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BIDENTATE GROUP VB LIGANDS

II*. MASS SPECTRAL STUDIES ON SOME ETHYLENIC DIPHOSPHINE, DIARSINE, AND PHOSPHINE–ARSINE LIGANDS

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SUMMARY

The mass spectra of *cis*- and *trans*-1,2-bis(diphenylphosphino)ethylene, *cis*- and *trans*-1,2-bis(diphenylarsino)ethylene, *cis*- and *trans*-1-diphenylphosphino-2-diphenylarsinoethylene, and the saturated 1-diphenylphosphino-2-diphenylarsinoethane are reported, and their fragmentation patterns, and those of some resulting intermediates, illustrated and discussed. The *cis* and *trans* isomers of the unsaturated ligands have identical mass spectra, suggesting that in the parent ion, $[H_2C_2E_2Ph_4]^{+\cdot}$ ($E=P$, As), free rotation about the C–C bond is possible. During fragmentation, phenyl migration from one Group VB atom to another occurs, but in the mixed phosphine–arsine ligands the phenyl group is transferred from arsenic to phosphorus, but not *vice-versa*.

INTRODUCTION

Despite the immense current interest in their preparation and complexing properties, few mass spectrophotometric data have been reported on phosphorus and arsenic donor ligands. The fragmentations induced by electron impact on triphenylphosphine[2], triphenylarsine[3], bis(diphenylphosphino)- and bis(diphenylarsino)-methane, 1,2-bis(diphenylphosphino)- and 1,2-bis(diphenylarsino)ethane[4] have been studied. The mass spectral patterns of *trans*-1-diphenylphosphino-2-diphenylarsinoethylene (*t*-vasp) and its saturated analogue have been briefly mentioned by King and Kapoor[5]. Feltham and Metzger[6] have studied the fragmentation patterns of three methyl-substituted diarsines—*o*-phenylenebis(diethylarsine) and *cis*- and *trans*-1,2-bis(dimethylarsino)ethylene—and it was shown that all four $CH_3\cdot$ groups are lost from the parent ions.

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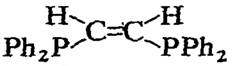
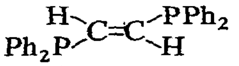
* For part 1 see ref. 1.

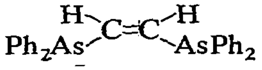
In this paper we report the mass spectra of *cis*- and *trans*-1,2-bis(diphenylphosphino)ethylene (vpp, I; *t*-vpp, II), *cis*- and *trans*-1,2-bis(diphenylarsino)ethylene (vaa, III; *t*-vaa, IV), *cis*- and *trans*-vasp (V and VI, respectively), and also of the saturated 1-diphenylphosphino-2-diphenylarsinoethane (pae, VII).



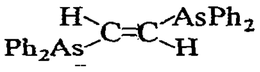
vpp (I)



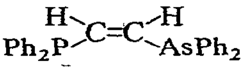
t-vpp (II)



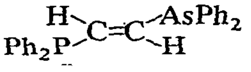
vaa (III)



t-vaa (IV)



vasp (V)



t-vasp (VI)

$Ph_2PCH_2CH_2AsPh_2$
pae (VII)

EXPERIMENTAL

The preparation of the ligands were carried out by standard methods[7] or will be reported in a future publication[8]. The mass spectra were recorded on an A.E.I. MS902 spectrometer with a source temperature of 100–110° at 70 eV using direct insertion technique.

DISCUSSION

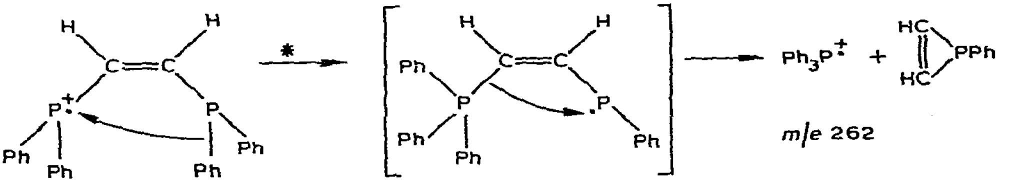
It was found that the *cis* and *trans* isomers of the vinyl ligands had identical mass spectra; the mass spectrum of vpp (I) and *t*-vpp (II) is included in Table 1. The fact that both isomers fragment in exactly the same manner suggests that in the parent ion, $[H_2C_2P_2Ph_4]^{+}$, free rotation about the C–C bond is possible. From both

TABLE 1

MASS SPECTRA OF THE LIGANDS

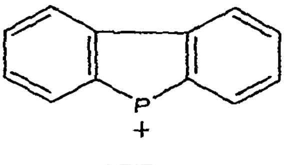
cis- and trans-vpp (I,II)			*pae (VII)*			*cis- and trans-vaa (III,IV)*			*cis- and trans-vasp (V,VI)*		
m/e	*I(%)*	*Fragment*	*m/e*	*I(%)*	*Fragment*	*m/e.*	*I(%)*	*Fragment*	*m/e*	*I(%)*	*Fragment*
396	100	$C_{26}H_{22}P_2$	442	100	$C_{26}H_{24}PAs$	484	100	$C_{26}H_{22}As_2$	440	100	$C_{26}H_{22}PAs$
370	10	$C_{24}H_{20}P_2$	414	17	$C_{24}H_{20}PAs$	458	11	$C_{24}H_{20}As_2$	414	13	$C_{24}H_{20}PAs$
319	11	$C_{20}H_{17}P_2$	365	7	$C_{20}H_{19}PAs$	407	9	$C_{20}H_{15}As_2$	365	15	$C_{20}H_{19}PAs$
287	16	$C_{20}H_{16}P$	337	7	$C_{18}H_{15}PAs$	381	10	$C_{18}H_{15}As_2$	337	6	$C_{18}H_{15}PAs$
262	22	$C_{18}H_{15}P$	289	68	$C_{20}H_{18}P$	306	15	$C_{18}H_{15}As$	287	34	$C_{20}H_{16}P$
185	27	$C_{12}H_{10}P$	275	15	$C_{19}H_{16}P$	229	70	$C_{12}H_{10}As$	262	90	$C_{18}H_{15}P$
184	13	$C_{12}H_9P$	262	90	$C_{18}H_{15}P$	227	86	$C_{12}H_8As$	229	18	$C_{12}H_{10}As$
183	59	$C_{12}H_8P$	229	21	$C_{12}H_{10}As$	180	14	C_8H_9As	227	23	$C_{12}H_8As$
154	5	$C_{12}H_{10}$	227	40	$C_{12}H_8As$	178	44	C_8H_7As	185	47	$C_{12}H_{10}P$
152	11	$C_{12}H_8$	185	56	$C_{12}H_{10}P$	154	33	$C_{12}H_{10}$	183	67	$C_{12}H_8P$
108	29	C_6H_5P	183	80	$C_{12}H_8P$	152	20	$C_{12}H_8$;	154	18	$C_{12}H_{10}$
107	21	C_6H_4P	154	19	$C_{12}H_{10}$			C_6H_5As	152	27	$C_{12}H_8$;
77	13	C_6H_5	153	17	$C_{12}H_{11}$	150	71	C_6H_3As			C_6H_5As
			152	39	$C_{12}H_8$				131	13	C_8H_6P
			108	20	C_6H_5P				108	17	C_6H_5P

vpp and *t*-vpp the ion $Ph_3P^{\cdot+}$ (*m/e* 262) was obtained, and this metastable ion results directly from the parent ion by loss of C_7H_7P and its origin is thus owed to a rearrangement of the parent ion involving a 1,4-five-centre phenyl migration[4]



(1)

The resultant fate of the $Ph_3P^{\cdot+}$ ion is illustrated in Fig. 1. In the mass spectrum of pae (VII) (see Table 1), as well as in that of vpp, the base peak is the cyclic species, (VIII), *m/e* 183. It can be seen from Fig. 1 that this cyclic ion is generated via several different pathways.



(VIII)

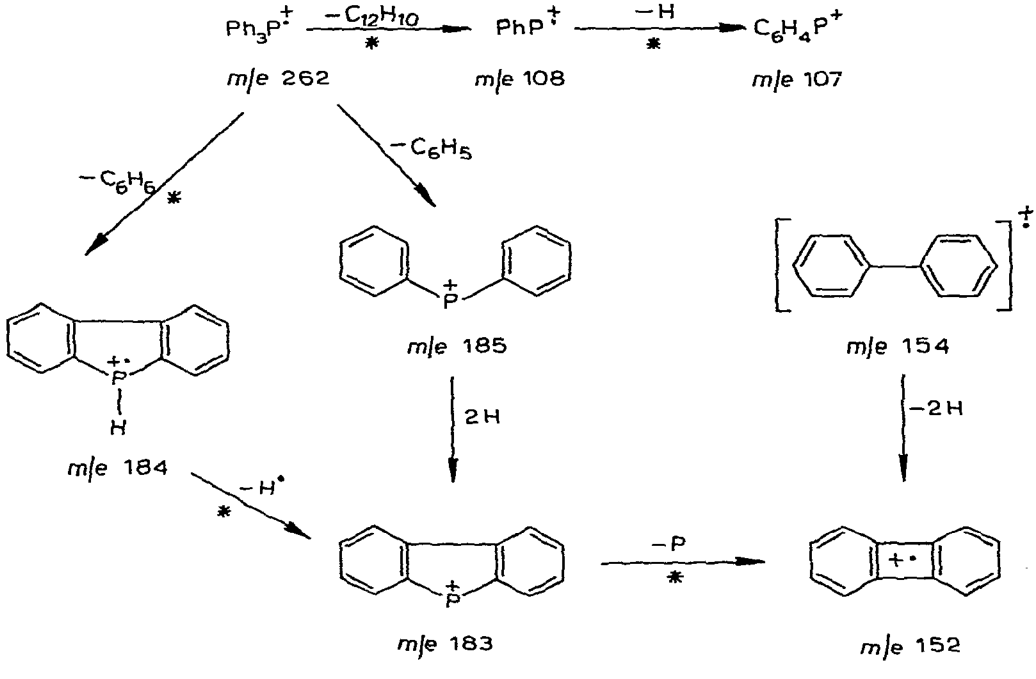


Fig. 1. Fragmentation of $Ph_3P^{\cdot+}$ to simpler molecules.

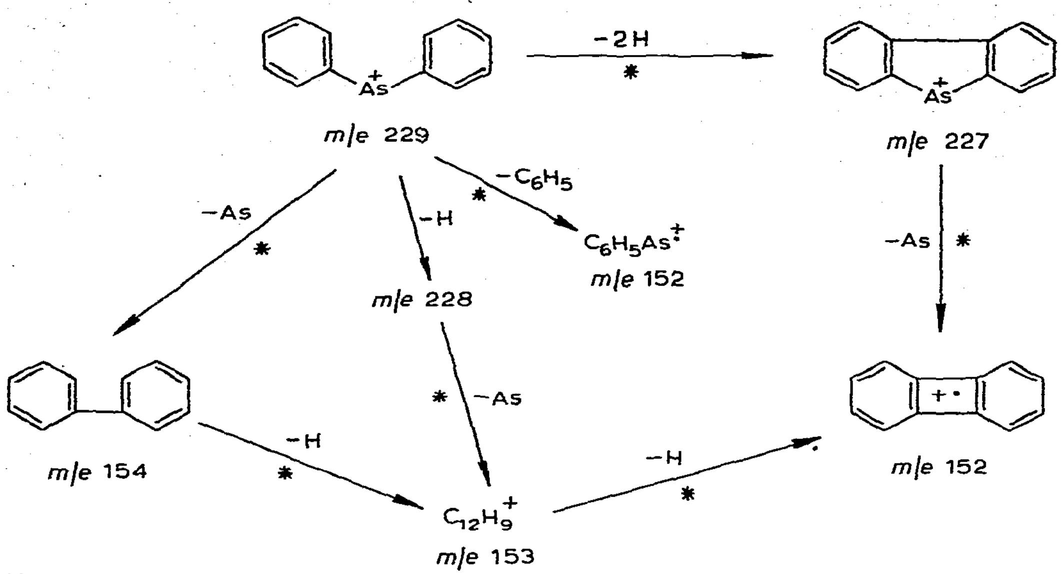


Fig. 2. Fragmentation of Ph_2As^+ to simpler organic molecules.

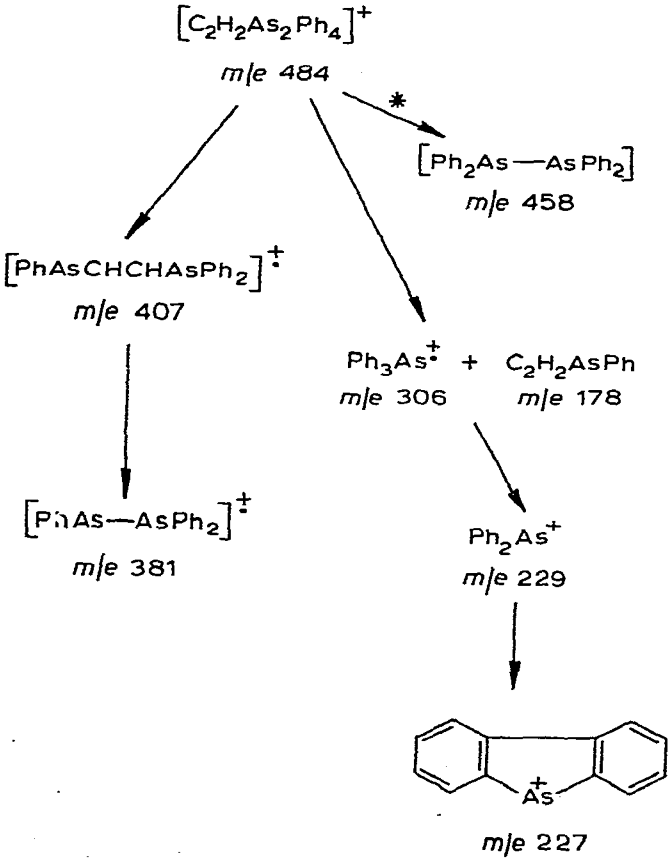


Fig. 3. Fragmentation of the diarsine ligand.

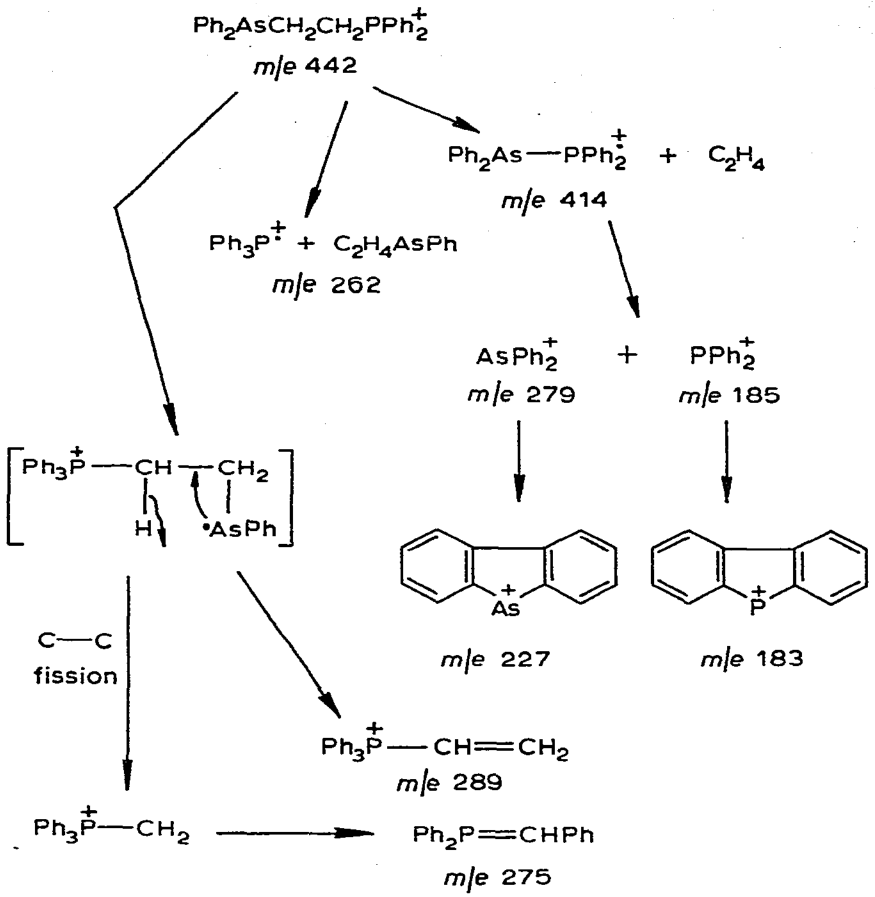
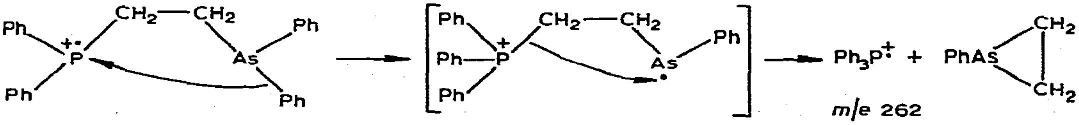


Fig. 4. Fragmentation of pae.

The mass spectrum of the isomeric diarsines is contained in Table 1, and the fragmentation generally resembles that of the analogous diphosphine pattern, the greater part of the current being carried by the species *m/e* 229 and 227 (Figs. 2 and 3).

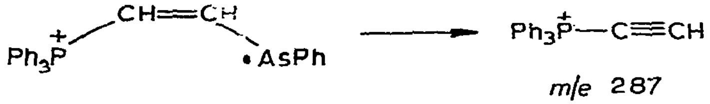
The most interesting spectra derive from the unsymmetrical phosphine–arsine ligands vasp (V, VI) and pae (VII). The mass spectral pattern of the vasp isomers is included in the Table as well as that of the saturated analogue, pae. The mass spectra of *t*-vasp and pae have been briefly reported by King and Kapoor[5], and these workers pointed out that cleavage of the carbon–phosphorus and/or carbon–arsenic predominated in the early stages of the fragmentation process. Phenyl migration occurs, as it did in the cases of vpp and vaa, but it is interesting to notice that there is no peak present assignable to $Ph_3As^{\cdot+}$ (*m/e* 306), thus indicating that in the phosphine–arsine ligands the phenyl group is transferred from arsenic to phosphorus, but not *vice-versa*:



The bond dissociation energies for C–P and C–As suggest that the C–As bond cleavage would be most likely[9].

The fragmentation of pae is shown in Fig. 4. One striking difference between the spectra of pae and vasp is that in the saturated pae a strong peak at *m/e* 289 results from the loss of C_6H_6As from the parent ion as follows:

The associated process in the case of vasp yields only an ion of much less intensity:



The spectra of all the mixed phosphine–arsenic ligands contain peaks with *m/e* 337, which can be attributed to Ph_3As^+ and ions of the type Ph_2E^+, $C_{12}H_8E^+$, and PhE^+ ($E=P, As$).

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