Electron Impact Studies on Triphenyl Derivatives of the Group IIIB Metals

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Only Ph_3Al and Ph_3Ga of the Group IIIB metal triphenyls produce ions derived from the dimers Ph_6M_2 under electron impact. Fragmentation behaviour reflects the progressive weakening of the Ph–M bond as the series is descended. Appearance potential measurements are reported for the major metal-containing ions and $D(Ph_2M^+–Ph)$ evaluated.

THIS paper is concerned with the mass spectroscopic behaviour of the triphenyl derivatives of B, Al, Ga, In, and Tl, and parallels similar studies on the Group IIIB metal alkyls.[1,2] We have examined evidence for associated species present in the vapour phase, and compared their fragmentation behaviour and measured appearance potentials.

Whereas triphenylboron is monomeric in solution and as a vapour, triphenylaluminium is dimeric in benzene solution. Its *X*-ray crystal structure shows that two phenyl groups function as bridging ligands and there is evidence that phenyl is a stronger bridging group than methyl.[3] All of the other triphenyls are monomeric in solution though there is weak interaction between monomer units of Ph_3Ga and Ph_3In in the crystalline state.[4] The phenyl groups in triphenylthallium exchange rapidly, possibly by a dimeric transition state.[5]

EXPERIMENTAL

Commercial Ph_3B was purified by crystallisation from ether. Ph_3Al, Ph_3Ga, and Ph_3In were prepared by heating the metal, present in excess, and diphenylmercury in an evacuated sealed tube at 140°. Biphenyl and mercury by-products were distilled at 130° into a cooled constricted portion of the tube which was then sealed off. Triphenylthallium was obtained as colourless needles by the action of PhLi in ether on Ph_2TlCl. Samples were either attached directly to an all-glass inlet system on the mass spectrometer *via* a break-seal, or opened in a nitrogen glove box and transferred to a direct insertion probe using an adaptor that allowed all operations to be carried out against a counter current of nitrogen.

Spectra were recorded on an MS 902 mass spectrometer, normally at 70 eV with an accelerator voltage of 6 kV. The source temperature was varied between 105 and 360 °C. Ion abundances were recorded at a resolution of 1 : 5000 at constant source pressure. Appearance potentials were measured at a high constant source pressure (7×10^{-6} mmHg) with the ion repeller voltage set between -1 and 5 V, the trap current at 20 μA, and a resolution of about 1 : 500. Where two peaks occurred at the same nominal mass a higher resolution was employed. Argon was used as a reference and the potentials were evaluated by the Warren method.[6] Impurities (Ph_2 and Hg) present in samples of Ph_3Al, Ph_3Ga, Ph_3In were reduced to a negligible level by maintaining the spectrometer at 100 °C for 1 h before recording the spectra.

RESULTS AND DISCUSSION

The metal-containing ions are listed in Table 1 and the abundances of the Ph_3M, Ph_2M, PhM, and M ions at 70, 20, and 10 eV in Table 2. Abundances of all metal containing and total hydrocarbon ions are deposited together with metastable supported transitions as Supplementary Publication No. 20711 (7 pp.).†

TABLE 1

Metal containing ions

Ph_3B	Ph_3Al	Ph_3Ga	Ph_3In	Ph_3Tl
$C_{18}H_{15}B$ *	$C_{30}H_{25}Al_2$ *	$C_{30}H_{25}Ga_2$	$C_{30}H_{23}In$ *	$C_{18}H_{15}Tl$ *
$C_{18}H_{15}B^{2+}$	$C_{30}H_{24}Al_2$	$C_{24}H_{20}Ga_2$ *	$C_{30}H_{22}In$ *	$C_{18}H_{14}Tl$ *
$C_{18}H_{14}B$ *	$C_{24}H_{20}Al_2$ *	$C_{18}H_{15}Ga$ *	$C_{24}H_{19}In$ *	$C_{12}H_{10}Tl$ *
$C_{18}H_{14}B^{2+}$	$C_{24}H_{19}Al_2$	$C_{18}H_{14}Ga$ *	$C_{24}H_{18}In$ *	C_6H_5Tl
$C_{18}H_{13}B$	$C_{18}H_{15}Al_2$ *	$C_{12}H_{10}Ga$ *	$C_{18}H_{15}In$ *	Tl *
$C_{18}H_{13}B^{2+}$	$C_{18}H_{14}Al_2$	C_6H_5Ga *	$C_{18}H_{14}In$ *	
$C_{16}H_{13}B$	$C_{18}H_{15}Al$ *	Ga *	$C_{12}H_{10}In$ *	
$C_{16}H_{13}B^{2+}$	$C_{18}H_{14}Al$ *		C_6H_5In *	
$C_{16}H_{12}B$	$C_{12}H_{10}Al$ *		In *	
$C_{16}H_{12}B^{2+}$	$C_{12}H_9Al$ *			
$C_{16}H_{11}B$	$C_{12}H_8Al$ *			
$C_{16}H_{11}B^{2+}$	C_6H_5Al *			
$C_{12}H_{10}B$ *	Al *			
$C_{12}H_9B$ *				
$C_{12}H_8B$ *				
$C_{10}H_8B$ *				
$C_{10}H_7B$ *				
$C_{10}H_6B$ *				
C_8H_6B				
C_6H_5B *				
C_6H_4B *				
C_4H_3B				
C_4H_2B				

* Confirmed by accurate mass measurement (agreement better than 5 p.p.m.).

No associated species were recorded in the spectra of triphenylboron or triphenylthallium, but ions of *m/e* greater than the parent monomer were observed for Ph_3Al, Ph_3Ga, and Ph_3In. In the cases of Ph_3Al and Ph_3Ga these provide convincing evidence for the existence of dimeric species in the vapour phase and result from fragmentation of the parent dimer although this was not observed. For aluminium, dimer ions resulting from both loss of phenyl and benzene were observed.

$$\begin{tikzcd}
 & Ph_5Al_2^{+} \arrow[r] & Ph_4Al_2^{+\cdot} \arrow[r] & Ph_3Al_2^{+} \\
Ph_6Al_2^{+\cdot} \arrow[ur] \arrow[dr] & & & \\
 & Ph_4C_6H_4Al_2^{+\cdot} \arrow[r] & Ph_3C_6H_4Al_2^{+\cdot} \arrow[r] & Ph_2C_6H_4Al_2^{+\cdot}
\end{tikzcd}$$

In contrast triphenylgallium produced only two associated ions, $Ph_5Ga_2^{+}$ and $Ph_4Ga_2^{+\cdot}$ which were present down to 8 eV. These dimer ions were of low abundance, carrying <1% of the total ion current. The spectrum of triphenylindium contained ions of higher mass than

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† See Notice to Authors *J. Chem. Soc.* (*A*), 1970, Index Issue. Items less than 10 pp. are supplied as full size copies.

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TABLE 2

Variation of abundances * of major ions with electron voltage

	B			Al			Ga			In			Tl		
eV	70	20	10	70	20	10	70	20	10	70	20	10	70	20	10
Ions$^+$															
$Ph_3M + C_{18}H_{14}M$	24·3	38·3	73·2	14·3	34·1	51·0	4·1	7·1	11·8	3·4	8·3	11·2	1·0	2·0	0·9
$Ph_2M + C_{12}H_9M + C_{12}H_8M$	52·8	60·2	27·9	25·4	36·7	28·5	58·7	84·4	85·6	39·4	67·7	73·6	56·3	80·0	85·9
PhM	2·0			14·0	21·1	18·7	1·3	1·7	1·3	2·9	3·3	3·3	4·0	3·4	2·8
M				41·4	8·1	1·8	29·3	6·8	1·3	50·2	18·9	11·2	38·7	14·5	9·6

* % of total metal-containing ions.

the parent but, since they contained only one indium atom, they were probably derived from pyrolysis of the sample at the high temperature (290 °C) necessary to obtain the mass spectrum.

Only in the spectrum of Ph_3B were doubly charged ions observed ($C_{18}H_nB^{2+}$, $n = 13$—15; $C_{16}H_nB^{2+}$, $n = 11$—13). At 120 °C and 70 eV they carried 8·4% of the total ion current, but were absent at 20 eV.

The mass spectra reflect the progressive decrease in M–C bond strength in going from boron to thallium. Thus B^+ was never observed, the ions of lowest mass in the spectrum of Ph_3B being derived from loss of acetylene from $C_6H_5B^{+\cdot}$ and $C_6H_4B^+$. Similar processes have been reported in the mass spectra of other phenyl-metal compounds [7] but more unusual is the successive loss of acetylene from Ph_2B^+ giving the ions $C_{10}H_8B^+$ and $C_8H_6B^+$. Many ions in the spectrum of Ph_3B resulted from C–H bond cleavage, and even at 20 eV the $PhB^{+\cdot}$ ion was absent. Elimination of benzene from $Ph_3B^{+\cdot}$ was metastable supported.

The variation of ion abundances with electron voltage (Table 2) suggests that the formation of M^+ results from both cleavage of a phenyl group from $PhM^{+\cdot}$ and elimination of biphenyl from Ph_2M^+, the latter process being strongly metastable-supported for Ph_2Ga^+.

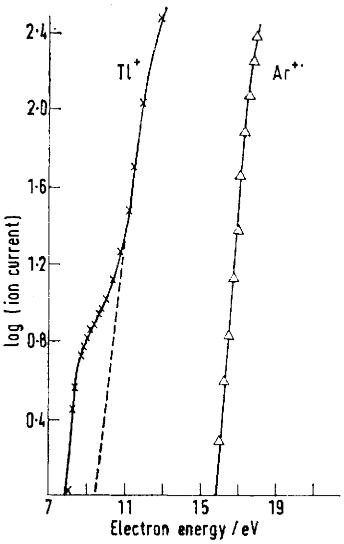
Hydrocarbon ions, principally $C_6H_6^{+\cdot}$ and $C_{12}H_{10}^{+\cdot}$, were present in all the spectra. For Ph_3B they carried 5·4—1·7% of the total ion current; for Ph_3Al the values were 62·6% at 70 eV and 27·8% at 5 eV. These were considerably higher than the corresponding values for Ph_3Ga, 6·6 and 11·7%, and may be attributed to occluded biphenyl contaminating the sample. In the cases of Ph_3In and Ph_3Tl, the major charge carrier was $C_{12}H_{10}^{+\cdot}$, hydrocarbon ions carrying about 99% of the total ion current.

Ionization and appearance potential data on the ions $Ph_3M^{+\cdot}$, Ph_2M^+, and M^+ are listed in Table 3. For aluminium and gallium the values reported could be derived from either monomer or dimer species; since the ionization efficiency curves were similar in form to those from boron and free from kinks, we are inclined to favour them being derived from monomer.

Comparative data are only available for boron where $A(Me_3B) = 8{\cdot}8 \pm 0{\cdot}2$ eV and $A(Et_3B) = 9{\cdot}0 \pm 0{\cdot}2$ eV.[8] Taking $\Delta H_f^0(Ph\cdot) = 325{\cdot}9$ kJ mol^{-1} and other published data [9,10] leads to a value of $\bar{D}(Ph{-}B)Ph_3B = 467$ kJ mol^{-1} which is twice our value for the cleavage of one Ph–B bond in the parent ion, $D(Ph_2B^+{-}Ph) = 232 \pm 20$ kJ mol^{-1}. The ionization efficiency curve for Tl^+ was unusual in showing a kink between 9 and 11 eV (Figure) similar to that reported for ferrocene.[11] Evaluation of $A(Tl^+)$ using the upper and lower linear portions of the curve gave values of 9·4 and 8 eV respectively, both lower than $A(Ph_2Tl^+)$. This behaviour is indicative of two processes contributing to the ionization efficiency curve and it is possible that the lower value results from thermal decomposition of Ph_3Tl to PhTl with subsequent ionization and fission of phenylthallium(I).

TABLE 3

Ion	Appearance potential, ±0·2 eV				
	B	Al	Ga	In	Tl
Ph_3M	9·2	9·0	9·0	9·0	
Ph_2M	11·6	10·3	9·6	9·4	9·8
M				9·3 ± 0·5	9·4
$D(Ph_2M{-}Ph)$	2·4	1·3	0·6	0·4	



Ionization efficiency curve for Tl^+

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