Metal Complexes formed by Some Substituted Phenyldialkyl-phosphines and -arsines.

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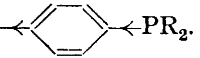
A number of complexes of silver(I), copper(I), zinc, cadmium, mercury, cobalt, and nickel halides with *p*-dimethylaminophenyldimethylphosphine and with the corresponding arsine have been prepared and compared with those formed by the unsubstituted ligands and ligands containing *p*-trifluoromethylphenyl groups. In all cases except that of mercury, which has a strong tendency to form d_π–d_π bonds, substitution of a *p*-dimethylamino-group in an arsine $Ph{\cdot}AsMe_2$ increases the stability of complexes, and a *p*-trifluoromethyl group has the reverse effect. With the phosphines, which are stronger donors, this effect is only apparent with zinc and cadmium, which also co-ordinate strongly to nitrogen and oxygen. This suggests that metals which co-ordinate by both a σ and a strong π bond are not appreciably affected by electronic effects which would greatly influence complexes involving only σ or weak π bonds. Several complexes have been prepared in which silver is three co-ordinated.

Electronegativity effects strongly influence the strengths of co-ordinate links. In the absence of any possible double bonding by *d* orbitals these effects are well understood, and may be illustrated by the strong acceptor properties of boron trifluoride relative to trimethylboron. Recently, however, *d* orbitals have been shown to contribute to whole or partial double bonds by forming d_π–p_π bonds (*e.g.*, in sulphates and phosphine oxides, Phillips, Hunter, and Sutton, *J.*, 1945, 146; and in transition-metal complexes with carbon monoxide and cyanides), and by forming d_π–d_π bonds in the complexes of Groups I*b*, II*b*, and VIII with heavier donors of Groups V and VI such as phosphorus, arsenic, or sulphur (Nyholm, *J.*, 1951, 3245; see Chatt, *J.*, 1952, 4300 for references). The overall effect of electronegativity on the stability of complexes in which *d* orbitals are involved is rather complicated as several factors are concerned, *viz.*, (*a*) the normal effect on the σ component of the co-ordinate link, (*b*) the effect on the π component (d_π–d_π bonding), and (*c*) the effect on matching of *d* with *s* and *p* orbitals in cases where dsp^2 or d^2sp^3 σ bonds are involved (see Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332).

The object of the present investigation was to compare the donor properties of some tertiary phosphines and arsines in which strong electronic effects may be transmitted to the phosphorus or arsenic atom without affecting its steric environment. *para*-Substituted phenyldimethyl(and diethyl)-phosphines and -arsines were selected, since electronic effects are strongly transmitted across a phenyl group, while the electronically active group remains at a distance from the co-ordinate link and does not affect its steric condition. Triarylphosphines were avoided since they tend to give inconveniently insoluble metal complexes in many cases, whereas the aryldialkylphosphines are sufficiently unsymmetrical to result in higher solubilities. The dimethylamino- (electron-repelling) and trifluoromethyl (electron-attracting) groups were used in the eight compounds, $NMe_2{\cdot}C_6H_4{\cdot}PMe_2$, $C_6H_5{\cdot}PMe_2$, $NMe_2{\cdot}C_6H_4{\cdot}PEt_2$, $C_6H_5{\cdot}PEt_2$, $CF_3{\cdot}C_6H_4{\cdot}PEt_2$, $NMe_2{\cdot}C_6H_4{\cdot}AsMe_2$, $C_6H_5{\cdot}AsMe_2$, $CF_3{\cdot}C_6H_4{\cdot}AsMe_2$. Unfortunately, attempts to prepare dimethyl-*p*-trifluoromethylphenylphosphine were not successful. In the absence of complications due to *d* orbitals the *p*-dimethylamino-compounds should be stronger donors than the unsubstituted phenyl compounds, owing to the effect: . Similarly the trifluoromethyl-substituted compounds should be weaker donors, CF_3. Strong d_π–d_π bonding, however, should be favoured by electronegative substituents.

The evidence about relative stabilities obtained in this work is of an entirely qualitative character; in some instances complexes were obtained and in others no compound could be prepared, some complexes were obviously unstable and very easily decomposed, some smelled strongly of the ligand while others did not. In experiments with nickel complexes, colour changes helped to show how far complex formation had taken place. In view, however, of the large number of experiments carried out, with eight different ligands and eight metals [Cu(I), Ag(I), Au(I), Zn, Cd, Hg, Co, and Ni], the overall result is quite informative. In the first place, attempts were made to prepare complexes between all these metals and dimethylaniline; only an unstable mercuric chloride complex resulted. Since complexes were obtained with phenyldimethylphosphine in all cases, it can be concluded that all these metals co-ordinate to the latter more strongly than to the former, and that co-ordination to the dimethylamino-group is not likely to complicate experiments with the *p*-dimethylaminophenyl series of phosphines and arsines.

Copper, Silver, and Gold.—Numerous tertiary phosphine and arsine complexes of these elements have been described previously, notably by Mann, Purdie, and Wells (*J.*, 1936, 1503; 1937, 1828; 1940, 1209, 1230, 1235) and by Kabesh and Nyholm (*J.*, 1951, 38, 3245; 1952, 1257). These investigations have shown that cuprous but not cupric copper forms complexes with phosphines and arsines, the co-ordination number of the copper being two or more generally four. Silver(I) behaves similarly, the majority of the compounds examined being of the type $[R_3P(\text{or As}){\cdot}AgI]_4$ in which the co-ordination number of the silver is four. Gold, on the other hand, forms complexes in both aurous and auric states, and the aurous complexes also differ in normally assuming a covalency of two (*e.g.*, $R_3P{\cdot}AuI$); however, a covalency of four is apparent in some chelate ditertiary arsine complexes, *e.g.*, $[Au(Diarsine)_2]X$ (Nyholm, *Nature*, 1951, **168**, 705).

In the present work few experiments were carried out with gold compounds, but the two compounds isolated, $[(NMe_2{\cdot}C_6H_4{\cdot}PMe_2)_2Au]I$ and $(Ph{\cdot}PMe_2)AuI_3$, conform to these rules. Dwyer and Stewart (*J. Proc. Roy. Soc. New South Wales*, 1950, **83**, 177) have described some rather unstable aurous halide complexes of $Ph{\cdot}AsMe_2$.

The experiments on copper(I) and silver were confined to the iodides, since far more earlier data concern iodides than the other halides, and can be compared with present results.

The effect of the *para*-substituents on the stability of complexes was only noticeable in the case of the arsine series. The arsine $NMe_2{\cdot}C_6H_4{\cdot}AsMe_2$ afforded a stable complex $(NMe_2{\cdot}C_6H_4{\cdot}AsMe_2)_2CuI$ with no indication of the formation of a 1 : 1 complex. Burrows and Sandford (*ibid.*, 1936, **69**, 182) described unstable 2 : 1 and 1 : 1 complexes between $Ph{\cdot}AsMe_2$ and cuprous iodide, and in the present work no $CF_3{\cdot}C_6H_4{\cdot}AsMe_2$ complex could be isolated at all. Similarly, silver iodide afforded the 2 : 1 complex $(NMe_2{\cdot}C_6H_4{\cdot}AsMe_2)_2AgI$, which decomposes when its solution in acetone or benzene is warmed, with deposition of silver iodide (which redissolves on cooling). Burrows and Parker (*J. Amer. Chem. Soc.*, 1933, **55**, 4133) failed to obtain a silver iodide complex with phenyldimethylarsine, and attempts at preparation of such a complex by the present authors also failed, neither could a derivative of $CF_3{\cdot}C_6H_4{\cdot}AsMe_2$ be prepared. Towards cuprous and silver iodide the donor character of arsenic in the series investigated is in the order $NMe_2 > H > CF_3$. The constitution of the 2 : 1 complexes formed by the amino-arsine $NMe_2{\cdot}C_6H_4{\cdot}AsMe_2$ is of some interest, since the copper or silver atoms would have the very unusual co-ordination number three if the complexes are monomeric and un-ionised. The cuprous iodide complex $(NMe_2{\cdot}C_6H_4{\cdot}AsMe_2)_2CuI$ was practically non-conducting in nitrobenzene solution, but its low solubility did not permit reliable measurements of molecular weight. The silver iodide complex was too unstable to investigate, and deposited silver iodide slowly in nitrobenzene solution.

In the phosphine series stable complexes were obtained with all the phosphines studied; phosphorus appears to be a stronger donor than arsenic to all types of acceptor. The most valuable information from this series concerns the possible occurrence of three-co-ordination, since many of the complexes were sufficiently stable to allow molecular-weight and conductivity measurements. The many cuprous and silver iodide complexes with tertiary phosphines previously described are tetrameric 1 : 1 compounds of the type $[PR_3{\cdot}Cu(\text{or } Ag)I]_4$. It was therefore surprising that only four complexes of this type were obtained in the present work, *viz.*, $[(Ph{\cdot}PEt_2)CuI]_{\sim 3}$, $[(CF_3{\cdot}C_6H_4{\cdot}PEt_2)CuI]_4$, $[(NMe_2{\cdot}C_6H_4{\cdot}PEt_2)AgI]_4$, and $[(Ph{\cdot}PEt_2)AgI]_4$. Several other 1 : 1 complexes were prepared, *viz.*, $(NMe_2{\cdot}C_6H_4{\cdot}PEt_2)CuI$, $(NMe_2{\cdot}C_6H_4{\cdot}PMe_2)AgI$, and $(Ph{\cdot}PMe_2)AgI$, but these were either too insoluble to permit molecular-weight measurement (CuI) or were unstable and decomposed rapidly in solution (AgI complexes).

One 3 : 1 complex was obtained, *viz.*, $(CF_3{\cdot}C_6H_4{\cdot}PEt_2)_3CuI$. This was evidently dissociated in solution in the manner suggested by Nyholm (*J.*, 1952, 1257) for the arsine complexes $(AsMePh_2)_3CuX$, since the measured molecular weight in boiling benzene varied with concentration from 520 to 580, the monomer requiring 892. This complex was virtually non-conducting in nitrobenzene solution. These data are consistent with the equilibria

$$4(CF_3{\cdot}C_6H_4{\cdot}PEt_2)_3CuI \rightleftharpoons [(CF_3{\cdot}C_6H_4{\cdot}PEt_2)CuI]_4 + 8CF_3{\cdot}C_6H_4{\cdot}PEt_2$$

or

$$(CF_3{\cdot}C_6H_4{\cdot}PEt_2)_3CuI \rightleftharpoons (CF_3{\cdot}C_6H_4{\cdot}PEt_2)_2CuI + CF_3{\cdot}C_6H_4{\cdot}PEt_2$$

Six phosphine complexes of the 2 : 1 type were prepared in addition to the two arsine complexes of this type already mentioned. Of these, the cuprous iodide compounds $(NMe_2{\cdot}C_6H_4{\cdot}PMe_2)_2CuI$ and $(Ph{\cdot}PMe_2)_2CuI$ are, like $(NMe_2{\cdot}C_6H_4{\cdot}AsMe_2)_2CuI$, too insoluble for molecular-weight measurements; they are, however, non-electrolytes in nitrobenzene. The silver iodide complexes $(NMe_2{\cdot}C_6H_4{\cdot}PMe_2)_2AgI$, $(Ph{\cdot}PMe_2)_2AgI$, $(NMe_2{\cdot}C_6H_4{\cdot}PEt_2)_2AgI$, and $(CF_3{\cdot}C_6H_4{\cdot}PEt_2)_2AgI$ are all quite stable and show no signs of decomposition in solution. Nyholm (*loc. cit.*) examined the 2 : 1 complexes of diphenylmethylarsine with cuprous chloride and bromide, and suggested that these were salts $[(R_3As)_4Cu][CuX_2]$ in the solid state, which dissociate in solution giving a mixture of $(AsR_3)_3CuX$ and $(AsR_3{\cdot}CuX)_4$. The cuprous chloride complex, $(AsMePh_2)_2CuCl$ (formula weight 587), had a molecular weight 626 (1·79% solution in nitrobenzene) and 758 (2·84% solution). Such a variation with concentration is consistent with an equilibrium between several species.

The four 2 : 1 phosphine–silver iodide complexes, mentioned above, can be crystallised from organic solvents in the normal way, unlike the arsine–cuprous iodide complexes studied by Nyholm. Their molecular weights (boiling benzene) and conductances (10^{-3} molal in nitrobenzene at 25°) are given in Table 1 and indicate that the compounds are monomeric and un-ionised in (benzene) solution. Compounds which do not ionise significantly in nitrobenzene would ionise even less in benzene on account of its lower dielectric constant. This was confirmed in several instances. The absence of any significant change of molecular weight with concentration suggests the absence of dissociation equilibria of the type which probably obtains in the case of Nyholm's arsine–cuprous iodide complexes. Further, some of the 1 : 1 complexes which would be involved in such equilibria have been prepared but immediately decompose in dilute benzene solution and, moreover, solutions of the 2 : 1 complexes do not smell of the phosphines (a fairly sensitive test in view of the very strong smells of the phosphines concerned). The presence of complexes involving $(AgI_2)^-$ ions is most improbable since no silver iodide is precipitated on addition of an acetone solution of silver nitrate.

TABLE 1. 2 : 1 *Phosphine–silver iodide complexes.*

Formula	M. p.	Formula weight	Λ_m in $PhNO_2$		*M* in C_6H_6				
$(NMe_2\cdot C_6H_4\cdot PMe_2)_2AgI$	177—178°	597	2·34	*M*	585	579	610	613	
				Wt. %	0·55	0·94	1·30	1·71	
$(Ph\cdot PMe_2)_2AgI$	114—115	511	0·93	*M*	568	560	545	515	
				Wt. %	0·56	1·20	1·80	2·45	
$(NMe_2\cdot C_6H_4\cdot PEt_2)_2AgI$	127—128	653	0·8	*M*	539	561	564	564	554
				Wt. %	0·79	0·94	1·1	1·25	1·7
$(CF_3\cdot C_6H_4\cdot PEt_2)_2AgI$ ...	94·5—95·5	703	0·4	*M*	710	715	667	682	
				Wt. %	0·69	1·6	2·45	3·15	

Although these results indicate a monomeric structure for the complexes in solution, with the silver exercising the co-ordination number three, they give no information about the structures of the solids. Only one of the phosphines, $(NMe_2\cdot C_6H_4\cdot PEt_2)$, afforded both types of complex (the tetrameric 1 : 1 and monomeric 2 : 1) with solubilities and stabilities adequate for molecular-weight measurement. The three-co-ordinated thiourea–silver complex has recently been investigated electrometrically (Fyfe, *J.*, 1955, 1032; see also Ahrland and Chatt, *Chem. and Ind.*, 1955, 96).

Zinc, Cadmium, and Mercury.—The tendency of these elements to co-ordinate to nitrogen and oxygen diminishes very markedly from zinc to mercury, and the tendency to co-ordinate to the phosphorus, arsenic, sulphur type of donor *increases* from zinc to mercury. It was therefore noteworthy that, in the present work, the effects of electronically active substituents were clearly evident in the case of zinc, less so for cadmium, and scarcely apparent in the case of mercury.

All the zinc complexes isolated were of the 2 : 1 type, *e.g.*, $(Ph\cdot PMe_2)_2ZnI_2$. The compounds $(NMe_2\cdot C_6H_4\cdot PMe_2)_2ZnX_2$ (X = Cl, Br, or I) could readily be crystallised unchanged, whereas $(Ph\cdot PMe_2)_2ZnI_2$ and $(Ph\cdot PEt_2)_2ZnI_2$ decomposed easily and smelled of the phosphine (no chlorides or bromides of this type could be prepared), and no trifluoromethyl derivative could be obtained. The arsine series was similar, and no derivative of $CF_3\cdot C_6H_4\cdot AsMe_2$ could be obtained. As expected, all the zinc complexes were decomposed by 2 : 2′-dipyridyl, with liberation of the free phosphine or arsine.

A large number of cadmium complexes was prepared, and both 1 : 1 and 2 : 1 types were formed. No derivative of $CF_3\cdot C_6H_4\cdot AsMe_2$ could be isolated, but the phosphine $CF_3\cdot C_6H_4\cdot PEt_2$ afforded the complex $(CF_3\cdot C_6H_4\cdot PEt_2)CdI_2$. That cadmium resembles zinc in the effects of the *para*-substituents also appeared from the observation that, whereas both $(NMe_2\cdot C_6H_4\cdot PMe_2)CdI_2$ and $(Ph\cdot PMe_2)CdI_2$ are decomposed by 2 : 2′-dipyridyl, yet the former is unaffected by *p*-toluidine while the latter is decomposed with liberation of phenyldimethylphosphine. The 1 : 1 complexes are often only slightly soluble (particularly chlorides and bromides), so readily separate from solution. The only 2 : 1 complexes that could be isolated were derived from the apparently stronger donors, $NMe_2\cdot C_6H_4\cdot PMe_2$, $NMe_2\cdot C_6H_4\cdot PEt_2$, $Ph\cdot PEt_2$, and $NMe_2\cdot C_6H_4\cdot AsMe_2$; iodides were easier to obtain than the bromides and chlorides.

Numerous 1 : 1 cadmium halide complexes with phosphines and arsines have previously been described, and have been assumed to have a halogen-bridged dimeric structure $R_3P(X)CdX_2Cd(X)PR_3$. The 1 : 1 cadmium chloride and bromide complexes were not sufficiently soluble to permit molecular-weight measurement, but the iodide $(NMe_2\cdot C_6H_4\cdot PMe_2)CdI_2$ was studied in several solvents. The analogous 1 : 1 diethyl compound rather surprisingly could not be prepared. The 1 : 1 complex $(NMe_2\cdot C_6H_4\cdot PMe_2)CdI_2$ was almost non-conducting in nitrobenzene and only slightly conducting in acetone (molal conductances 1 and 5 respectively at 10^{-3}; compare cadmium iodide, 790 at 10^{-3}m in acetone). The molecular weight of this complex, measured ebullioscopically, varied with solvent and concentration, but was generally within the range 500—1000 corresponding to a monomer (*M*, 547)–dimer equilibrium. Except in ethanol, in which the complex was monomeric (observed molecular weights from 482 to

569), the degree of association increased with concentration, and association to the dimer was favoured by non-polar solvents. For example, the observed degree of association was 1·0—1·2 in acetone, 1·5—1·8 in chloroform, and 1·5—2·0 in benzene. Although interaction with alcohol or acetone to give four-co-ordinate complexes is possible, this could not occur in chloroform or benzene. In nitrobenzene (cryoscopically) the complex was monomeric, with some apparent dissociation at the lower concentrations; there was evidently some interaction with the solvent since the solutions were deep orange. Since the monomeric form of the complex, whether bonded to solvent molecules or not, is likely to be more polar than the bridged dimeric form, association to the dimer should, as observed, be favoured by low polarity of solvent. The trifluoromethyl complex $(CF_3{\cdot}C_6H_4{\cdot}PEt_2)CdI_2$ behaved in a similar way; dimeric in benzene, it was only slightly associated in acetone in which its molal conductance was only 1·3 at 10^{-3}M (25°). The 1 : 1 tri-*n*-propylphosphine complex *n*-Pr_3P,CdI_2, one of many described by Evans, Mann, Peiser, and Purdie (*J.*, 1940, 1208), was re-examined and found to be monomeric in acetone, but dimeric in benzene and chloroform. This behaviour may very well be due to co-ordination with acetone.*

Mercury co-ordinates very strongly with donors of the phosphine and arsine type, capable of d_π bonding, and among the many complexes prepared in the present work there was none which suggested that *para*-substitution of trifluoromethyl for hydrogen reduced the stability of a complex. All the mercury complexes prepared were odourless and readily recrystallised from solvents in the absence of any added phosphine or arsine. Both 1 : 1 and 2 : 1 complexes were prepared. The former resemble their cadmium analogues in respect of solubility, but several were sufficiently soluble to allow molecular-weight measurement. The complex $(Ph{\cdot}PEt_2)HgBr_2$ was dimeric in benzene, but the degree of association in acetone varied from 1·2 to 1·6. Similarly, the complex $(CF_3{\cdot}C_6H_4{\cdot}PEt_2)HgBr_2$, dimeric in benzene, was partly associated in acetone (1·4—1·7). The tri-*n*-propylphosphine complexes $Pr^n{}_3P,HgBr_2$ and $Pr^n{}_3P,HgI_2$ (Mann *et al.*, *loc. cit.*) were also only partly associated to the dimers in boiling acetone, the observed degrees of association being 1·5—1·85 and 1·2—1·7, respectively.

The compound $(NMe_2{\cdot}C_6H_4{\cdot}PMe_2)_2HgI_2$ reacts with two mols. of methyl iodide in acetone solution at room temperature. The product is a *P*-methiodide since the same substance was formed from the phosphine methiodide and potassium mercuri-iodide, and a similar dimethiodide was obtained from $(Ph{\cdot}PMe_2)_2HgI_2$ in which there are no dimethylamino-groups in the ligand. Several phosphonium and arsonium mercuri-iodides have been prepared and are described in the Experimental section; their molal conductances in nitrobenzene at 25° are all about 60—70. The cadmium complexes did not react with methyl iodide directly, but the phosphonium and arsonium cadmi-iodides were readily obtained from the quarternary iodides and cadmium iodide in ethanol.

Cobalt and Nickel.—Only the phosphine $NMe_2{\cdot}C_6H_4{\cdot}PMe_2$ afforded isolable complexes with cobalt(II) chloride and bromide, and these were difficult to purify. No cobalt arsine complexes could be obtained with the ligands investigated.

All the phosphines studied formed red 2 : 1 complexes with nickel, of the type $(R_3P)_2NiX_2$ (X = Cl, Br, I). Of the arsines, however, only $NMe_2{\cdot}C_6H_4{\cdot}AsMe_2$ afforded isolable complexes, $(NMe_2{\cdot}C_6H_4{\cdot}AsMe_2)_2NiBr_2$ and the iodide. Since the reactants are colourless or green and the complexes are red or brown-red, colour changes provided useful qualitative information about relative stabilities. Thus, addition of $NMe_2{\cdot}C_6H_4{\cdot}AsMe_2$ to a green ethanolic solution of nickel chloride caused no colour change, though the bromide and iodide gave deep red solutions from which the solid complexes could be isolated. Similarly, addition of the same quantity of $Ph{\cdot}AsMe_2$ to equimolar amounts of the three halides in equal volumes of ethanol caused a colour change only with nickel iodide, and the arsine $CF_3{\cdot}C_6H_4{\cdot}AsMe_2$ produced a faint brown colour only with the iodide. Consequently, the stability order in co-ordination with these arsines is I > Br > Cl but this apparent order may well be determined by variations in the solvation energies of the three halide ions.* Addition of $NMe_2{\cdot}C_6H_4{\cdot}AsMe_2$ to ethanolic nickel iodide results in a deep red colour

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* The authors are indebted to a Referee for this point.

and the solid complex can be separated, while Ph·AsMe$_2$ produces a brown colour and no product can be isolated, and CF$_3$·C$_6$H$_4$·AsMe$_2$ causes only a very pale brown colour. Hence it is safe to conclude that the order of donor strength to nickel iodide is NMe$_2$·C$_6$H$_4$·AsMe$_2$ $>$ Ph·AsMe$_2$ $>$ CF$_3$·C$_6$H$_4$·AsMe$_2$.

EXPERIMENTAL

Preparation of Ligands.—The phosphines Ph·PMe$_2$, Ph·PEt$_2$, NMe$_2$·C$_6$H$_4$·PMe$_2$, and NMe$_2$·C$_6$H$_4$·PEt$_2$ were prepared as previously described, by the action of methyl- or ethyl-magnesium halide on the dichlorophosphine, except that separation of the reaction product (after hydrolysis) by steam-distillation was found to be better than other methods described.

*Diethyl-*p-*trifluoromethylphenylphosphine.*—*p*-Bromobenzotrifluoride (76·4 g.) was added slowly to magnesium (8·3 g.) in dry ether (500 c.c.). Diethylchlorophosphine (Beeby and Mann, *J.*, 1951, 411) (43·2 g.) in ether (100 c.c.) was added to the resulting Grignard solution during 40 min. The mixture was then refluxed for ½ hr. and hydrolysed with water (60 c.c.) followed by 6N-sodium hydroxide (150 c.c.). The phosphine was separated by steam-distillation (N$_2$ atmosphere), after previous removal of most of the ether, extracted with ether, dried, and distilled under nitrogen. The *phosphine*, b. p. 106—108°/13 mm. (26 g., 33%), which oxidises in the air more easily than the others prepared, was distributed in a number of sealed tubes under nitrogen (Found: F, 24·7. C$_{11}$H$_{14}$F$_3$P requires F, 24·4%).

For characterisation the phosphine was added to methyl iodide (excess) in benzene, and the *methiodide* separated as an oil which crystallised slowly; recrystallised from ethanol, it had m. p. 108—109° (Found: I, 33·5. C$_{12}$H$_{17}$F$_3$PI requires I, 33·8%).

p-*Dimethylaminophenyldimethylarsine.*—*p*-Bromodimethylaniline (14·5 g.) in dry ether (20 c.c.) was slowly added to lithium (1·0 g.) in dry ether (40 c.c.) under a nitrogen atmosphere. When reaction was finished, cacodyl iodide (8·0 g.) in ether (20 c.c.) was slowly added. The mixture was refluxed for 1 hr. and then hydrolysed. The arsine was extracted with ether, dried (MgSO$_4$), and separated by distillation, which yielded dimethylaniline (2 c.c.) followed by the arsine, b. p. 147—150°/82 mm. (5·5 g., 70%). For characterisation the arsine was added to methyl iodide (excess) in ether; the *methiodide* which separated was crystallised from ethanol, and formed colourless plates, m. p. 259—260° (decomp.) (Found: C, 35·9; H, 5·0. C$_{11}$H$_{19}$NIAs requires C, 35·95; H, 5·2%).

Phenyldimethylarsine was prepared as previously described.

*Dimethyl-*p-*trifluoromethylphenylarsine.*—This was prepared from *p*-trifluoromethylphenylmagnesium bromide and cacodyl iodide by a method similar to that used to prepare diethyl-*p*-trifluoromethylphenylphosphine, and was obtained in 75% yield, as a pale yellow oil, b. p. 202—204°. The *methiodide* formed colourless needles (from ethanol), m. p. 168° (Found: C, 30·0; H, 3·5; I, 32·3. C$_{10}$H$_{13}$F$_3$IAs requires C, 30·6; H, 3·35; I, 32·4%).

Since carbon and hydrogen analyses of compounds containing fluorine often gave erratic results, such compounds were generally analysed by determination of metal and halogen. Molecular weights were determined ebullioscopically, unless otherwise stated, in a Swiętoslawski apparatus, two thermistors being used to measure temperature differences. Molal conductances are for 10^{-3}M-solutions in nitrobenzene at 25°.

Copper and silver complexes were prepared by addition of a concentrated ethanolic solution of the ligand (1 mol.) to cuprous or silver iodide (1 mol.) dissolved in concentrated aqueous potassium iodide. The mixture was shaken, and the complex separated and crystallised from a suitable solvent.

Complexes of zinc, cadmium, mercury, cobalt, and nickel were prepared by addition of an ethanolic solution of the ligand to an ethanolic solution of the appropriate metal halide. Complexes of mercuric iodide were prepared by dissolving the solid iodide in an ethanolic or acetone solution of the ligand, or by addition of an ethanolic solution of the ligand to aqueous potassium mercuri-iodide. The *complexes* listed in Table 2 were prepared by these methods, except those whose preparation is described below.

Tris-(p-*dimethylaminophenyldiethylphosphine*)*monoiodocopper.*—Cuprous iodide (1 mol.) was dissolved in a solution of the phosphine (NMe$_2$·C$_6$H$_4$·PEt$_2$) (16 mols.) in ethanol. The *complex* which separated was crystallised from ethanol–benzene (1 : 1) and formed large colourless crystals, m. p. 89—91° (Found: C, 51·4; H, 7·0; N, 5·1. C$_{36}$H$_{60}$N$_3$IP$_3$Cu requires C, 52·7; H, 7·3; N, 5·1%).

Tris(*diethyl-*p-*trifluoromethylphenylphosphine*)*monoiodocopper.*—This *complex* separated when the phosphine (CF$_3$·C$_6$H$_4$·PEt$_2$) (6 mols.) was shaken with a solution of cuprous iodide

TABLE 2.

Complex number	Substance	M. p.*	Found (%)		Formula	Reqd. (%)	
			C	H		C	H
I	$(NMe_2\cdot C_6H_4\cdot PMe_2)_2CuI$	156—157° ^{c}	42·4	5·9	$C_{20}H_{32}N_2IP_2Cu$	42·2	5·8
II	$(Ph\cdot PMe_2)_2CuI$	98·5—99 ^{c}	41·1	4·4	$C_{16}H_{22}IP_2Cu$	41·3	4·7
III	$(NMe_2\cdot C_6H_4\cdot PEt_2)_2CuI$	210—212 ^{c}	36·4	4·85	$C_{12}H_{20}NIPCu$ ^{g}	36·0	5·0
IV	$(Ph\cdot PEt_2)CuI$	153·5—155 ^{a}	33·8	4·4	$C_{10}H_{15}IPCu$	33·6	4·2
V	$[(CF_3\cdot C_6H_4\cdot PEt_2)CuI]_4$	165—166 ^{e}	—	—	$C_{44}H_{56}F_{12}I_4P_4Cu_4$ ^{h}	—	—
VI	$(NMe_2\cdot C_6H_4\cdot AsMe_2)_2CuI$	135—136 ^{c}	37·8	4·9	$C_{20}H_{32}N_2IAs_2Cu$	37·5	5·0
VII	$(NMe_2\cdot C_6H_4\cdot PMe_2)_2AgI$	177—178 ^{c}	39·7	5·0	$C_{20}H_{32}N_2IP_2Ag$	40·1	5·3
VIII	$(Ph\cdot PMe_2)_2AgI$	114—115 ^{c}	37·4	4·4	$C_{16}H_{22}IP_2Ag$	37·5	4·3
IX	$[(NMe_2\cdot C_6H_4\cdot PEt_2)AgI]_4$	203—205 ^{b}	32·5	4·3	$C_{48}H_{80}N_4I_4P_4Ag_4$ ^{i}	32·4	4·5
X	$[(Ph\cdot PEt_2)AgI]_4$	138—139 ^{e}	30·2	4·05	$C_{40}H_{60}I_4P_4Ag_4$ ^{j}	29·9	3·7
XI	$(CF_3\cdot C_6H_4\cdot PEt_2)_2AgI$	94·5—95·5 ^{a}	—	—	$C_{22}H_{28}F_6IP_2Ag$ ^{k}	—	—
XII	$(NMe_2\cdot C_6H_4\cdot AsMe_2)_2AgI$	146—148 ^{c}	34·5	4·6	$C_{20}H_{32}N_2IAs_2Ag$	34·8	4·6
XIII	$(NMe_2\cdot C_6H_4\cdot PMe_2)_2ZnCl_2$	151·5—152 ^{a}	48·4	6·8	$C_{20}H_{32}N_2Cl_2P_2Zn$	48·1	6·4
XIV	$(NMe_2\cdot C_6H_4\cdot PMe_2)_2ZnBr_2$	146 ^{a}	40·6	5·4	$C_{20}H_{32}N_2Br_2P_2Zn$	40·8	5·4
XV	$(NMe_2\cdot C_6H_4\cdot PMe_2)_2ZnI_2$	159—160 ^{a}	35·2	4·7	$C_{20}H_{32}N_2I_2P_2Zn$	35·3	4·7
XVI	$(Ph\cdot PMe_2)_2ZnI_2$	135 ^{a}	32·1	3·7	$C_{16}H_{22}I_2P_2Zn$	32·1	3·7
XVII	$(NMe_2\cdot C_6H_4\cdot PEt_2)_2ZnI_2$	115—117 ^{e}	38·8	5·6	$C_{24}H_{40}N_2I_2P_2Zn$ ^{l}	39·1	5·4
XVIII	$(Ph\cdot PEt_2)_2ZnI_2$	172·5—174 ^{e}	36·8	5·0	$C_{20}H_{30}I_2P_2Zn$	36·8	4·6
XIX	$(NMe_2\cdot C_6H_4\cdot AsMe_2)_2ZnI_2$	118 ^{a}	30·8	4·0	$C_{20}H_{32}N_2I_2As_2Zn$	31·2	4·2
XX	$(NMe_2\cdot C_6H_4\cdot PMe_2)CdCl_2$	215—217 ^{f}	32·7	4·4	$C_{10}H_{16}NCl_2PCd$	32·9	4·4
XXI	$(Ph\cdot PMe_2)CdCl_2$	302—304 ^{a} *	29·6	3·4	$C_8H_{10}Cl_2PCd$	29·9	3·1
XXII	$(NMe_2\cdot C_6H_4\cdot AsMe_2)CdCl_2$	180 ^{a} *	29·4	3·9	$C_{10}H_{16}NCl_2AsCd$ ^{m}	29·2	4·05
XXIII	$(NMe_2\cdot C_6H_4\cdot PMe_2)CdBr_2$	221—222 ^{f}	26·7	3·2	$C_{10}H_{16}NBr_2PCd$	26·5	3·5
XXIV	$(Ph\cdot PMe_2)CdBr_2$	~180 ^{e} *	23·4	2·7	$C_8H_{10}Br_2PCd$	23·4	2·7
XXV	$(NMe_2\cdot C_6H_4\cdot AsMe_2)CdBr_2$	210—212 ^{a}	24·45	3·5	$C_{10}H_{16}NBr_2AsCd$ ^{n}	24·2	3·2
XXVI	$(NMe_2\cdot C_6H_4\cdot PMe_2)CdI_2$	144—145 ^{a}	21·9	2·8	$C_{10}H_{16}NI_2PCd$	21·9	2·9
XXVII	$(Ph\cdot PMe_2)CdI_2$	75 ^{d}	19·7	2·2	$C_8H_{11}I_2PCd$	19·1	2·2
XXVIII	$(NMe_2\cdot C_6H_4\cdot PEt_2)_2CdI_2$	116—118 ^{a}	37·1	4·8	$C_{24}H_{40}N_2I_2P_2Cd$ ^{o}	36·8	5·1
XXIX	$(Ph\cdot PEt_2)_2CdI_2$	102—103 ^{a}	—	—	$C_{20}H_{30}I_2PCd$ ^{p}	—	—
XXX	$(CF_3\cdot C_6H_4\cdot PEt_2)CdI_2$	123·5—124·5 ^{e}	—	—	$C_{11}H_{14}F_3I_2PCd$ ^{q}	—	—
XXXI	$(NMe_2\cdot C_6H_4\cdot AsMe_2)_2CdI_2$	116 ^{e}	29·8	4·2	$C_{20}H_{32}N_2I_2As_2Cd$	29·4	3·9
XXXII	$(NMe_2\cdot C_6H_4\cdot PMe_2)HgCl_2$	233—235 ^{b} ^{e}	26·8	4·0	$C_{10}H_{16}NCl_2Hg$	26·6	3·5
XXXIII	$(Ph\cdot PMe_2)HgCl_2$	168—169 ^{f}	23·2	2·5	$C_8H_{11}Cl_2PHg$	23·4	2·7
XXXIV	$(NMe_2\cdot C_6H_4\cdot AsMe_2)HgCl_2$	199 ^{b} *	24·4	3·1	$C_{10}H_{16}NCl_2AsHg$ ^{r}	24·2	3·2
XXXV	$(NMe_2\cdot C_6H_4\cdot PMe_2)HgBr_2$	201—204 ^{b}	22·6	3·1	$C_{10}H_{16}NBr_2PHg$	22·2	3·0
XXXVI	$(Ph\cdot PMe_2)HgBr_2$	133—135 ^{b}	19·4	2·2	$C_8H_{11}Br_2PHg$	19·3	2·2
XXXVII	$(NMe_2\cdot C_6H_4\cdot PEt_2)HgBr_2$	170·5—173 ^{b}	26·0	3·7	$C_{12}H_{20}NBr_2PHg$ ^{s}	25·3	3·5
XXXVIII	$(Ph\cdot PEt_2)HgBr_2$	120—121 ^{e}	23·2	2·8	$C_{10}H_{15}Br_2PHg$	22·8	2·8
XXXIX	$(CF_3\cdot C_6H_4\cdot PEt_2)HgBr_2$	116·5—117·5 ^{e}	—	—	$C_{11}H_{14}F_3Br_2PHg$ ^{t}	—	—
XL	$(NMe_2\cdot C_6H_4\cdot AsMe_2)HgBr_2$	171 ^{b} *	20·8	2·7	$C_{10}H_{16}NBr_2AsHg$	20·6	2·7
XLI	$(NMe_2\cdot C_6H_4\cdot PMe_2)_2HgI_2$	170—171 ^{b}	29·2	3·9	$C_{20}H_{32}N_2I_2P_2Hg$	29·4	3·9
XLII	$(Ph\cdot PMe_2)_2HgI_2$	115—117 ^{c}	26·6	3·2	$C_{16}H_{22}I_2P_2Hg$	26·2	3·0
XLIII	$(NMe_2\cdot C_6H_4\cdot PEt_2)_2HgI_2$	157—159 ^{e}	32·8	4·7	$C_{24}H_{40}N_2I_2P_2Hg$	33·0	4·6
XLIV	$(Ph\cdot PEt_2)_2HgI_2$	130—131 ^{e}	30·9	3·8	$C_{20}H_{30}I_2P_2Hg$	30·5	3·8
XLV	$(CF_3\cdot C_6H_4\cdot PEt_2)HgI_2$	130·5—132 ^{e}	—	—	$C_{11}H_{14}F_3I_2PHg$ ^{u}	—	—
XLVI	$(NMe_2\cdot C_6H_4\cdot PMe_2)_2NiCl_2$	205·5 ^{c}	48·6	6·3	$C_{20}H_{32}N_2Cl_2P_2Ni$	48·8	6·5
XLVII	$(Ph\cdot PMe_2)_2NiCl_2$	152·5—153 ^{e}	47·4	5·6	$C_{16}H_{22}Cl_2P_2Ni$	47·3	5·4
XLVIII	$(NMe_2\cdot C_6H_4\cdot PEt_2)_2NiCl_2$	110—111 ^{e}	52·8	7·7	$C_{24}H_{40}N_2Cl_2P_2Ni$ ^{v}	52·5	7·3
XLIX	$(CF_3\cdot C_6H_4\cdot PEt_2)_2NiCl_2$	137·5—139·5 ^{e}	—	—	$C_{22}H_{28}F_6Cl_2P_2Ni$ ^{w}	—	—
L	$(NMe_2\cdot C_6H_4\cdot PMe_2)_2NiBr_2$	179—181 ^{c} *	41·5	5·8	$C_{20}H_{32}N_2Br_2P_2Ni$	41·6	5·5
LI	$(Ph\cdot PMe_2)_2NiBr_2$	137·5—138·5 ^{e}	39·2	4·8	$C_{16}H_{22}Br_2P_2Ni$	38·9	4·5
LII	$(NMe_2\cdot C_6H_4\cdot AsMe_2)_2NiBr_2$	183—184 ^{a}	36·1	4·5	$C_{20}H_{32}N_2Br_2As_2Ni$	35·9	4·8
LIII	$(NMe_2\cdot C_6H_4\cdot PMe_2)_2NiI_2$	173—175 ^{e}	35·6	4·8	$C_{20}H_{32}N_2I_2P_2Ni$	35·5	4·7
LIV	$(NMe_2\cdot C_6H_4\cdot AsMe_2)_2NiI_2$	175—177 ^{a}	31·6	4·3	$C_{20}H_{32}N_2I_2As_2Ni$	31·5	4·2

* Denotes with decomposition.

Molal conductances; (III), 0·72; (IV), 2·58; (VI), 1·32. Crystallised from ^{a} ethanol, ^{b} acetone, ^{c} benzene, ^{d} chloroform, ^{e} ethanol–acetone. ^{f} Insoluble in common solvents, washed with much hot ethanol. ^{g} Found: N, 3·1. Reqd.: N, 3·5%. ^{h} Found: Cu, 15·0; I, 30·0%; *M*, 1600. Reqd.: Cu, 14·95; I, 29·9%; *M*, 1698. ^{i} Found: *M*, 1590, 1664. Reqd.: *M*, 1776. ^{j} Found: AgI, 58·5%; *M*, 1460, 1640, 1785. Reqd.: AgI, 58·4%; *M*, 1604. ^{k} Found: AgI, 33·4. Reqd.: 33·4%. ^{l} Found: N, 3·4%; *M*, 680, 684. Reqd.: N, 3·8%; *M*, 737. ^{m} Found: N, 3·4. Reqd.: N, 3·4%. ^{n} Found: N, 2·7. Reqd.: N, 2·8%. ^{o} Found: *M*, 763, 745. Reqd.: *M*, 784. ^{p} Found: Cd, 16·1%; *M*, 688, 710. Reqd.: Cd, 16·1%; *M*, 698. ^{q} Found: Cd, 18·7; I, 41·9. Reqd.: Cd, 18·8; I, 42·2%. ^{r} Found: N, 3·1. Reqd.: N, 2·8%. ^{s} Found: N, 2·5; Br, 28·4. Reqd.: N, 2·5; Br, 28·1%. ^{t} Found: Br, 26·8. Reqd.: Br, 26·9%. ^{u} Found: I, 36·7. Reqd.: I, 36·8%. Found: N, 4·6%; *M*, 528, 522, 602, 550. Reqd.: N, 5·1% ; *M*, 548. ^{w} Found: Ni, 9·65; Cl, 12·1. Reqd.: Ni, 9·8; Cl, 11·9%.

(1 mol.) in concentrated aqueous potassium iodide, and crystallised from ethanol as colourless needles, m. p. 94—95° [Found: Cu, 7·1; I, 14·4%; *M*, 525 (0·20% solution in benzene), 555 (0·43%), 548 (0·70%), 577 (0·96%) 582 (1·35%). $C_{33}H_{42}F_9IP_3Cu$ requires Cu, 7·1; I, 14·2%; *M*, 892·5].

p-*Dimethylaminophenyldimethylphosphineiodosilver*.—A suspension of silver iodide (0·3 g., 1·3 mols.) in a solution of the 2 : 1 complex $(NMe_2{\cdot}C_6H_4{\cdot}PMe_2)_2AgI$ (0·59 g., 1 mol.) in benzene (15 c.c.) was boiled under reflux for 5 hr. During this time small crystals separated and adhered to the side of the flask; they were washed from unchanged silver iodide by light petroleum. The mixture was filtered, and colourless crystals were deposited from the cold filtrate. Both crops of crystals (0·6 g.) had the same m. p. and mixed m. p. (204—205°). Attempts at recrystallisation or dissolution for molecular-weight measurement caused decomposition to silver iodide and the 2 : 1 compound $(NMe_2{\cdot}C_6H_4{\cdot}PMe_2)_2AgI$ (Found: C, 29·2; H, 3·9. $C_{10}H_{16}NIPAg$ requires C, 28·9; H, 4·2%). The complex $(Ph{\cdot}PMe_2)AgI$ was prepared in a similar way, but could not be obtained pure; it had m. p. 80·5—83° (Found: C, 26·4; H, 3·1. Calc. for $C_8H_{11}IPAg$: C, 25·7; H, 3·4%). Dissolution in an organic solvent resulted in decomposition to silver iodide and $(Ph{\cdot}PMe_2)_2AgI$.

Bis-(p-*dimethylaminophenyldiethylphosphine*)*monoiodosilver*.—The diethylphosphine $(NMe_2{\cdot}C_6H_4{\cdot}PEt_2)$ (4 mols.) was shaken with a solution of silver iodide (1 mol.) in concentrated aqueous potassium iodide. The white *complex* which separated was crystallised from acetone, and formed colourless rhombs, m. p. 127—128° (Found: C, 44·0; H, 6·3; N, 4·6. $C_{24}H_{40}N_2IP_2Ag$ requires C, 44·1; H, 6·1; N, 4·3%). The molal conductance in nitrobenzene and the molecular weight are given in Table 1.

Bis-(p-*dimethylaminophenyldimethylphosphine*)*monoiodogold*.—The dimethylphosphine $NMe_2{\cdot}C_6H_4{\cdot}PMe_2$ (0·1 g.) in ethanol (6 c.c.) was slowly added to a solution of potassium auri-iodide (0·2 g.) in ethanol (10 c.c.). After the first portion of the phosphine had been added the brown solution became colourless. When the addition was complete the solution was concentrated to 5 c.c. by boiling. The pale cream crystals which separated from the cold solution were crystallised from benzene; they had m. p. 198—199°, molal conductance 12·5 (Found: C, 34·8; H, 4·4. $C_{20}H_{32}N_2IP_2Au$ requires C, 35·0; H, 4·4%).

Phenyldimethylphosphinetri-iodogold.—Phenyldimethylphosphine dissolved in 6 vols. of ethanol was added to a solution of potassium auri-iodide (0·1 g.) in ethanol containing a trace of iodine until the solution became colourless. When the solution was concentrated to 10 c.c. and set aside for several hours colourless lustrous plates separated (0·4 g.) and were recrystallised from ethanol; they had m. p. 142° (slight decomp.) (Found: C, 13·7; H, 1·6. $C_8H_{11}I_3PAu$ requires C, 13·4; H, 1·5%). When pure potassium auri-iodide free from iodine was used a yellow oil separated, which could not be induced to crystallise.

Bis-(p-*dimethylaminophenyldimethylphosphine*)*dichlorocadmium*.—The complex (XX) (1 mol.) was dissolved in a solution of the phosphine $NMe_2{\cdot}C_6H_4{\cdot}PMe_2$ (2 mols., 100% excess) in acetone, and the cooled solution deposited the 2 : 1 *complex* as large colourless plates, m. p. 138—139° (Found: C, 43·8; H, 6·1; N, 5·25. $C_{20}H_{32}N_2Cl_2P_2Cd$ requires C, 44·0; H, 5·9; N, 5·14%).

Bis-(p-*dimethylaminophenyldimethylphosphine*)*dibromocadmium*.—This was prepared similarly, from (XXIII), and separated from acetone as large rhombohedral crystals, m. p. 154—155° (Found: C, 37·7; H, 5·05; N, 4·30. $C_{20}H_{32}N_2Br_2P_2Cd$ requires C, 37·8; H, 5·05; N, 4·42%).

Bis-(p-*dimethylaminophenyldimethylarsine*)*dibromocadmium*.—This was prepared similarly, from (XXV), and formed colourless crystals (from acetone), decomp. 230° with previous softening at 100° (Found: C, 33·5; H, 4·45; N, 3·6. $C_{20}H_{32}N_2Br_2As_2Cd$ requires C, 33·2; H, 4·43; N, 3·9%).

Reaction of Zinc and Cadmium Complexes with 2 : 2′-*Dipyridyl and with* p-*Toluidine*.—2 : 2′-Dipyridyl (0·08 g.) in ethanol (10 c.c.) was added to a solution of the complex (XV) (0·34 g.) in ethanol. A white crystalline precipitate of dipyridyldi-iodozinc, m. p. ~370°, was formed when the solution was heated to boiling, and was removed by filtration (Found: N, 6·1. Calc. for $C_{10}H_8N_2I_2Zn$: N, 5·9%). The filtrate was concentrated to about 2 c.c. and a solution of methyl iodide (1 c.c.) in ether (20 c.c.) was added; the resulting white precipitate was identified as *p*-dimethylaminophenyltrimethylphosphonium iodide by m. p. and mixed m. p., both 264—265°.

When 2 : 2′-dipyridyl (0·1 g.) in ethanol (5 c.c.) was added to a solution of the complex (XXVI) (0·11 g.) in ethanol (25 c.c.), the white precipitate which formed immediately was collected and identified as dipyridyldi-iodocadmium by m. p. 354—356°, mixed m. p. 356—358°. The filtrate smelled strongly of the liberated phosphine, which was identified (as above) as the methiodide.

No detectable odour of the free phosphine resulted when the same complex was boiled under reflux with *p*-toluidine in excess.

2 : 2′-Dipyridyldi-iodocadmium was precipitated immediately in the cold when 2 : 2′-dipyridyl in ethanol was added to an ethanol solution of the compound (XXVII), and phenyldimethylphosphine was identified in the filtrate by precipitation as methiodide. This phosphine was also displaced from the same complex by *p*-toluidine, with formation of *di*-p-*toluidinedi-iodocadmium*, m. p. 179—180° (from ethanol) (Found : C, 28·3; H, 2·9. $C_{14}H_{18}N_2I_2Cd$ requires C, 28·1; H, 3·1%).

Bis-(p-*dimethylaminophenyldimethylarsine*)*dichloromercury*.—This *complex* crystallises in large colourless plates when a hot acetone solution of the 1 : 1 complex, to which excess of the arsine has been added, is cooled; it has m. p. 137·5—138·5° (Found : C, 33·4; H, 4·4; N, 4·25. $C_{20}H_{32}N_2Cl_2As_2Hg$ requires C, 33·2; H, 4·4; N, 3·9%). The *dibromo-complex*, prepared similarly, has m. p. 140—141·5° (from acetone) (Found : C, 29·6; H, 4·0. $C_{20}H_{32}N_2Br_2As_2Hg$ requires C, 29·6; H, 4·0%).

Reaction between Bis-(p-*dimethylaminophenyldimethylphosphine*)*mercuric Iodide and Methyl Iodide*.—Methyl iodide (2·8 g.) in acetone (10 c.c.) was added to a solution of the complex (XLI) (1 g.) in acetone (20 c.c.). Pale yellow crystals (0·44 g.) of *bis*-(p-*dimethylaminophenyltrimethylphosphonium*)*mercuri-iodide* separated during 2 hr. at room temperature, and were crystallised from acetone (m. p. 171—172°) (Found : C, 23·9; H, 3·7. $C_{22}H_{38}N_2I_4P_2Hg$ requires C, 24·0; H, 3·7%). The molal conductance was 72·7.

Bis(*trimethylphenylphosphonium*) *mercuri-iodide* was prepared similarly, from the complex (XLII), and afforded pale yellow crystals (from acetone), m. p. 187—188° (Found : C, 20·3; H, 2·8. $C_{18}H_{28}I_4P_2Hg$ requires C, 20·6; H, 2·7%). The molal conductance was 69·0.

These mercuri-iodides, and others listed below together with some cadmi-iodides, were also prepared by addition of the appropriate quaternary iodide in ethanol to aqueous-alcoholic potassium mercuri-iodide, or to ethanolic cadmium iodide. The mercuri-iodides were all pale yellow and the cadmi-iodides colourless.

Bis(*trimethylphenylammonium*) *mercuri-iodide* (from ethanol), m. p. 186°, molal conductance 67·6 (Found : C, 22·2; H, 2·9. $C_{18}H_{28}N_2I_4Hg$ requires C, 22·0; H, 3·2%). *Bis*(*trimethylphenylarsonium*) *mercuri-iodide* (from ethanol), m. p. 192°, molal conductance 67·3 (Found : C, 19·2; H, 2·2. $C_{18}H_{28}I_4As_2Hg$ requires C, 19·5; H, 2·5%). *Bis*-(p-*dimethylaminophenyltrimethylarsonium*) *mercuri-iodide* (from ethanol), m. p. 164°, molal conductance 72·7 (Found : C, 21·9; H, 3·35. $C_{22}H_{38}N_2I_4As_2Hg$ requires C, 22·2; H, 3·2%). *Bis*(*trimethylphenylammonium*) *cadmi-iodide* (from ethanol), m. p. 195° (Found : C, 24·4; H, 3·1. $C_{18}H_{28}N_2I_4Cd$ requires C, 24·2; H, 3·1%). *Bis*(*trimethylphenylphosphonium*) *cadmi-iodide* (from ethanol), m. p. 190° (Found : C, 23·3; H, 3·2. $C_{18}H_{28}I_4P_2Cd$ requires C, 23·3; H, 3·0%). *Bis*-(p-*dimethylaminophenyltrimethylphosphonium*) *cadmi-iodide* (from ethanol), m. p. 177°, molal conductance 60·0 (Found : C, 25·9; H, 3·7. $C_{22}H_{38}N_2I_4P_2Cd$ requires C, 26·1; H, 3·7%). *Bis*(*trimethylphenylarsonium*) *cadmi-iodide* (from ethanol), m. p. 193·5—194° (Found : C, 21·6; H, 2·8. $C_{18}H_{28}I_4As_2Cd$ requires C, 21·4; H, 2·8%). *Bis*-(p-*dimethylaminophenyltrimethylarsonium*) *cadmi-iodide* (from ethanol), m. p. 170·5° (Found : C, 24·0; H, 3·45. $C_{22}H_{38}N_2I_4As_2Cd$ requires C, 24·0; H, 3·45%).

Complexes of p-*Dimethylaminophenyldimethylarsine and Mercuric Iodide*.—The arsine (2·25 g., 1 mol.) in ethanol (6 c.c.) was added to a solution of mercuric iodide (4·5 g., 1 mol.) in aqueous-alcoholic potassium iodide. The resulting pale yellow precipitate was separated and extracted with ethanol. Concentration of the ethanol extract yielded colourless crystals of *bis*-(p-*dimethylaminophenyldimethylarsine*)*di-iodomercury*, m. p. 137—137·5° (Found : C, 26·6; H, 3·4. $C_{20}H_{32}N_2I_2As_2Hg$ requires C, 26·5; H, 3·5%). The yellow residue from the ethanol-extraction separated from acetone as bright yellow crystals, m. p. 148°, of the 1 : 1 complex, *di-iodobis*-(p-*dimethylaminophenyldimethylarsine*)-μμ′-*di-iododimercury* (Found : C, 17·8; H, 2·3. $C_{10}H_{16}NI_2AsHg$ requires C, 17·7; H, 2·2%).

Bis-(p-*dimethylaminophenyldimethylphosphine*)*dichlorocobalt*.—The phosphine (1·81 g., 4 mols.) in ethanol (10 c.c.) was slowly added to a well-stirred solution of cobalt(II) chloride 6-hydrate (0·6 g., 1 mol.) in ethanol (25 c.c.). During the addition the solution became dark green and no solid was formed. When the solution was boiled it became blue and a dark blue oil separated from the cooled solution. This was dissolved in hot acetone, from which it separated as a blue microcrystalline solid (m. p. 138°). The substance smelled strongly of the phosphine, even after much washing with ether and further crystallisation from acetone. After two crystallisations the *complex* melted at 140—141° (Found : C, 47·4; H, 6·3. $C_{20}H_{32}N_2Cl_2P_2Co$ requires C, 48·5; H, 6·5%). The *dibromo-complex* was prepared similarly, and separated from acetone as deep blue needles, m. p. 153·5° (Found : C, 41·0; H, 5·5. $C_{20}H_{32}N_2Br_2P_2Co$ requires C, 41·4; H, 5·5%).

Bis(triethylphosphine)di-iodomercury.—This *compound* does not appear to have been described, and was prepared by addition of ethanolic triethylphosphine to aqueous-alcoholic potassium mercuri-iodide. It afforded colourless needles, m. p. 156—157°, from acetone (Found : C, 21·2; H, 4·8. $C_{12}H_{30}I_2P_2Hg$ requires C, 20·9; H, 4·4%).

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