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SOME TRIS(*para*-SUBSTITUTED PHENYL)ARSINE–HALOGEN ADDUCTS—A CONDUCTANCE STUDY

GORDON S. HARRIS,* ABDULLAH KHAN† and AMINA MAHOMEDY

School of Chemistry, University of St Andrews, St Andrews, Scotland, U.K.

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Abstract—Conductometric titration studies have been made of some tris(*para*-substituted phenyl)arsine–halogen systems $(p\text{-}YC_6H_4)_3As\text{–}X_2$ [Y = CH_3, F, and CF_3; X_2 = Br_2, I_2, and IBr] in acetonitrile. When $X_2 = Br_2$ evidence was obtained in each case for the formation of 1 : 1 and 2 : 1 adducts [$(p\text{-}YC_6H_4)_3AsBr_2$ and $(p\text{-}YC_6H_4)_3AsBr_4$] in solution but for $X_2 = I_2$ and IBr there was no evidence for 1 : 1 adduct formation, and only two 2 : 1 adducts, $(p\text{-}CH_3C_6H_4)_3AsI_4$ and $(p\text{-}CH_3C_6H_4)_3AsI_2Br_2$, were indicated. All of the 1 : 1 adducts [$(p\text{-}YC_6H_4)_3AsBr_2$; Y = CH_3, F, and CF_3] and some of the 2 : 1 adducts [$(p\text{-}CH_3C_6H_4)_3AsX_4$; X_2 = Br_2, I_2, and IBr] shown by conductometric titration to form in solution have been isolated as crystalline solids. Electrolytic conductance studies of the dichlorides, $(p\text{-}YC_6H_4)_3AsCl_2$, and dibromides, $(p\text{-}YC_6H_4)_3AsBr_2$, in acetonitrile give molar conductivity values which indicate that these compounds are weak electrolytes, and Hammett plots show that for each series there is a good correlation between molar conductivity and the electronic effect of substituent Y—the smaller the electron withdrawing power of Y, the larger the value of molar conductivity.

It is well known that the trialkyl and triaryl derivatives of Group 15 elements (R_3E) have, in general, a strong tendency to react with halogens (X_2) to form 1 : 1 adducts (R_3EX_2) and that in some cases 2 : 1 adducts (R_3EX_4) are formed.[1–3] These adduct types are the so-called dihalides and tetrahalides respectively of R_3E, and this nomenclature will, for convenience, also be used in this paper; it is emphasised that only the stoichiometry of compounds is implied by these names.

Our previous studies of the electrolytic conductance of the dihalides, R_3EX_2, in non-aqueous solvents have clearly demonstrated that the conductance properties of such compounds, when R and X remain the same, depend on the identity of the atom E.[3,4] For example, acetonitrile solutions of Ph_3PCl_2 have high values of molar conductivity ($\Lambda \approx 80$ S cm^2 mol^{-1}) whereas solutions of Ph_3SbCl_2 are virtually non-conducting ($\Lambda < 1$ S cm^2 mol^{-1}); Ph_3AsCl_2 is intermediate in its behaviour giving molar conductivity values between these extremes ($\Lambda \approx 4$ S cm^2 mol^{-1}).‡ Thus Ph_3PCl_2 is regarded as a strong 1 : 1 electrolyte, Ph_3AsCl_2 a weak electrolyte, and Ph_3SbCl_2 a non-electrolyte in acetonitrile.[4]

It has likewise been observed that changing R in R_3PX_2 and in R_3AsX_2 (X being kept the same) results in a change in molar conductivity—an effect which in some cases is substantial. For example, whereas acetonitrile solutions of $(C_6H_5)_3PCl_2$ have high values of molar conductivity ($\Lambda \approx 80$ S cm^2 mol^{-1}) the values for similar solutions of $(C_6F_5)_3PCl_2$ are very low ($\Lambda < 1$ S cm^2 mol^{-1}).[4,5] This strongly suggests that the electronic effect of the organic group attached to atom E in the compounds R_3EX_2 plays an important role in determining the extent to which these compounds form ions in a non-aqueous ionising solvent. To examine

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* Author to whom correspondence should be addressed.

† Present address: Chemistry Department, University of Baluchistan, Quetta, Pakistan.

‡ The quoted values of molar conductivity refer to solutions of comparable concentrations (*ca* 0.01 mol dm^{-3}), and this applies throughout this paper when relative values of molar conductivity of compounds are being discussed.

this idea further we have prepared and carried out a conductance study of a series of arsenic compounds, R_3AsX_2, in which R is a *para*-substituted phenyl group, YC_6H_4; the reason for introducing substituent Y was to alter, to varying degrees, the overall electronic effect of YC_6H_4 relative to that of the phenyl group (Y = H). The substituents (Y) selected were CF_3, F, and CH_3 which vary widely in their electronic effect, and *para* substitution was chosen to eliminate any steric effect of Y. The choice of arsenic as the Group 15 element was made because solutions of the phenyl compounds Ph_3AsX_2 (X = Cl, Br) in acetonitrile have intermediate values of molar conductivity, indicating weak electrolyte behaviour,[3]

$$Ph_3AsX_2 \rightleftarrows Ph_3AsX^+ + X^-.$$

Consequently in the *para*-substituted derivatives any significant change in the position of the ionisation equilibrium,

$$(p\text{-}YC_6H_4)_3AsX_2 \rightleftarrows (p\text{-}YC_6H_4)_3AsX^+ + X^-,$$

arising from Y being a group other than H, should result in an observable increase or decrease in molar conductivity relative to that of Ph_3AsX_2 at similar concentrations.

As a preliminary to our investigation of the electrolytic conductance of the dihalides $(p\text{-}YC_6H_4)_3AsX_2$, we carried out conductometric titrations of the parent $(p\text{-}YC_6H_4)_3As\text{–}X_2$ systems (except those for which $X_2 = Cl_2$) to obtain information on the stoichiometry of the adducts formed in acetonitrile and to gain preliminary information on their conducting properties. Also, to identify any trihalide ions formed in each reaction, the ultra-violet spectrum of the solution being titrated was recorded at selected stages. These techniques have previously proved to be very informative when applied to other $R_3E\text{–}X_2$ systems.[3,4,6]

RESULTS AND DISCUSSION

Conductometric titrations

Nine $(p\text{-}YC_6H_4)_3As\text{–}X_2$ systems were studied, involving the arsines, tris(*p*-methylphenyl)arsine, tris(*p*-fluorophenyl)arsine, and tris(*p*-trifluoromethylphenyl)arsine, and the halogens, bromine, iodine, and iodine bromide. The conductometric titration graphs fell into three categories, henceforth referred to as Types I, II, and III graphs; these are exemplified in Figs 1–3 by the graphs of the systems, $(p\text{-}FC_6H_4)_3As\text{–}Br_2$, $(p\text{-}CH_3C_6H_4)_3As\text{–}I_2$, and $(p\text{-}CF_3C_6H_4)_3As\text{–}IBr$, respectively.

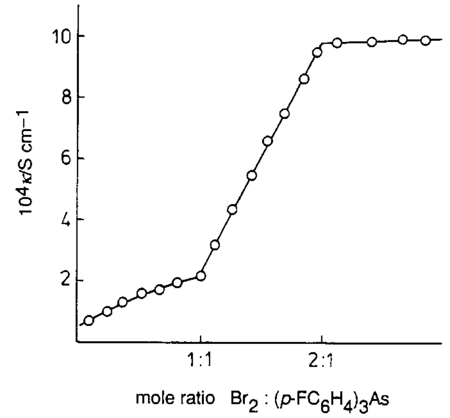

Fig. 1. Conductometric tritration of $(p\text{-}FC_6H_4)_3As$ with Br_2 (Type I graph).

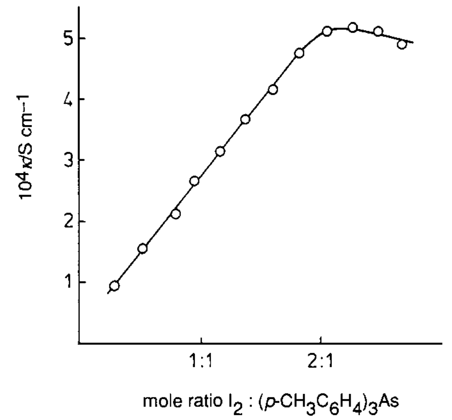

Fig. 2. Conductometric titration of $(p\text{-}CH_3C_6H_4)_3As$ with I_2 (Type II graph).

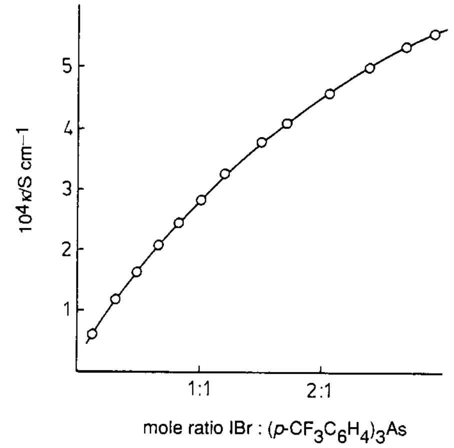

Fig. 3. Conductometric titration of $(p\text{-}CF_3C_6H_4)_3As$ with IBr (Type III graph).

$(p\text{-}YC_6H_4)_3As\text{–}Br_2$ *systems.* Each of the three systems gives a Type I graph, the two breaks in which indicate a two-stage reaction producing firstly the 1 : 1 adduct followed by the 2 : 1 adduct:

$$(p\text{-YC}_6\text{H}_4)_3\text{As} \xrightarrow{\text{Br}_2} (p\text{-YC}_6\text{H}_4)_3\text{AsBr}_2 \xrightarrow{\text{Br}_2} (p\text{-YC}_6\text{H}_4)_3\text{AsBr}_4.$$

A colour change (colourless to yellow) occurs at the first end-point due to the formation of tribromide ion after the 1 : 1 molar ratio. In each case the 1 : 1 adduct has a lower conductivity (κ) than the 2 : 1 adduct; for the 1 : 1 adducts molar conductivity (Λ) values fall in the range 3.9–51.5 S cm^2 mol^{-1}, whereas for the 2 : 1 adducts the range is 112.1–121.0 S cm^2 mol^{-1}. These values indicate that the 1 : 1 adducts behave as very weak to weak 1 : 1 electrolytes in acetonitrile,

$$(p\text{-YC}_6\text{H}_4)_3\text{AsBr}_2 \rightleftharpoons (p\text{-YC}_6\text{H}_4)_3\text{AsBr}^+ + \text{Br}^-$$

whilst the 2 : 1 compounds are all strong 1 : 1 electrolytes,

$$(p\text{-YC}_6\text{H}_4)_3\text{AsBr}_4 \rightarrow (p\text{-YC}_6\text{H}_4)_3\text{AsBr}^+ + \text{Br}_3^-.$$

These three systems behave in a like-manner to the triphenylarsine–bromine system.[3]

$(p\text{-YC}_6\text{H}_4)_3\text{As-I}_2$ *and* $(p\text{-YC}_6\text{H}_4)_3\text{As–IBr}$ *systems.* None of the six systems which come under this heading gave any evidence for the formation of a 1 : 1 adduct in acetonitrile. Two of the systems, $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As–I}_2$ and $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As–IBr}$, did however give a clear indication of the formation of 2 : 1 adducts; each gave a Type II graph showing that a one stage reaction occurs:

$$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As} + 2\text{I}_2 \rightarrow (p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$$

$$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As} + 2\text{IBr} \rightarrow (p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2\text{Br}_2.$$

The ions I_3^- and I_2Br^- respectively were detected in solution from the commencement of these titrations; the molar conductivity of the solutions at the 2 : 1 mole ratio is high in each case (114.4 S cm^2 mol^{-1} and 113.0 S cm^2 mol^{-1} respectively) which indicates strong 1 : 1 electrolytes:

$$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4 \rightarrow (p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}^+ + \text{I}_3^-$$

$$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2\text{Br}_2 \rightarrow (p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}^+ + \text{I}_2\text{Br}^-.$$

These two systems parallel the triphenylarsine–iodine and triphenylarsine–iodine bromide systems respectively in their behaviour.[3]

The remaining four systems of this group [$(p\text{-FC}_6\text{H}_4)_3\text{As–I}_2$, $(p\text{-FC}_6\text{H}_4)_3\text{As–IBr}$, $(p\text{-CF}_3\text{C}_6\text{H}_4)_3\text{As–I}_2$, and $(p\text{-CF}_3\text{C}_6\text{H}_4)_3\text{As–IBr}$] all gave conductometric titration graphs of Type III. The observed increase in conductivity as titration proceeds points to the formation of a product which forms ions in solution, and this accords with the detection of trihalide ion in solution from the beginning of each titration. Again it is clear that 2 : 1 adducts are being formed directly from the start of titration, but the continued increase in conductivity beyond the 2 : 1 mole ratio and absence of a sharp break in the titration graph suggests incomplete reaction at the equivalence point. In these four systems therefore we are dealing with equilibrium reactions, for example,

$$(p\text{-FC}_6\text{H}_4)_3\text{As} + 2\text{I}_2 \rightleftarrows (p\text{-FC}_6\text{H}_4)_3\text{AsI}_4 \quad [\equiv (p\text{-FC}_6\text{H}_4)_3\text{AsI}^+ + \text{I}_3^-]$$

in which a significant amount of the reactants is present in solution at the (2 : 1) equivalence point.

Isolation of adducts

The 1 : 1 adducts (dihalides) shown by conductometric titration to form in acetonitrile solution are all dibromides namely, $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$, $(p\text{-FC}_6\text{H}_4)_3\text{AsBr}_2$, and $(p\text{-CF}_3\text{C}_6\text{H}_4)_3\text{AsBr}_2$. These were readily obtained as crystalline solids from a solution containing 1 : 1 molar proportions of the arsine and bromine. The corresponding dichlorides, $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$, $(p\text{-FC}_6\text{H}_4)_3\text{AsCl}_2$, and $(p\text{-CF}_3\text{C}_6\text{H}_4)_3\text{AsCl}_2$ were also obtained readily by passage of excess chlorine into a solution of the arsine. Although the conductometric titrations gave no indication of the formation of 1 : 1 adducts by any of the arsines with iodine or iodine bromide, three of these have in fact been isolated as crystalline solids [$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2$, $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsIBr}$, and $(p\text{-CF}_3\text{C}_6\text{H}_4)_3\text{AsI}_2$]. The isolation of solid adducts which were not indicated by conductometric titration has been observed before; for example, Ph_3AsI_2, which does not show up in the conductometric titration graph of the $\text{Ph}_3\text{As–I}_2$ system, can be obtained as a crystalline solid.[3] It has been noted however that on dissolving this solid in acetonitrile, disproportionation (to $\text{Ph}_3\text{As} + \text{Ph}_3\text{AsI}_4$) occurs, thus explaining the conductometric titration results in such cases.

Of the nine 2 : 1 adducts possible in principle in these systems only $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsBr}_4$, $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_4$, and $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{AsI}_2\text{Br}_2$ have been prepared as analytically pure compounds. Attempts were not made to prepare the other possible 2 : 1 adducts, whether indicated by conductometric titration or not, since the present work is primarily concerned with (an electrolytic conductance study of) the 1 : 1 adducts.

Table 1. Molar conductivity (Λ) at 25°C of $(p\text{-}YC_6H_4)_3AsCl_2$ and $(p\text{-}YC_6H_4)_3AsBr_2$ [Y = CH_3, H, F, and CF_3] at concentration 0.01 mol dm^{-3} in acetronitrile

Compound	Λ S cm^2 mol^{-1}	Compound	Λ S cm^2 mol^{-1}
$(p\text{-}CH_3C_6H_4)_3AsCl_2$	5.4	$(p\text{-}CH_3C_6H_4)_3AsBr_2$	53.0
$(C_6H_5)_3AsCl_2$	4.0	$(C_6H_5)_3AsBr_2$	25.3
$(p\text{-}FC_6H_4)_3AsCl_2$	2.5	$(p\text{-}FC_6H_4)_3AsBr_2$	20.0
$(p\text{-}CF_3C_6H_4)_3AsCl_2$	0.5	$(p\text{-}CF_3C_6H_4)_3AsBr_2$	2.5

Electrolytic conductance of the dihalides

Electrolytic conductance measurements were made on acetonitrile solutions of the 1 : 1 adducts $(p\text{-}YC_6H_4)_3AsX_2$ (dichlorides and dibromides) in the concentration range 0.002–0.03 mol dm^{-3}. The observed values of molar conductivity were relatively low and the graph of molar conductivity against square root of concentration was typical of a weak electrolyte in each case. For comparison purposes, values of molar conductivity at concentration 0.01 mol dm^{-3} were taken from the graphs and recorded in Table 1. From these results it can be seen that for a given arsine the dibromide is more highly conducting that the dichloride; also, values of molar conductivity, with one exception, fall in the range 0–25.5 S cm^2 mol^{-1}. Additionally it is noticed that within each series, $(p\text{-}YC_6H_4)_3AsCl_2$ and $(p\text{-}YC_6H_4)_3AsBr_2$, molar conductivities show a marked dependence on the nature of the substituent Y.

On the basis of the latter observation, for each series a plot was made of $\log_{10}(\Lambda_Y/\Lambda_H)$ against the values of Hammett substituent constant σ_Y* for each substituent Y, in order to investigate more closely the relation between molar conductivity and the electronic effect (electron withdrawing or releasing effect) of the substituent. From the graphs obtained (Fig. 4) it is seen that for each series of compounds the points lie approximately on a straight line (of negative slope) indicating a good Hammett correlation in each case. That is, molar conductivity of the compounds correlates well with the electronic effect of substituent Y, which implies correlation of molar conductivity with the electronic effect of the group YC_6H_5 (as a whole) attached to the arsenic atom. Thus for each series, $(p\text{-}YC_6H_4)_3AsCl_2$ and $(p\text{-}YC_6H_4)_3AsBr_2$, the smaller the electron withdrawing power of Y, and hence of the group YC_6H_4, the higher is the observed value of molar conductivity.

It seems reasonable therefore to suggest that for compounds R_3AsX_2 in general, in the absence of steric effects, the electronic effect of group R plays a major role in determining the tendency of a given compound to form ions when dissolved in a non-aqueous ionising solvent, the rule apparently being, the tendency of R_3AsX_2 (X being specified) to form ions increases as the electron withdrawing power of group R decreases.

The explanation of this behaviour follows lines similar to those advanced (by organic chemists) to explain the dependence of acid strength of carboxylic acids, RCOOH, on the precise nature of R.[7]

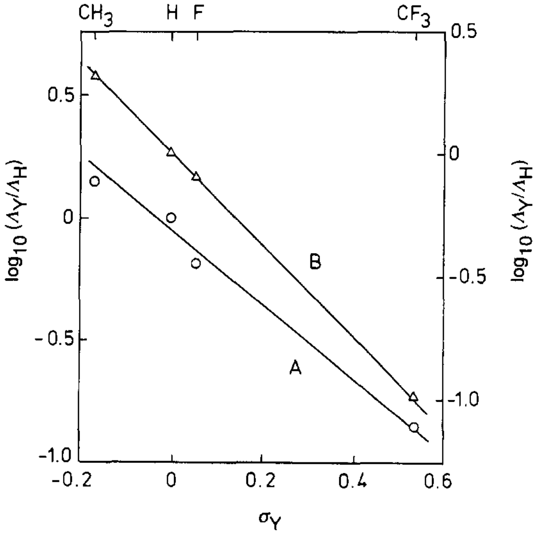

Fig. 4. Hammett plots for the conductivity (molar) of $(p\text{-}YC_6H_4)_3AsCl_2$ [graph A; left-hand ordinate] and $(p\text{-}YC_6H_4)_3AsBr_2$ [graph B; right-hand ordinate] in acetonitrile solution. On the upper abscissa the σ_Y values of the groups (Y) involved are indicated. The two ordinates have the same scale but these are displaced relative to one another to avoid overlap of the two graphs.

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*The conventional symbol for the Hammett substituent constant is σ_X but in this paper σ_Y is used instead since we use Y as the general symbol for a substituent and X as the general symbol for a halogen atom.

However, for the compounds under consideration (R_3AsX_2) the arguments are reversed. This is because on ionisation of R_3AsX_2 the group R becomes part of the positive ion; (this is also the reason for the negative slope of the Hammett plots referred to earlier).

Explanation of the observed conductivity behaviour of R_3AsX_2, as with the carboxylic acids, involves bond strength and entropy considerations:

(a) If the unionised R_3AsX_2 molecule in solution has a pentacoordinate (e.g. trigonal bipyramidal) covalent structure, ionisation must involve an As—X (axial, most likely) bond-breaking step; thus any change in the strength of the As—X bond brought about by changing group R will influence the tendency of R_3AsX_2 to ionise in non-aqueous ionising solvents. It is, for example, likely that an electron releasing group will have a slight weakening effect on the As—X bond whilst an electron withdrawing group will have the opposite effect. Support for this suggestion comes from the work of Bartell and Hansen (electron diffraction)[8] and of Downs and Schmutzler (vibrational spectroscopy)[9] on the related fluoromethylphosphoranes, $(CH_3)_nPF_{5-n}$ (trigonal bipyramidal structures). In these compounds it has been shown that the P—F (axial) bonds are weaker than in phosphorus pentafluoride and that they become progressively weaker as n, the number of electron releasing methyl groups, increases.

If, on the other hand the unionised R_3AsX_2 molecule in solution is a donor–acceptor complex of the type R_3E–X–X, as has been shown recently by McAuliffe *et al.* to be the case for Ph_3AsI_2 in the solid state[10] (crystalline Ph_3PI_2 and Ph_3PBr_2 have analogous structures[11,12]) then ionisation involves cleavage of the X—X bond. Structural data for donor–acceptor compounds of this kind clearly show that the X—X bond is longer, and by inference weaker, than in the parent dihalogen molecule.[10–12] The extent of X—X bond weakening is, as expected, greater the greater the donor strength of R_3E[11,13,14] which in turn depends, when E is specified, on the electronic effect of R (if R is electron withdrawing R_3E is a weak donor: if R is electron releasing, R_3E is a stronger donor).

(b) An entropy factor which depends on the electronic effect of R is likely to be more important than the bond energy considerations discussed under (a) above.[7] In the cation R_3AsX^+, the smaller the electron withdrawing power of R the greater will be the spreading out of the cationic charge. This will result in a lessening of order in the arrangement of solvent molecules in the vicinity of the cation thus favouring the right-hand side of the ionisation equilibrium.

The phosphorus compounds, R_3PX_2, like their arsenic analogues discussed above vary widely in their conductance behaviour,[4,5,15] and it seems reasonable to assume that for them also the electronic effect of the group R is, in the absence of any steric effect, the main factor influencing the molar conductivities of these compounds in non-aqueous ionising solvents.

EXPERIMENTAL

As most of the compounds involved in this work are hydrolytically unstable, strict precautions were taken to ensure the exclusion of moisture at all times; thus manipulations were carried out in a dry-box through which a flow of dry nitrogen was passed, all apparatus and solvents were thoroughly dried before use, and a vacuum system was used in the purification and handling of volatile compounds.

Standard reagents and solvents used were of the best quality available commercially and these were further purified by conventional methods. Acetonitrile suitable for conductivity studies was obtained using the purification method described by Smith and Witten.[16]

For conductance measurements of solutions a sealed cell of the dipping electrodes type was used. The platinum electrode supports were mounted on a glass cone which fitted the vessel containing the solution which was prepared *in situ* in the dry-box. The apparatus and techniques used for the conductometric titrations have been described previously.[4,17] Conductance was measured using a Phillips resistance bridge (type GM 4249). Ultraviolet spectra were recorded on a Unicam SP800B ultra-violet-visible recording spectrophotometer; measurements were made in stoppered quartz cells of path lengths in the range 5–0.1 mm. Analytical data (C, H, and N) were obtained using a Perkin–Elmer Model 240 and a Carlo Erba strumetazione Mod 1106 elemental analyser. Halogen analysis was carried out potentiometrically using an adaptation of the method described by Lingane.[18]

Preparation of arsines

Tris(p-methylphenyl)arsine was prepared by a standard Wurtz-type reaction between p-bromotoluene and arsenic trichloride in dry diethyl ether.[1] The product was purified by column chromatography (alumina) using petroleum (40–60°C) as eluant. Removal of solvent gave a white solid m.p. 46°C. Found: C, 72.4; H, 6.0. Calc. for $C_{21}H_{21}As$: C, 72.4; H, 6.0%.

Tris(p-fluorophenyl)arsine was made from the reaction between the Grignard reagent of *p*-bromofluorobenzene and arsenic trichloride in diethyl ether; the reactants were refluxed for 2 h. Decomposition of the reaction product (using dilute sulphuric acid) followed by extraction with diethyl ether gave an oily liquid. This was passed through a silica gel column (eluant benzene/petroleum (40–60°C) [1 : 4 mixture]). Removal of solvent gave a clear viscous liquid which, on standing, gave a white solid, m.p. 75–77°C. Found: C, 60.6; H, 3.4. $C_{18}H_{12}AsF_3$ requires C, 60.0; H, 3.3%.

Tris(*p*-trifluoromethylphenyl)arsine was made by adding (dropwise with constant stirring) arsenic trichloride in diethyl ether to *p*-trifluoromethyl phenyllithium in diethyl ether at 0–5°C. After complete addition of the arsenic trichloride the mixture was stirred for 3 h then hydrolysed with dilute hydrochloric acid. The ether layer was separated off, dried (over anhydrous sodium sulphate), and evaporated to yield crude product which was purified by passage through a silica gel column as in the previous preparation. This yielded, after evaporation of the solvent, a solid which was recrystallised from ethanol/water to give a white solid, m.p. 81–83°C. Found: C, 50.5; H, 2.6. $C_{21}H_{12}AsF_9$ requires C, 49.4; H, 2.4%.

Preparation of halogen adducts

The dichlorides were prepared by passage of a stream of dry chlorine gas, diluted in a stream of dry nitrogen, through a cooled solution of the triarylarsine in chloroform, until the solution acquired a pale yellow–green colour. The dichlorides were obtained as crystalline solids either by adding dry diethyl ether to the chloroform solution or by removal of the solvent under vacuum. The dibromides, di-iodides, and bromide iodides were prepared by the addition (dropwise with shaking) of the appropriate halogen or interhalogen (*x* moles) in dry acetonitrile to a solution or suspension of the triarylarsine (*x* moles) in the same solvent. The crystalline dihalide was obtained from the resulting solution by removal of solvent under vacuum or by

Table 2. Elemental analysis (%)[a] and properties of the adducts

Adduct[b]	Colour	m.p.[c] (°C)	C	H	Cl	Br	I
$(CH_3C_6H_4)_3AsCl_2$[d]	White	220–224	59.8	5.4	17.0	—	—
			(60.1)	(5.1)	(16.9)	—	—
$(FC_6H_4)_3AsCl_2$	White	206–208	49.2	2.7	17.0	—	—
			(50.1)	(2.8)	(16.5)	—	—
$(CF_3C_6H_4)_3AsCl_2$	White	214–216	43.4	2.1	12.5	—	—
			(43.4)	(2.1)	(12.2)	—	—
$(CH_3C_6H_4)_3AsBr_2$[d]	White	236–238	50.4	4.0	—	31.1	—
			(49.6)	(4.2)	—	(31.4)	—
$(FC_6H_4)_3AsBr_2$	White	244–246	42.5	2.4	—	30.4	—
			(41.6)	(2.3)	—	(30.7)	—
$(CF_3C_6H_4)_3AsBr_2$	White	210–212	38.2	1.8	—	23.4	—
			(37.6)	(1.8)	—	(23.9)	—
$(CH_3C_6H_4)_3AsIBr$	Yellow	149–151	45.0	3.9	—	14.0	22.2
			(45.4)	(3.8)	—	(14.4)	(22.8)
$(CH_3C_6H_4)_3AsI_2$[d]	Red–brown	166–167	42.0	3.5	—	—	41.4
			(41.9)	(3.5)	—	—	(42.1)
$(CF_3C_6H_4)_3AsI_2$	Dark brown	116–118	33.8	1.7	—	—	33.0
			(33.0)	(1.6)	—	—	(33.2)
$(CH_3C_6H_4)_3AsBr_4$	Dark orange	120–121	37.8	3.1	—	47.4	—
			(37.8)	(3.1)	—	(47.8)	—
$(CH_3C_6H_4)_3AsI_2Br_2$	Brown	132–133	33.1	2.7	—	19.1	33.4
			(33.1)	(2.8)	—	(20.9)	(33.3)
$(CH_3C_6H_4)_3AsI_4$	Dark brown	152–153	29.6	2.4	—	—	58.6
			(29.5)	(2.5)	—	—	(59.3)

[a] Theoretical values in parentheses.
[b] All *para*-substituted compounds.
[c] With decomposition.
[d] These adducts have been reported previously.[1]

reduction of the volume of the solution followed by the addition of dry diethyl ether. The tetrahalides were prepared by adding (dropwise with stirring) the appropriate halogen or interhalogen (x moles) in dry acetonitrile to the triarylarsine ($x/2$ moles) dissolved in the same solvent. After reducing the volume of the resultant solution, the crystalline tetrahalide was obtained by the addition of dry diethyl ether. Analytical and m.p. data for all the adducts prepared are given in Table 2.

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