# Triphenylphosphine–Halogen Adducts of Novel Stoicheiometry

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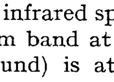
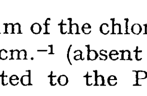
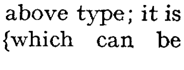
IN a recent communication[1] we recorded the isolation of a solid whose composition corresponded analytically to $Ph_3PBr_{0\cdot5}I_{1\cdot5}$. That this is not a unique example of this unexpected stoicheiometry is revealed by our isolation of $Ph_3PCl_{0\cdot5}I_{1\cdot5}$ as a yellow crystalline solid (m.p. 218° decomp.) when ether is added to methyl cyanide containing equimolar quantities of triphenylphosphine and iodine chloride. The ultraviolet spectrum of methyl cyanide solutions of both of these compounds shows strong tri-iodide ion absorption suggesting that the above formulæ should be doubled and written as the ionic structures, $[(Ph_3P)_2Br]^+I_3^-$ and $[(Ph_3P)_2Cl]^+I_3^-$. The values of specific conductance of the methyl cyanide solutions are high, and the molar conductance values calculated on the basis of the doubled formulæ are 95·0 and 127·2 ohm$^{-1}$cm.$^2$mole$^{-1}$ (0·01M solutions) for the bromo- and chloro-compound, respectively: that is, values as expected for strong 1 : 1 electrolytes in methyl cyanide. Nitrobenzene solutions of the compounds are likewise good electrolytic conductors, and cryoscopic determination of the average molecular weight of the species present accords with the postulated formulation, $[(Ph_3P)_2Hal]^+I_3^-$.

Compounds containing cations of the type $[(Ph_3P)_2Hal]^+$ have not, to our knowledge, been reported so far: however, it has been suggested[2] that in the formation of the phenylphosphorus halide,  $\underset{\mathrm{Br}}{\mathrm{Ph_3P}}-\underset{\mathrm{Br}}{\mathrm{PPh_3}}$ the ion  $\mathrm{Ph_3P}-\underset{\mathrm{Br}}{\overset{+}{\mathrm{P}}}\mathrm{Ph_3}$ participates as an intermediate. Thus it seems reasonable to suggest that the structure of the cations of the compounds presently described may be  $\mathrm{Ph_3P}-\underset{\mathrm{Cl(Br)}}{\overset{+}{\mathrm{P}}}\mathrm{Ph_3}$.

In the infrared spectrum of the chloro-compound a medium band at 580 cm.$^{-1}$ (absent in the bromo-compound) is attributed to the P–Cl stretching vibration. A shoulder at 490 cm.$^{-1}$ in the bromo-compound is possibly the P–Br stretching frequency.

So far we have prepared only one other compound which may contain a cation of the above type; it is the adduct $(Ph_3P)_2HgBr_2,Br_2$ {which can be written $[(Ph_3P)_2Br]^+HgBr_3^-\}$ obtained as a white crystalline solid, m.p. 130°, on adding ether to an equimolar mixture of $(Ph_3P)_2HgBr_2$ and bromine in methyl cyanide. The molar conductance of the compound in methyl cyanide is 117·5 ohm$^{-1}$ cm.$^2$ mole$^{-1}$ ($C_m$ = 0·01).

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[1] A. D. Beveridge, G. S. Harris, and (in part) F. Inglis, *J. Chem. Soc.* (*A*), 1966, 520.

[2] B. Miller, in "Topics in Phosphorus Chemistry", Interscience, New York, 1965, vol. 2, p. 195.