Journal of Organometallic Chemistry, 84 (1975) 239—245
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BIDENTATE GROUP VB LIGANDS

XII*. MASS SPECTRAL STUDIES ON SOME *o*-PHENYLENE CHELATES CONTAINING PHOSPHORUS, ARSENIC AND ANTIMONY DONOR ATOMS

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(Received July 18th, 1974)

Summary

The mass spectra of five bidentate chelates containing the *o*-phenylene linkage, $o\text{-}C_6H_4(EPh_2)(E'Ph_2)$ (E = E' = P; E = E' = As; E = P, E' = As; E = P, E' = Sb; E = As, E' = Sb), are reported. The fragmentation patterns reflect the effect of decreasing C—Group VB bond strength as the mass of the VB element increases. Thus the intensity of the parent ion M and $M-1$ decrease along the series P → Sb. The base peak in each ligand is a cyclic ion $C_{12}H_8E^+$, and in the case of the mixed bidentates E is the lighter Group VB element. Unlike those bidentate ligands with the alkane or alkene backbones, these *o*-phenylene ligand fragmentation patterns show that $Ph_2EEPh_2^+$ ions are not formed to any appreciable extent, and phenyl migration reactions to give Ph_3E^+ ions are unimportant. The fragmentation of two ditertiary stibines, $Ph_2Sb(CH_2)_nSbPh_2$ (n = 1, 3) are also reported. In these cases the major fragments are Ph_2Sb^+, $PhSb^+$ and $C_{12}H_{10}^+$.

Introduction

The recent extensive studies on the synthesis and coordination chemistry of heavy Group VB donor ligands have, rather surprisingly, prompted few studies of the mass spectra of the ligands themselves. The fragmentation patterns of triphenyl-phosphine [2, 3], -arsine, and -stibine [3], and of the bidentate chelating $Ph_2ECH_2EPh_2$ [4], $Ph_2ECH_2CH_2EPh_2$ [4], and *cis*- and *trans*-$Ph_2ECH{=}CHEPh_2$ [5] (E = P, As), $Ph_2PCH_2CH_2AsPh_2$ [5], and *cis*- and *trans*-$Ph_2PCH{=}CHAsPh_2$ [5] have been reported. Feltham and Metzger [6] examined the

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* For Parts X and XI see ref. 1.

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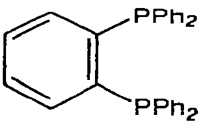
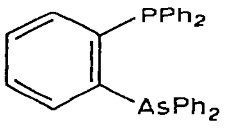
products of the reaction of Me_2As^- ions with *o*-dichlorobenzene by mass spectro etry, and also recorded the fragmentation patterns of *o*-phenylenebis(dimethylarsine) and of *cis*- and *trans*-1,2-bis(dimethylarsino)ethylene.

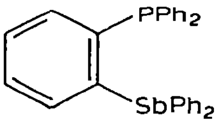
Here we report the mass spectra of five *o*-phenylene ligands: *o*-phenylenebis(diphenylphosphine) (I), [*o*-(diphenylarsino)phenyl]diphenylphosphine (II), [*o*-(diphenylphosphino)phenyl]diphenylstibine (III), *o*-phenylenebis(diphenylarsine) (IV), and [*o*-(diphenylarsino)phenyl]diphenylstibine (V); and of two ditertiary stibines: bis(diphenylstibino)methane (VI) and 1,3-bis(diphenylstibino)propane (VII).



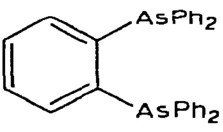
(I, pp)



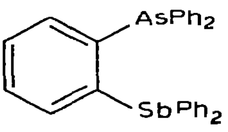
(II, ap)



(III, sbp)



(IV, aa)



(V, sba)

$Ph_2SbCH_2SbPh_2$

(VI, dsbm)

$Pn_2SbCH_2CH_2CH_2SbPh_2$

(VII, dsbp)

Experimental

The ligands were obtained by literature methods, viz.: pp [7], ap [8], sbp [9], sba [9], aa [10], dsbm [11] and dsbp [12].

The 70 eV mass spectra were obtained using an AEI MS 902 mass spectrometer and a DS 30 Data System. Spectra were recorded at a resolving power of 2000 and the atomic compositions confirmed by accurate mass measurements (RP = 10,000).

Results and discussion

The major fragments of the *o*-phenylene ligands are listed in Table 1. The effect of decreasing bond strength C—Group VB element as the atomic number of the latter increases is particularly noticeable along the series, particularly in the decreased importance of the parent ion. The base peaks for all five ligands*

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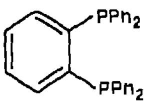
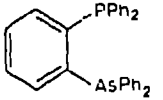
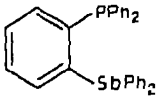
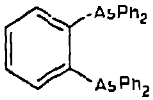
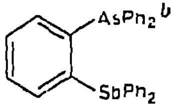
* sba was isolated as a n-butanol solvate and as such gave a base peak of *m/e* 56 (butene). The spectrum was recomputed to eliminate the solvate.

TABLE 1. MASS SPECTRA OF THE LIGANDS o-$C_6H_4(EPh_2)(E'Ph_2)$ [E, E' = P, As, Sb][a]

												 [b]		
Mass	Rel. Int.	Fragment	Mass.	Rel. Int.	Fragment	Mass.	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment	Mass	Rel. Int.	Fragment
446	73	$C_{30}H_{24}P_2$	490	58	$C_{30}H_{24}PAs$	536	36	$C_{30}H_{24}PSb$	534	46	$C_{30}H_{24}As_2$	580	14	$C_{30}H_{24}AsSb$
445	21	$C_{30}H_{23}P_2$	489	3	$C_{30}H_{23}PAs$	535	0.9	$C_{30}H_{23}PSb$	533	1	$C_{30}H_{23}As_2$	503	34	$C_{24}H_{19}AsSb$
369	79	$C_{24}H_{19}P_2$	413	84	$C_{24}H_{19}PAs$	459	56	$C_{24}H_{19}PSb$	457	60	$C_{24}H_{19}As_2$	426	0.5	$C_{18}H_{14}AsSb$
368	3	$C_{24}H_{18}P_2$	412	5	$C_{24}H_{18}PAs$	382	17	$C_{18}H_{14}PSb$	380	0.6	$C_{18}H_{14}As_2$			
367	2.5	$C_{24}H_{17}P_2$	337	10	$C_{24}H_{18}P$	338	16	$C_{24}H_{19}P$	306	3	$C_{18}H_{15}As$			
337	2.5	$C_{24}H_{18}P$				337	37	$C_{24}H_{18}P$	304	3	$C_{18}H_{13}As$			
291	5	$C_{18}H_{13}P_2$				275	5	$C_{12}H_{10}Sb$	303	4.5	$C_{18}H_{12}As$	306	13	$C_{18}H_{15}As$
290	3.5	$C_{18}H_{12}P_2$				273	4	$C_{12}H_8Sb$	229	13	$C_{12}H_{10}As$	304	4	$C_{18}H_{13}As$
289	14	$C_{18}H_{11}P_2$				262	8	$C_{18}H_{15}P$	228	9	$C_{12}H_9As$	303	2	$C_{18}H_{12}As$
288	2.5	$C_{18}H_{10}P_2$				261	6	$C_{18}H_{14}P$	227	100	$C_{12}H_8As$	275	8	$C_{12}H_{10}Sb$
262	7	$C_{18}H_{15}P$	262	2	$C_{18}H_{15}P$	260	12	$C_{18}H_{13}P$	154	11	$C_{12}H_{10}$	273	8	$C_{12}H_8Sb$
261	10	$C_{18}H_{14}P$	261	4	$C_{18}H_{14}P$	259	7	$C_{18}H_{12}P$	152	38	$C_{12}H_8$, C_6H_5As	229	13	$C_{12}H_{10}As$
260	8	$C_{18}H_{13}P$	260	7	$C_{18}H_{13}P$	257	4	$C_{18}H_{10}P$	151	16	C_6H_4As	228	31	$C_{12}H_9As$
259	5	$C_{18}H_{12}P$	259	4	$C_{18}H_{12}P$	198	18	C_6H_5Sb	78	9	C_6H_6	227	100	$C_{12}H_8As$
257	12.5	$C_{18}H_{10}P$	257	4	$C_{18}H_{10}P$	197	9	C_6H_4Sb	77	8	C_6H_5	198	5.5	C_6H_5Sb
186	6.5	$C_{12}H_{11}P$	228	4	$C_{12}H_9As$	185	4	$C_{12}H_{10}P$				197	2	C_6H_4Sb
185	9	$C_{12}H_{10}P$	186	12	$C_{12}H_{11}P$	184	15	$C_{12}H_9P$				154	43	$C_{12}H_{10}$
184	23	$C_{12}H_9P$	185	10	$C_{12}H_{10}P$	183	100	$C_{12}H_8P$				153	22	$C_{12}H_9$
183	100	$C_{12}H_8P$	184	19.5	$C_{12}H_9P$	154	51	$C_{12}H_{10}$				152	91	$C_{12}H_8$, C_6H_5As
154	1	$C_{12}H_{10}$	183	100	$C_{12}H_8P$	152	22	$C_{12}H_8$				151	19	C_6H_4As
153	2	$C_{12}H_9$	154	8	$C_{12}H_{10}$	121	3	Sb						
152	10	$C_{12}H_8$	153	4	$C_{12}H_9$	108	7	C_6H_5P				78	33	C_6H_6
108	18	C_6H_5P	152	13	$C_{12}H_8$, C_6H_5As	107	15	C_6H_4P				77	19.5	C_6H_5
107	19	C_6H_4P	108	4	C_6H_5P	78	13	C_6H_6						
78	12	C_6H_6	107	3	C_6H_4P	77	28	C_6H_5						
77	9	C_6H_5	78	15	C_6H_6									
			77	9.5	C_6H_5									

[a] For antimony-containing species only m/e for ^{121}Sb are given; relative intensities are uncorrected. [b] Occurs as n-butanol solvate, and as such has base peak m/e 56 (butene). Spectrum is recalculated to eliminate solvent.

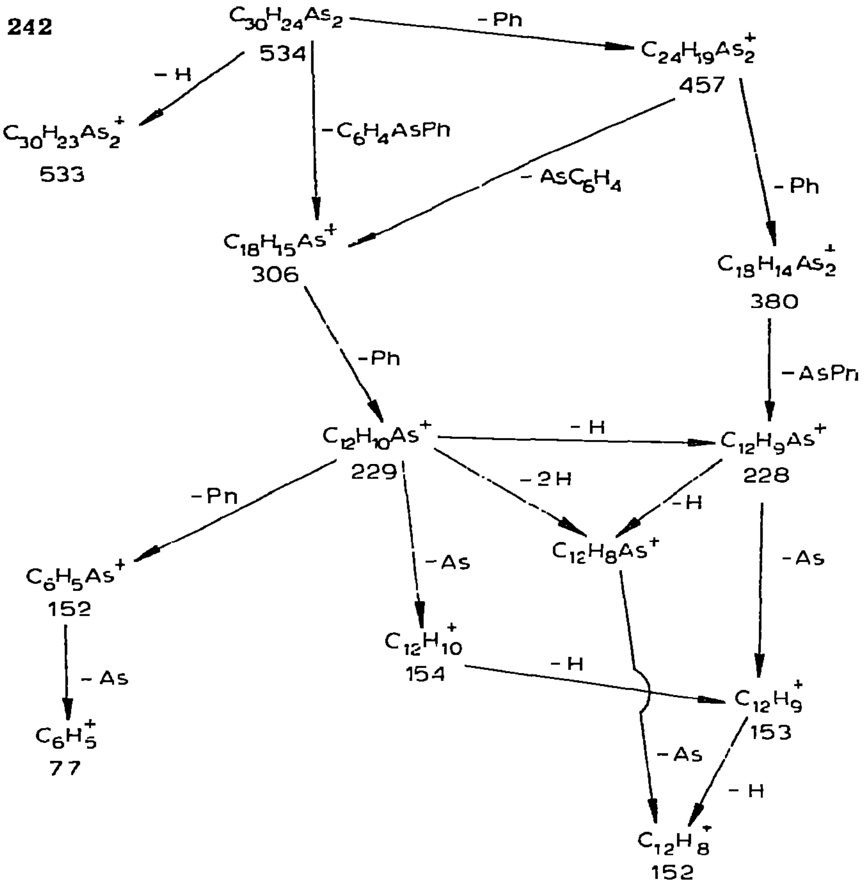


Fig. 1. Fragmentation of aa.

TABLE 2[a]

MASS SPECTRA OF dsbm AND dsbp

dsbm			dsbp		
Mass	Rel. int.	Fragment	Mass	Rel. int.	Fragment
564	11.5	$C_{25}H_{22}Sb_2$	592	1.4	$C_{27}H_{26}Sb_2$
550	1.6	$C_{24}H_{20}Sb_2$	550	3.6	$C_{24}H_{20}Sb_2$
352	7.4	$C_{18}H_{15}Sb$	515	10.1	$C_{21}H_{21}Sb_2$
319	2.6	$C_6H_5Sb_2$	438	3.6	$C_{15}H_{16}Sb_2$
290	4.5	$C_{13}H_{13}Sb$	352	5.4	$C_{18}H_{15}Sb$
289	1.6	$C_{13}H_{12}Sb$	319	5.2	$C_6H_5Sb_2$
275	19.5	$C_{12}H_{10}Sb$	317	10.7	$C_{15}H_{16}Sb$
273	8.1	$C_{12}H_8Sb$	276	5.5	$C_{12}H_{11}Sb$
198	80.2	C_6H_5Sb	275	39	$C_{12}H_{10}Sb$
197	8.5	C_6H_4Sb	273	6.1	$C_{12}H_8Sb$
154	100	$C_{12}H_{10}$	240	1.3	$C_9H_{11}Sb$
153	19	$C_{12}H_9$	239	4.0	$C_9H_{10}Sb$
152	14.6	$C_{12}H_8$	198	65.3	C_6H_5Sb
121	4.1	Sb	197	8.7	C_6H_4Sb
			154	100	$C_{12}H_{10}$
			153	17.6	$C_{12}H_9$
			152	12.9	$C_{12}H_8$
			121	6.8	Sb

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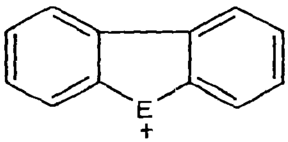
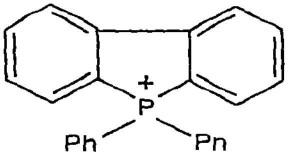
[a] Only data for ^{121}Sb containing fragments is given, and the I% are *not* corrected to take into account ^{123}Sb containing ions.

are cyclic ions of the type:



(VIII)

where E = P for pp, ap, sbp, and = As for aa, sba. The mixed ligands produce particularly clear evidence of the effect of decreasing C—E bond strength — for example the relative intensities of the $C_{12}H_8P^+$ and $C_{12}H_8As^+$ ions in ap are 100 and 24.5% respectively. In contrast to alkane or alkene backboned di-Group VB donor ligands [4, 5], the elimination of the backbone to give $Ph_2EEPh_2^+$ ions is unimportant here, as is phenyl migration to give Ph_3E^+, since only weak peaks due to the latter are observed. As previously noted [5] in mixed donor ligands, where phenyl migration does occur, the phenyl group is transferred from the heavier to the lighter E atom, but not vice versa. The phosphorus containing ligands all show a strong peak at *m/e* 337 which is due to $C_{24}H_{18}P^+$ and which probably has the structure:



Similar As and Sb containing fragments do not appear to form to any extent.

The fragmentation of aa is relatively simple and in shown in Fig. 1. The peak *m/e* 152 consists of $PhAs^+$ and $C_{12}H_8^{+\cdot}$ (this is confirmed by high resolution studies).

The basic fragmentation patterns of the other ligands appear to be essentially similar, although those containing at least one P atom show quite complex behaviour.

*Distibines**

The fragmentation pattern of dsbm is fairly similar to those reported for the phosphorus and arsenic analogues [4]; the differences observed can be attributed to the much weaker C—Sb bond [13] and to the unimportance of species containing multiple bonds to the antimony. From Table 2, where only the ^{121}Sb fragments are listed, it appears that the base peak of the dsbm spectrum is the ion *m/e* 154 (biphenyl). If, however, the ^{123}Sb fragments are also considered the base peak is $PhSb^+$. The corresponding base peaks in the phosphorus and arsenic analogues are the cyclic ion VIII and the parent, respectively [4]. As previously mentioned, species containing multiple bonds to antimony are unimportant — for example $Ph_2P^+{=}CH_2$ has I = 62% in the spectrum of

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* See footnote to Table 2.

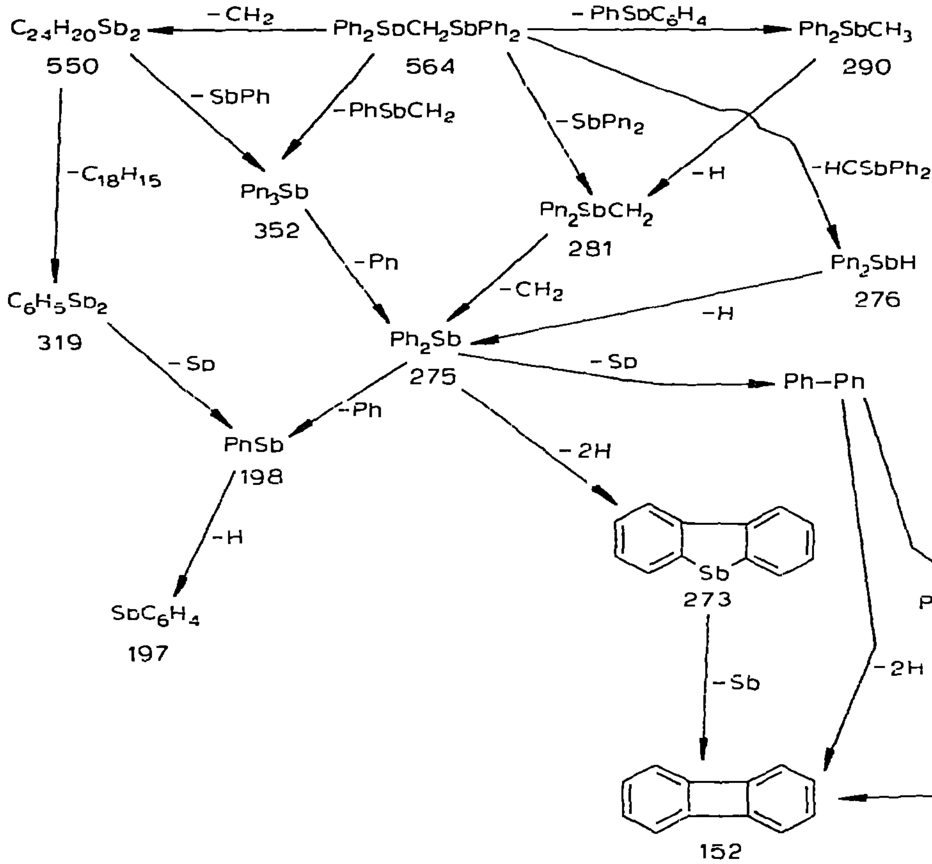
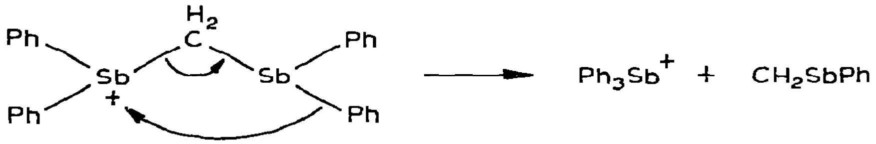


Fig. 2. Fragmentation of dsbm (^{121}Sb).

$Ph_2\underset{+}{P}CH_2PPh_2$ and $Ph_2As^+{=}CH_2$ I = 7% in that of the arsenic analogue, whilst $Ph_2Sb{=}CH_2$ has only I = 1.6% (^{121}Sb + ^{123}Sb), and there is no ion at all corresponding to the *m/e* of PhSb≡CH ion. The phenyl migration reaction:



is also relatively less important since Ph_3Sb (*m/e* = 352) has I = 7.5%, compared with I = 81% for Ph_3P^+ and I = 64% for Ph_3As^+ in the phosphorous and arsenic analogues [4]. The major antimony containing species are ions of *m/e* 275, 198 which are attributed to Ph_2Sb^+ and $PhSb^+$, respectively. The proposed fragmentation patterns for dsbm and dsbp are shown in Figs. 2 and 3. The dsbp spectrum has a base peak of Ph—Ph *m/e* 154 (^{121}Sb data only), but the sum of ^{121}Sb and ^{123}Sb fragments for $PhSb^+$ is 115% of the Ph—Ph peak.

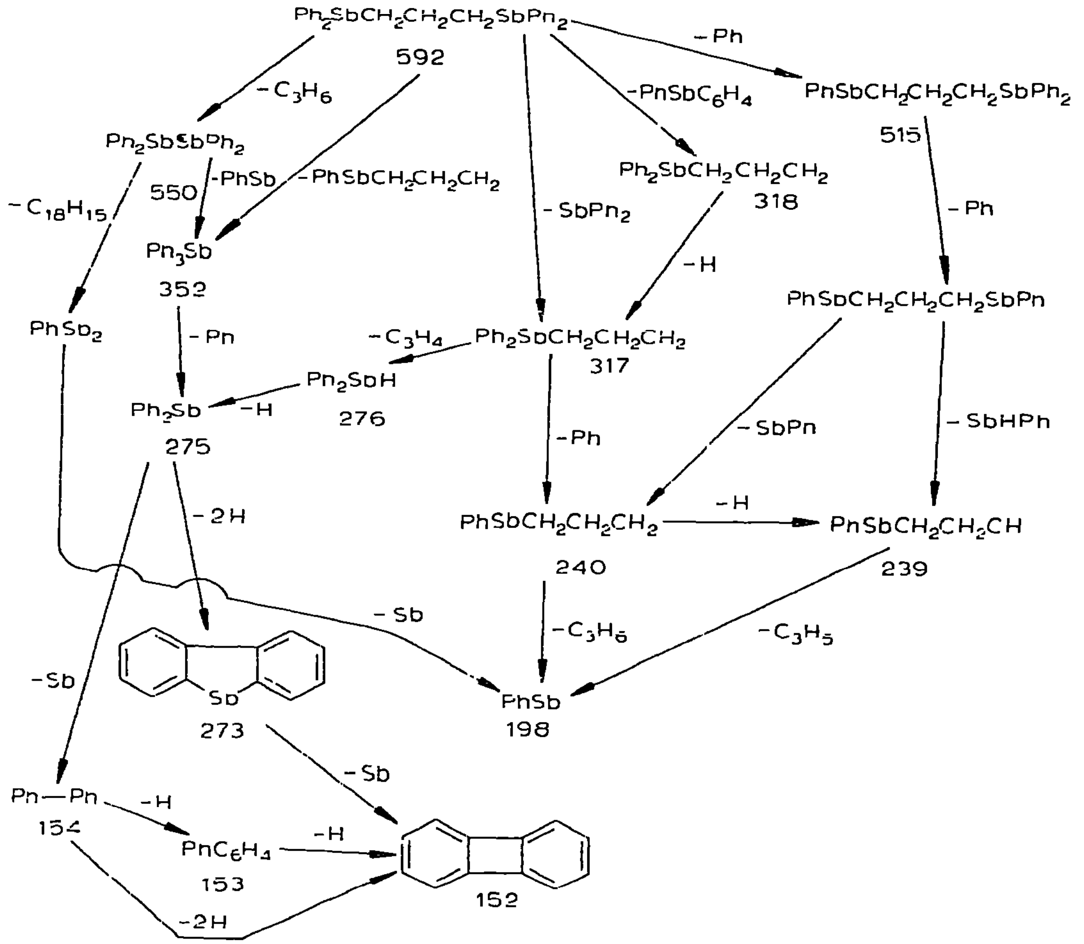


Fig. 3. Fragmentation of dsbp (^{121}Sb)

Acknowledgement

WL is grateful to The Science Research Council for the award of a Research Studentship.

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