Journal of Organometallic Chemistry, 125 (1977) 209—214

COMPLEXES OF BIDENTATE GROUP VB CHELATES

XX *. MASS SPECTRAL STUDIES ON SOME DIPHOSPHINE AND DISTIBINE LIGANDS WITH BACKBONES OF VARYING LENGTH

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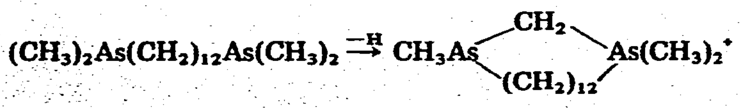
(Received July 9th, 1976)

Summary

The mass spectral fragmentation patterns of the diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 6, 8, 10, 12) and the distibines $Me_2Sb(CH_2)_nSbMe_2$ (n = 6, 10) are reported and compared with those of $Me_2As(CH_2)_{12}AsMe_2$ and the analogous ligands with C_2 and C_3 backbones.

Introduction

Mass spectra of several types of bidentate Group VB donor ligands have been reported over the past few years, including $Ph_2E(CH_2)_nEPh_2$ (E = P, As, [2,3] Sb [4]), *cis*- and *trans*-$Ph_2ECHCHEPh_2$ (E = P, As) [3], *o*-$C_6H_4(EPh_2)(E'Ph_2)$ (E, E' = P, As, Sb) [4]. Not surprisingly the type of ligand backbone (alkane, alkene or *o*-phenylene) has a profound effect upon the mode(s) of fragmentation of the ligands. Recently we reported [1] the mass spectrum of the long chain diarsine, $Me_2As(CH_2)_{12}AsMe_2$, which exhibited an unexpected tendency to cyclise and lose C_2H_4 fragments progressively. We are currently [5,6] examining the coordination chemistry of a range of α,ω-alkane diphosphines, diarsines and distibines with medium (n = 4—8) and long (n = 10—14) backbones in order to try to elucidate the varying importance of backbone length and donors upon their ability to function as *trans* chelating or bridging ligands, i.e. to see if the reaction seen [1] in the mass spectral beam



$$(CH_3)_2As(CH_2)_{12}As(CH_3)_2 \xrightarrow{-H} CH_3As\begin{matrix}CH_2\\ \\ (CH_2)_{12}\end{matrix}As(CH_3)_2^{+}$$

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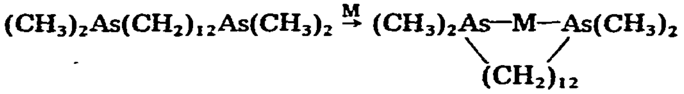
[*] For part XIX see ref. 1.

gave us any information about the tendency for the coordination reaction



$$(CH_3)_2As(CH_2)_{12}As(CH_3)_2 \xrightarrow{M} (CH_3)_2As\text{—}M\text{—}As(CH_3)_2 \quad \underbrace{}_{(CH_2)_{12}}$$

Thus, the mass spectra of several ligands have been examined to see if the variation in backbone length exerted any marked effect upon the fragmentation modes.

Experimental

Mass spectra were recorded as described previously [4]. The synthesis of the ligands will be described elsewhere [6].

TABLE 1

FRAGMENTATION PATTERNS OF COMPOUNDS I—IV

$Ph_2P(CH_2)_{12}PPh_2$			$Ph_2P(CH_2)_{10}PPh_2$		
Mass	Rel. int.	Fragment	Mass	Rel. int.	Fragment
538	32.1	$C_{36}H_{44}P_2$	510	11.4	$C_{34}H_{40}P_2$
537	7.4	$C_{36}H_{43}P_2$	509	3.9	$C_{34}H_{39}P_2$
509	1.5	$C_{34}H_{39}P_2$	467	1.7	
495	9.0		433	7.6	$C_{28}H_{35}P_2$
481	2.4	$C_{32}H_{35}P_2$	370	21.6	$C_{24}H_{20}P_2$
461	14.4	$C_{30}H_{39}P_2$	325	65.7	$C_{22}H_{30}P$
370	24.0	$C_{24}H_{20}P_2$	311	9.9	$C_{21}H_{28}P$
353	65.6	$C_{24}H_{34}P$	297	7.1	$C_{20}H_{26}P$
339	10.7	$C_{23}H_{32}P$	283	8.2	$C_{19}H_{24}P$
325	8.9	$C_{22}H_{30}P$	269	13.7	$C_{18}H_{22}P$
311	7.0	$C_{21}H_{28}P$	255	25.4	$C_{17}H_{20}P$
297	4.6	$C_{20}H_{26}P$	241	16.2	$C_{16}H_{18}P$
283	8.5	$C_{19}H_{24}P$	213	18.2	$C_{14}H_{14}P$
269	26.5	$C_{18}H_{22}P$	200	18.0	$C_{13}H_{13}P$
262	3.4	$C_{18}H_{15}P$	199	84.0	$C_{13}H_{12}P$
255	22.5	$C_{17}H_{20}P$	186	42.3	$C_{12}H_{11}P$
241	15.6	$C_{16}H_{18}P$	185	40.8	$C_{12}H_{10}P$
227	1.8	$C_{15}H_{16}P$	183	75.0	$C_{12}H_8P$
213	20.5	$C_{14}H_{14}P$	154	2.4	$C_{12}H_{10}$
200	41.1	$C_{13}C_{13}P$	152	8.3	$C_{12}H_8$
199	100	$C_{13}H_{12}P$	121	22.8	C_7H_6P
186	50.3	$C_{12}H_{11}P$	109	37.9	C_6H_6P
185	40.9	$C_{12}H_{10}P$	108	100	C_6H_5P
183	80.7	$C_{12}H_8P$	107	26.4	C_6H_4P
154	9.8	$C_{12}H_{10}$	91	50.7	C_7H_7
152	14.4	$C_{12}H_8$	78	26.0	C_6H_6
121	13.3	C_7H_6P	77	28.1	C_6H_5
109	36.5	C_6H_6P			
108	93.3	C_6H_5P			
107	27.1	C_6H_4P			
91	29.4	C_7H_7			
78	65.3	C_6H_6			
77	96.9	C_6H_5			

Results and discussion

(a) The diphosphines, $Ph_2P(CH_2)_nPPh_2$ (n = 6, 8, 10, 12)

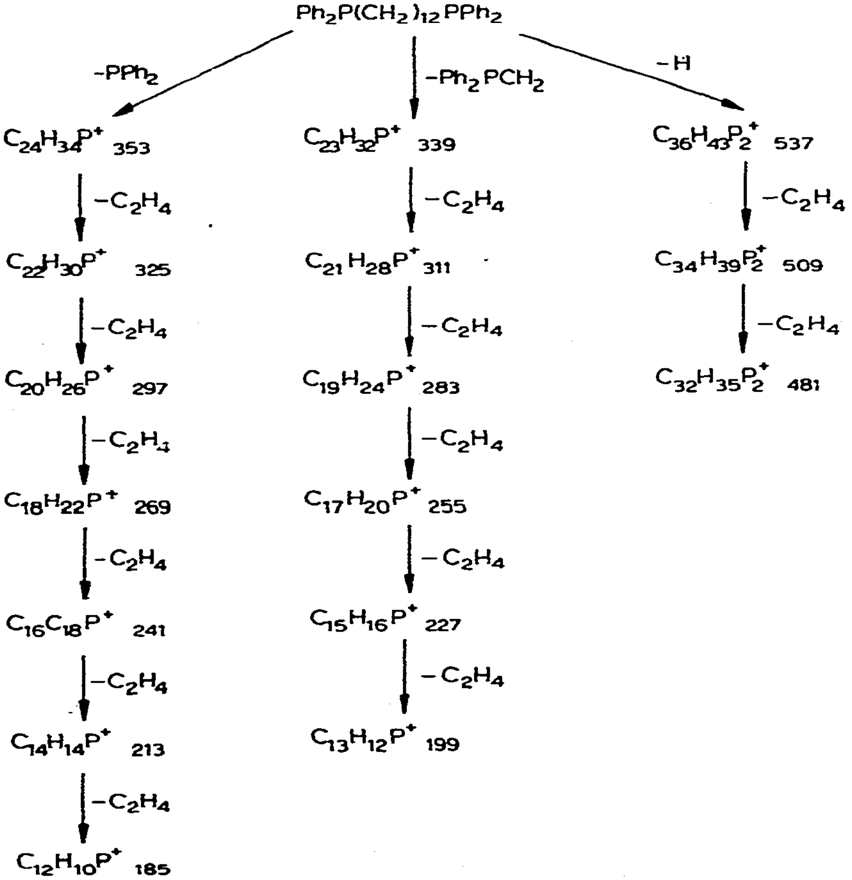
The prominent ions in the mass spectra of 1,12-bis(diphenylphosphino)-dodecane, (n = 12), (I), 1,10-bis(diphenylphosphino)decane, (n = 10), (II), 1,8-bis(diphenylphosphino)octane, (n = 8), (III), and 1,6-bis(diphenylphosphino)-hexane, (n = 6), (IV), are listed in Table 1. All four ligands exhibit parent and $P - 1$ ions, although for IV the ions are of very low intensity. The ion $\text{Ph}_2\text{PPPh}_2^+$, formed by elimination of the backbone, is an important one in the spectra of I, II and III, but occurs with only very low intensity for IV, perhaps a reflection of the increasing strain involved in ring closure which must precede elimination. Phenyl migration reactions are unimportant. Fragments containing two phosphorus atoms are rather rare, in marked contrast to the case for the o-phenylene analogue [4]; only one phenyl group can be lost, $(P - \text{Ph})^+$, before $-(\text{CH}_2)_n - \text{P}$ cleavage occurs; there is no evidence for $P - 2\text{Ph}^+$ ions.

Loss of PPh_2 from the parent ion is a prominent decomposition route, the $\text{Ph}_2\text{P(CH}_2)_n^+$ (n = 12, 10, 8, 6 for I—IV, respectively) ions are all of high intensity, and for III this ion is the base peak. All the succeeding $\text{Ph}_2\text{P(CH}_2)^+_{(n-1),(n-2)\ldots}$ down to Ph_2P^+ (m/e 185) are present. Loss of successive methylene groups is most unlikely [2]; these ions no doubt result from progressive ethylene (C_2H_4) loss from $\text{Ph}_2\text{P(CH}_2)_n^+$ and $\text{Ph}_2\text{P(CH}_2)^+_{n-1}$ resulting in two overlapping series (Scheme 1 shows the proposed fragmentation for I). The $\text{Ph}_2\text{P(CH}_2)^+_{n-1}$ ion

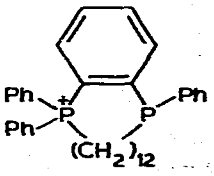
$Ph_2P(CH_2)_8PPh_2$			$Ph_2P(CH_2)_6PPh_2$		
Mass	Rel. int.	Fragment	Mass	Rel. int.	Fragment
482	7.5	$C_{32}H_{36}P_2$	454	0.6	$C_{30}H_{32}P_2$
481	3.9	$C_{32}H_{35}P_2$	453	0.3	$C_{30}H_{31}P_2$
439	1.2		377	1.1	$C_{24}H_{27}P_2$
405	7.8	$C_{26}H_{31}P_2$	370	0.8	$C_{24}H_{20}P_2$
370	6.8	$C_{24}H_{20}P_2$	269	96.9	$C_{18}H_{22}P$
297	100	$C_{20}H_{26}P$	262	4.8	$C_{18}H_{15}P$
283	9.7	$C_{19}H_{24}P$	255	4.6	$C_{17}H_{20}P$
269	9.0	$C_{18}H_{22}P$	241	3.2	$C_{16}H_{18}P$
255	12.5	$C_{17}H_{20}P$	227	2.8	$C_{15}H_{16}P$
241	17.1	$C_{16}H_{18}P$	213	3.3	$C_{14}H_{14}P$
227	1.0	$C_{15}H_{16}P$	200	7.4	$C_{13}H_{13}P$
213	12.1	$C_{14}H_{14}P$	199	24.7	$C_{13}H_{12}P$
200	15.8	$C_{13}H_{13}P$	186	35.5	$C_{12}H_{11}P$
199	64.2	$C_{13}H_{12}P$	185	15.4	$C_{12}H_{10}P$
186	24.8	$C_{12}H_{11}P$	183	64.1	$C_{12}H_8P$
185	12.0	$C_{12}H_{10}P$	154	6.3	$C_{12}H_{10}$
183	84.2	$C_{12}H_8P$	152	14.2	$C_{12}H_8$
154	1.7	$C_{12}H_{10}$	121	11.2	C_7H_6P
152	8.3	$C_{12}H_8$	109	24.0	C_6H_6P
121	22.9	C_7H_6P	108	100	C_6H_5P
109	32.4	C_6H_6P	107	45.5	C_6H_4P
108	77.2	C_6H_5P	91	33.9	C_7H_7
107	24.6	C_6H_4P	78	42.3	C_6H_6
91	30.9	C_7H_7	77	64.3	C_6H_5
78	14.0	C_6H_6			
77	16.0	C_6H_5			

SCHEME 1

Fragmentation pattern of $Ph_2P(CH_2)_{12}PPh_2$



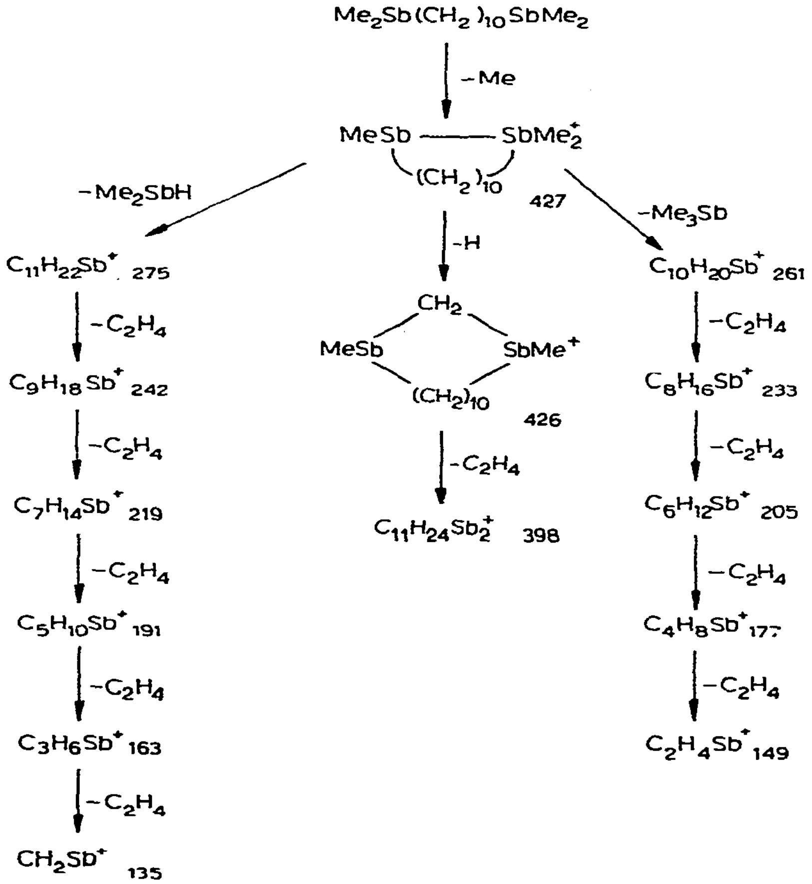
presumably arises by loss of Ph_2PCH_2 from the parent. Only ligand I shows any evidence for a third series of progressive C_2H_4 loss beginning at $P-1^+$, presumably the cyclic ion V. The ions corresponding to Ph_2P^+ and PhP^+ are of high intensity, as they usually are in the spectra of phenylphosphines. The spectra also contain a long series of ions at low *m/e* (not shown) corresponding to the normal fragments derived from the alkane backbone.



(V)

SCHEME 2

Fragmentation pattern of $Me_2Sb(CH_2)_{10}SbMe_2$



(b) The distibines, $Me_2Sb(CH_2)_nSbMe_2$ ($n = 6, 10$)

The spectra of 1,10-bis(dimethylstibino)decane, (VI), and 1,6-bis(dimethylstibino)hexane, (VII), are shown in Table 2. These spectra illustrate the weakness of the C—Sb bond. In both cases, based upon ^{121}Sb only, the base peaks are hydrocarbon fragments (although for VI, if ^{123}Sb is also considered, $^{121}Sb + ^{123}Sb$ yields a base peak of Me_2Sb^+ ~ 105% of the hydrocarbon base). There are extensive series of hydrocarbon fragments at low *m/e* (not shown). The major antimony peaks are, as expected, Me_2Sb^+, $C_2H_4Sb^+$ and $MeSb^+$, characteristic of methylstibines [1]. Both VI and VII resemble $Me_2Sb(CH_2)_3SbMe_2$ [1] in that the reasonably intense peak at highest *m/e* observed corresponds to $P - Me^+$ rather than P^+, although VI does, in fact, exhibit a very weak P^+ ($I = 0.9\%$). The spectrum of VI again shows two series of C_2H_4 loss, beginning at $C_{11}H_{22}Sb^+$ (*m/e* = 275) and $C_{10}H_{20}Sb$ (*m/e* = 261) which may result by loss of Me_2SbH and Me_3Sb from P—Me (Scheme 2). A comparison with $Me_2As(CH_2)_{12}AsMe_2$ [1] shows that the mass spectrum of VI differs in lacking series containing two

TABLE 2

FRAGMENTATION PATTERNS OF COMPOUNDS VI AND VII

Me$_2$Sb(CH$_2$)$_6$SbMe			Me$_2$Sb(CH$_2$)$_{10}$SbMe$_2$		
Mass	Rel. int.	Fragment	Mass	Rel. int.	Fragment
371	19.2	$C_9H_{21}Sb_2$	442	0.9	$C_{14}H_{32}Sb_2$
356	0.1	$C_8H_{18}Sb_2$	426	22.5	$C_{13}H_{28}Sb_2$
302	3.2	$C_4H_{12}Sb_2$	398	1.3	$C_{11}H_{24}Sb_2$
287	2.4	$C_3H_9Sb_2$	302	3.3	$C_4H_{12}Sb_2$
257	1.8	CH_3Sb_2	291	2.3	$C_{12}H_{26}Sb$
235	3.4	$C_8H_{18}Sb$	290	5.7	$C_{12}H_{25}Sb$
234	2.2	$C_8H_{17}Sb$	276	2.7	$C_{11}H_{23}Sb$
220	3.7	$C_7H_{15}Sb$	275	14.1	$C_{11}H_{22}Sb$
219	13.2	$C_7H_{14}Sb$	261	1.9	$C_{10}H_{20}Sb$
207	3.0	$C_6H_{14}Sb$	247	0.4	$C_9H_{18}Sb$
205	8.8	$C_6H_{12}Sb$	233	0.4	$C_8H_{16}Sb$
191	5.1	$C_5H_{10}Sb$	219	2.6	$C_7H_{14}Sb$
177	11.0	C_4H_8Sb	205	1.3	$C_6H_{12}Sb$
166	6.2	C_3H_9Sb	191	1.6	$C_5H_{10}Sb$
163	3.0	C_3H_6Sb	177	1.7	C_4H_8Sb
151	80.0	C_2H_6Sb	166	9.8	C_3H_9Sb
149	25.9	C_2H_4Sb	163	0.9	C_3H_6Sb
136	46.9	CH_3Sb	151	61.9	C_2H_6Sb
135	9.5	CH_2Sb	149	16.8	C_2H_4Sb
122	7.3	SbH	136	23.0	CH_3Sb
121	23.3	Sb	135	9.0	CH_2Sb
81	100	C_6H_9	122	3.3	SbH
			121	11.3	Sb
			55	100	C_4H_7

Group VB atoms, again a manifestation of the weakness of the C—Sb bond. Ligand VII shows similar series of C_2H_4 loss from the monoantimony ions $C_6H_{12}Sb^+$ and $C_7H_{14}Sb^+$.

A comparison of the spectra of I—VII and that of Me$_2$As(CH$_2$)$_{12}$AsMe$_2$ reveals that progressive loss of C_2H_4 from the backbone is a characteristic of this type of ligand, but the effect on the spectra of varying backbone length (at least over the (CH$_2$)$_{12}$ to (CH$_2$)$_6$ range) is considerably less than that produced by changes in the Group VB element or the terminal substituents.

Acknowledgment

We are grateful to the Science Research Council for the award of Research Studentships to IEN and PDR.

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