	12.8	C_2H_7P	59	11.0	C_2H_4P						
61	19.6	C_2H_6P	46	3.3	CH_3P						
59	17.3	C_2H_4P	45	8.8	CH_2P						
57	10.8	C_2H_2P	41	18.3	C_3H_5						
45	15.7	CH_2P									
41	13.6	C_3H_5									

[a] Only ^{121}Sb fragments listed.

Here we report the mass spectra of a series of predominantly alkyl substituted ligands: 1,3-bis(dimethylphosphino) propane (dmp) (I), 1,3-bis(dimethylarsino)propane (dma) (II), (3-dimethylphosphinopropyl)dimethylarsine (dmap) (III), 1,3-bis(dimethylstibino)propane (dmsb) (IV), 1,2-bis(phenylmethylarsino)ethane (dase) (V), 1,3-bis(phenylmethylarsino)propane (dasp) (VI), bis(3-dimethylarsinopropyl)phenylarsine (tasp) (VII), bis(3-dimethylarsinopropyl)phenylphosphine (tap) (VIII), and 1,12-bis(dimethylarsino)dodecane (dmd) (IX) *.

Experimental

The 70 eV mass spectra were obtained using an A.E.I. MS 902 mass spectrometer linked to a DS 30 data system. Spectra were recorded at a resolving power of 2000, and atomic compositions confirmed by accurate mass measurements (RP = 10000).

The ligands were obtained by literature methods: dmp [10], dma [11], dmap [10], dmsb [12], dase [13], dasp [14], tasp [15], tap [16], and dmd by a method [17] similar to that used to prepare dma.

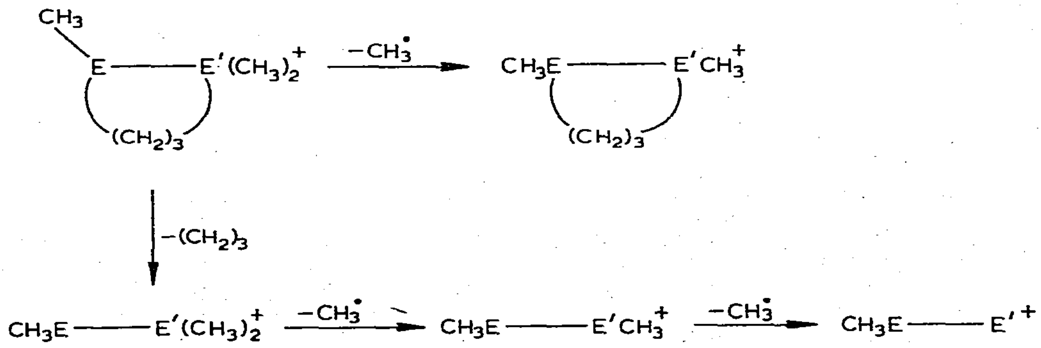
Results and discussion

The prominent ions in the mass spectra of these ligands are listed in Tables 1 (I-IV), 2 (V and VI), 3 (VII and VIII) and 4 (IX).

Ligands I-IV (Table 1)

These ligands $Me_2E(CH_2)_3EMe_2$ do not exhibit a parent ion in their spectra, the heaviest fragment observed corresponding to $P - CH_3^+$. For I-III the ion having *m/e* $P - CH_3^+$ is also the base peak, but for IV the base peak corresponds to *m/e* 151, Me_2Sb^+. All four spectra show the propensity of this type of ligand to lose methyl radicals from the parent and subsequent daughter ions. Also all four spectra exhibit ions containing two Group VB atoms, $P - CH_3^+$, $P - 2CH_3^+$, $C_3H_9EE'^+$, $C_2H_6EE'^+$, $CH_3EE'^+$, etc., suggesting that there is a linking of the pnictogen atoms probably after loss of a methyl radical from the parent as shown in Scheme 1.

SCHEME 1



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* $Me_2P(CH_2)_3PMe_2$, I; $Me_2As(CH_2)_3AsMe_2$, II; $Me_2P(CH_2)_3AsMe_2$, III; $Me_2Sb(CH_2)_3SbMe_2$, IV; $PhMeAs(CH_2)_2AsMePh$, V; $PhMeAs(CH_2)_3AsMePh$, VI; $PhAs\{(CH_2)_3AsMe_2\}_2$, VII; $PhP\{(CH_2)_3AsMe_2\}_2$, VIII; $Me_2As(CH_2)_{12}AsMe_2$, IX.

The cleavage of an $—E(CH_3)_2$ fragment from the backbone is also evident by the occurrence of $C_4H_8E^+$ ions. The presence of $C_3H_9E^+$ ions show that the methyl groups can migrate from one pnictogen atom to the other in the compound as previously noted [4,6]. In unsymmetrical ligands the migration only occurs from the heavier pnictogen atom to the lighter since the spectrum of ligand II exhibite a peak at *m/e* 86, $(CH_3)_3P^{+\cdot}$ but not at *m/e* 120, $(CH_3)_3As^{+\cdot}$.

Ligands V and VI (Table 2)

The fragmentation patterns of the two α,ω-bis(phenylmethylarsino)alkanes show interesting differences. Ligand V exhibits a parent ion *m/e* 362 and the base peak at *m/e* 167, $C_7H_8As^+(PhMeAs^+)$. Ligand VI resembles the tetramethyl analogue II in that the heaviest fragment observed is *m/e* 361 which is also the base peak, $P — CH_3^+$. Ligand V unlike ligand VI drops out the backbone to give *m/e* 334, $C_{14}H_{16}As_2^{+\cdot}$ which then loses a methyl radical to give *m/e* 319, $C_{13}H_{16}As_2^+$, or undergoes As—As bond fission to give *m/e* 167, $C_7H_8As^+$. Phenyl migration also occurs since a prominent ion occurs at *m/e* 229, $C_{12}H_{10}As^+(Ph_2As^+)$, the subsequent decomposition of which is a characteristic feature of the spectra of arylarsines [5,6]. In the spectra of both V and VI there is no evidence for methyl migration.

A comparison of the fragmentation patterns of V and of $Ph_2As(CH_2)_2AsPh_2$ [7] does not provide any clue to the reasons for the instability of $Me_2As(CH_2)_2$-$AsMe_2$ [18], the tendency to eliminate the backbone is greater for both ligands than for the trimethylene linked II and VI but partial replacement of phenyl by methyl groups [$Ph_2As(CH_2)_2AsPh_2$ vs. $MePhAs(CH_2)_2AsPhMe$] does not cause any profound change in the spectra.

TABLE 2

FRAGMENTATION PATTERNS OF COMPOUNDS V AND VI

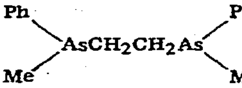
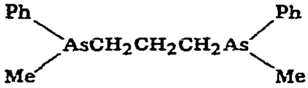
					
Mass	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment
362	13.0	$C_{16}H_{20}As_2$	361	100	$C_{16}H_{19}As_2$
347	3.4	$C_{15}H_{17}As_2$	319	2.4	$C_{13}H_{13}As_2$
334	15.2	$C_{14}H_{16}As_2$	299	8.0	$C_{11}H_{17}As_2$
319	3.6	$C_{13}H_{13}As_2$	229	6.8	$C_{12}H_{10}As$
244	17.3	$C_{13}H_{13}As$	227	6.2	$C_{12}H_8As$
229	32.6	$C_{12}H_{10}As$	193	6.2	$C_9H_{10}As$
227	13.4	$C_{12}H_8As$	180	5.4	$C_2H_6As_2$
182	4.4	$C_8H_{11}As$	167	36.1	C_7H_8As
167	100	C_7H_8As	165	10.5	CH_3As_2, C_7H_6As
165	10.7	CH_3As_2, C_7H_6As	154	3.3	$C_{12}H_{10}$
154	10.6	$C_{12}H_{10}$	152	12.1	$C_{12}H_8$, C_6H_5As
152	22.3	C_6H_5As, $C_{12}H_8$	151	8.5	C_6H_4As
151	26.7	C_6H_4As	117	6.0	C_3H_6As
91	97.2	C_7H_7, CH_4As	104	3.8	C_2H_5As
89	9.8	CH_2As	91	64.9	C_7H_7, CH_4As
78	11.7	C_6H_6	89	5.6	CH_2As
77	15.3	C_6H_5	78	10.1	C_6H_6
75	2.3	As	77	10.7	C_6H_5
			75	0.3	As

TABLE 3

FRAGMENTATION PATTERNS OF COMPOUNDS VII AND VIII

$Me_2AsCH_2CH_2CH_2As(Ph)CH_2CH_2CH_2AsMe_2$ (VII)						$Me_2AsCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2AsMe_2$ (VIII)					
Mass	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment
431	26.7	$C_{15}H_{26}As_3$	90	11.0	CH_3As	387	100	$C_{15}H_{26}As_2P$	140	5.6	$C_8H_{13}P$
401	1.2	$C_{13}H_{20}As_3$	89	13.9	CH_2As	357	9.0	$C_{13}H_{20}As_2P$	137	2.7	$C_8H_{10}P$
362	2.1	$C_{10}H_{17}As_3$	78	21.0	C_6H_6	300	6.4		133	6.9	$C_4H_{10}As$
300	39.6	$C_{11}H_{18}As_2$	77	10.5	C_6H_5	283	42.8	$C_{13}H_{21}AsP$	131	22.0	C_4H_8As
299	100.0	$C_{11}H_{17}As_2$	75	2.6	As	281	23.8	$C_{13}H_{19}AsP$	127	2.8	C_4H_4As
284	10.2	$C_{10}H_{14}As_2$				279	14.0	$C_{13}H_{17}AsP$	125	8.1	C_4H_2As
257	8.4	$C_8H_{11}As_2$				267	10.0	$C_{12}H_{17}AsP$	123	7.7	C_7H_8P
227	12.7	$C_6H_5As_2$				255	18.2	$C_{11}H_{17}AsP$	122	6.1	C_7H_7P
221	6.2	$C_5H_{11}As_2$				248	4.3		121	10.6	CH_3AsP
207	2.7	$C_4H_9As_2$				241	3.0	$C_{10}H_{15}AsP$	120	6.6	C_3H_9As
193	3.3	$C_3H_7As_2$				240	7.8	$C_{10}H_{14}AsP$	119	5.6	C_3H_8As
189	3.1	$C_3H_3As_2$				239	3.8	$C_{10}H_{13}AsP$	117	6.0	C_3H_6As
180	3.1	$C_2H_6As_2$									
179	7.3	$C_2H_5As_2$				226	7.4	$C_9H_{12}AsP$	116	13.0	C_3H_5As or $C_6H_{13}P$
167	29.3	C_7H_8As							115	5.4	$C_6H_{12}P$
165	15.2	CH_3As_2				225	7.4	$C_9H_{11}AsP$	109	22.1	C_6H_6P
153	19.7	C_6H_6As				210	4.1	$C_4H_{10}As_2$	108	6.9	C_6H_5P
152	12.2	C_6H_5As				207	5.2	$C_4H_9As_2$	107	32.6	C_6H_4P
151	8.7	C_6H_4As HAs_2				199	2.1	C_7H_9AsP			
150	5.0	As_2				186	4.8	C_6H_8AsP	105	24.3	C_2H_6As
147	25.9	$C_5H_{12}As$				183	8.6	C_6H_5AsP	103	20.4	C_2H_4As
146	5.4	$C_5H_{11}As$				181	4.3	$C_2H_7As_2$	102	5.9	C_2H_3As
131	15.0	C_4H_8As				179	5.1	$C_2H_5As_2$	101	10.9	C_2H_2As
127	2.0	C_4H_4As				178	2.6	$C_2H_4As_2$ $C_5H_{12}AsP$	91	25.0	CH_4As, C_7H_7
125	3.1	C_4H_2As									
117	10.7	C_3H_6As				167	4.3	C_7H_8As	90	30.1	CH_3As
105	31.0	C_2H_6As				165	3.0	CH_3As_2	89	30.0	CH_2As
103	22.8	C_2H_4As				164	10.2	$C_4H_{10}AsP$	88	9.0	C_4H_9P
91	36.4	CH_4As C_7H_7				163	6.0	C_4H_9AsP	78	11.3	C_6H_6
						151	5.6	C_6H_4As	77	8.6	C_6H_5
						150	9.6	$C_8H_{11}P$, As_2	75	7.1	As
						149	24.4	$C_9H_{10}P$			
						147	8.6	$C_5H_{12}As$			
						146	3.3	$C_5H_{11}As$			

TABLE 4

FRAGMENTATION PATTERN OF $Me_2As(CH_2)_{12}AsMe_2$ (IX)

Mass	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment
378	1.7	$C_{16}H_{36}As_2$	133	3.5	$C_4H_{10}As$
377	1.7	$C_{16}H_{35}As_2$	131	1.5	C_4H_8As
363	100.0	$C_{15}H_{33}As_2$	120	3.3	C_3H_9As
349	6.1	$C_{14}H_{31}As_2$	119	5.4	C_3H_8As
347	2.1	$C_{14}H_{29}As_2$	117	4.3	C_3H_6As
335	21.1	$C_{13}H_{29}As_2$	107	6.9	C_8H_{11}
321	1.8	$C_{12}H_{27}As_2$	106	13.8	C_2H_7As
307	4.0	$C_{11}H_{25}As_2$	105	31.6	C_2H_6As
293	1.9	$C_{10}H_{23}As_2$	103	9.6	C_2H_4As
279	2.8	$C_9H_{21}As_2$	101	2.3	C_2H_2As
274	2.1	$C_{14}H_{31}As$	95	3.7	C_7H_{11}
273	1.3	$C_{14}H_{30}As$	91	2.8	CH_4As
272	1.4	$C_{14}H_{29}As$	90	4.2	CH_3As
265	1.2	$C_8H_{19}As_2$	89	4.8	CH_2As
251	2.6	$C_7H_{17}As_2$	83	4.9	C_6H_{11}
245	2.5	$C_{12}H_{26}As$	81	4.1	C_6H_9
237	2.8	$C_6H_{15}As_2$	75	2.0	As
231	2.1	$C_{11}H_{24}As$	71	3.8	C_5H_{11}
217	1.1	$C_{10}H_{12}As$	69	18.9	C_5H_9
210	16.3	$C_4H_{12}As_2$	67	7.0	C_5H_7
201	2.9	$C_9H_{18}As$	57	13.6	C_4H_9
196	1.5	$C_3H_{10}As_2$	56	5.7	C_4H_8
195	2.4	$C_3H_9As_2$	55	41.5	C_4H_7
189	0.7	$C_8H_{18}As$			
187	2.2	$C_8H_{16}As$			
182	2.4	$C_2H_8As_2$			
181	1.7	$C_8H_{10}As$			
175	1.5	$C_7H_{16}As$			
161	1.4	$C_6H_{14}As$			
159	1.3	$C_6H_{12}As$			

Ligands VII and VIII (Table 3)

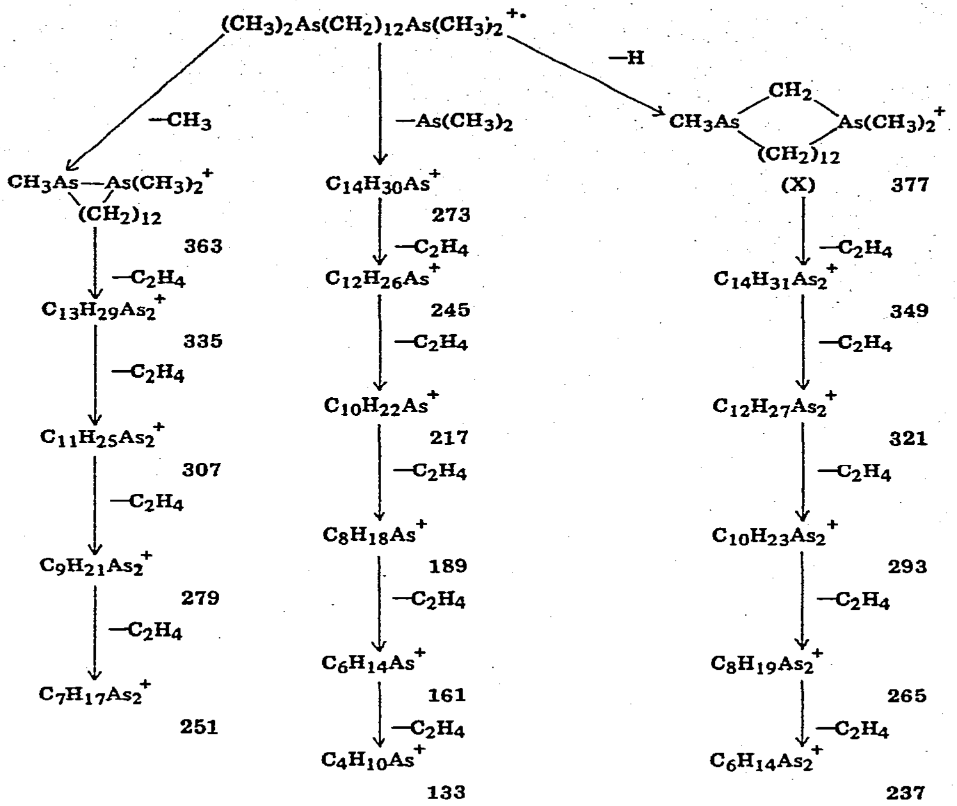
The fragmentation patterns of the two tridentates are complex but show similar fragmentation routes to the bidentates previously discussed. As in the trimethylene backboned bidentates no parent ion is seen, the heaviest fragment being $P - CH_3^+$. In the case of VIII this ion is also the base peak *m/e* 387, however, the base peak for VII occurs at *m/e* 299 corresponding to $P - (CH_2)_3$-$AsMe_2^+$. This is a reflection of the relatively stronger C—P bond against the C—As bond. The loss of $-(CH_2)_3AsMe_2$ from the parent does occur for VIII but with a relative intensity of 18.2%, *m/e* 255. All expected ions of lower *m/e* are found.

Ligand IX (Table 4)

The ligand 1,12-bis(dimethylarsino)dodecane gives a complex fragmentation pattern. The parent ion is seen at low relative intensity *m/e* 378, 1.7%, and analogous to II and VI the base peak corresponds to $P - CH_3^+$, *m/e* 363. A weak $P - 1$ peak occurs probably corresponding to the cyclic ion (X), which then loses ethylene progressively. Two other series of progressive ethylene loss are seen beginning with the ions $P - CH_3^+$, *m/e* 363, and $P - As(CH_3)_2^+$, *m/e* 273. (Scheme 2). The other most prominent arsenic containing fragments are *m/e* 210, $(CH_3)_2AsAs(CH_3)_2^{+\cdot}$ and *m/e* 105, $(CH_3)_2As^+$.

SCHEME 2

FRAGMENTATION OF $Me_2As(CH_2)_{12}AsMe_2$



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