170. *Studies in Co-ordination Chemistry. Part I. Complexes of Quadrivalent Platinum with Tertiary Arsines.*

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A series of octahedral complexes of quadrivalent platinum which have the general formula $Pt(Hal)_4,2AsR_3$ have been prepared by using various halides and tertiary arsines. They are all very stable compounds which are difficult to reduce. The complexes are more deeply coloured than their bivalent, planar analogues and are less soluble than these in organic solvents. Differences in reactivity between *cis*- and *trans*-isomers of these octahedral complexes similar to those shown by the bivalent square complexes have been observed. The properties of the compounds are discussed.

This paper is the first of a series dealing with the complexes of metal salts with tertiary arsines. It is proposed to investigate the properties of these complexes as a function of the valency state of the metal and of the anion present and to attempt the preparation of halogen-bridged complexes. Initially the investigation is confined to the elements of Group VIII. Tertiary arsines and phosphines show many properties as ligands which distinguish them from ammonia and amines; they have a very marked tendency to form non-ionic complexes which are freely soluble in organic solvents rather than salt-like substances which are formed so readily by ammonia. It is thus possible to apply a variety of techniques to the study of these compounds which cannot be used with ammines because of their insolubility in organic solvents. A detailed discussion of these differences and an attempt to explain them with particular reference to the nature of the metal–arsenic bond will be given in a later communication. However, the complexes of the elements in many of their valency states with tertiary arsines have not been investigated, and as a first step the preparation of these and a study of their properties were considered desirable.

Tertiary arsines have been used frequently for the stabilisation of lower-valency states, for which purposes their reducing properties are an advantage. In higher-valency states, however, any tendency towards dissociation of the complex might be expected to lead to decomposition, since the compound contains both an oxidising and a reducing agent combined. For instance, Mann and Purdie (*J.*, **1940**, 1235) observed that several of the complexes of tervalent gold with triethylphosphine were unstable on standing; triethylphosphinetrichlorogold(III), $[AuCl_3,PEt_3]$, for example, decomposed within a few days on standing at room temperature, even when kept in the dark, metallic gold being deposited. The tri-iodide decomposed within a few weeks but the tribromide was stable indefinitely. Although tertiary phosphines are as a rule stronger ligands than tertiary arsines, they are similar to them in many ways; thus both tend to form non-ionic complexes with metal salts of the same general type and both are strong reducing agents.

No complexes of quadrivalent platinum with tertiary arsines have been described previously. Of similar complexes with tertiary phosphines, Cahours and Gal (*Compt. rend.*, 1870, **70**, 902) mentioned two platinic complexes with triethylphosphine but no analyses were given. Also, Rosenheim and Lowenstamm (*Z. anorg. Chem.*, 1903, **37**, 400) prepared the compound $PtCl_4,2P(OC_2H_5)_3$ but no analyses were reported.

All the platinic complexes described in this paper have the general formula $Pt(Hal)_4,2AsR_3$, and where solubilities permitted the determination of molecular weights in freezing benzene or freezing bromoform they were monomeric. All were prepared by adding the appropriate amount of the required halogen dissolved in carbon tetrachloride to the planar four-covalent complex of bivalent platinum dissolved in chloroform or benzene. The solvent used was very important in many cases, for the chloride complexes were often obtained as difficultly crystallisable oils from solvents other than benzene. Complexes of triethyl-, triphenyl-, and diphenylmethylarsine have been studied; the last has been found convenient for many other Group VIII metals but on occasions it led to the formation of isomeric mixtures. In all cases the platinic complexes were less soluble in organic solvents than the corresponding bivalent compounds from which they were derived. As with the bivalent complexes, solubility of the *cis*-bisarsine compounds was much less than that of the corresponding *trans*-isomers. For any given isomer the solubility decreased in the sequence chloride > bromide > iodide. As expected, the solubility of the bistriethylarsine complexes was much greater than that of the triphenyl or mixed aryl–alkyl derivatives.

The complexes were all highly coloured, the colour deepening in passing from the bivalent to the quadrivalent state and also in passing from the chloride through the bromide to the iodide. Where obtained, the *cis*-isomers were lighter in colour than the *trans*-isomers. The properties of a typical series are shown in the table

			Bivalent compounds.	
Platinic complex.	Colour.	M. p.	Colour.	M. p.
cis-$PtCl_4,2AsEt_3$	Pale yellow	125°	White	142°
trans-$PtCl_4,2AsEt_3$	Dark yellow	155	Yellow	120
trans-$PtBr_4,2AsEt_3$	Scarlet	173	Deep yellow	120
trans-$PtI_4,2AsEt_3$	Purplish-black	144	Orange	94

Probably the most noteworthy property of the complexes was their stability on standing and towards reducing agents. Only with the *cis*- and the *trans*-form of the *chloride* $PtCl_4,2AsEt_3$ was instability on standing observed; these two substances became oily after several months but the corresponding *tetrabromide* and *tetraiodide* were stable indefinitely Complexes of the other arsines showed no sign of decomposition after several months. On heating, the complexes melted without decomposition as a rule, in some cases above 200°. Unlike the triethylphosphine–gold complexes, they could be boiled with alcohol or acetone without reduction taking place. Sulphur dioxide similarly did not cause reduction except in one or two cases. Thus, although the *compounds* $PtCl_4,2AsMePh_2$ and $PtI_4,AsMePh_2$ were not reduced by sulphur dioxide in chloroform solution, the *complex trans*-$PtCl_2I_2,2AsMePh_2$ was reduced in $\frac{1}{2}$ hour by this means; the product was *trans*-$PtI_2,2AsMePh_2$, the more electronegative halogen being removed. On the other hand, if one attempted to reduce the *cis*-dichloro-*trans*-di-iodo-compound, disproportionation to form the tetrachloro- and tetraiodo-compounds occurred without reduction taking place. Throughout the investigation it was observed that the mixed halogen compounds disproportionated very easily.

Towards most chemical reagents the *trans*-compounds were less reactive than the corresponding *cis*-isomers. For instance, an alcoholic solution of *cis*-$PtCl_4,2AsEt_3$ reacted instantly with aqueous silver nitrate but the corresponding *trans*-complex gave no precipitate for some hours. Similarly, the *cis*-compound reacted vigorously with concentrated sulphuric acid, an effervescence occurring with the evolution of hydrogen chloride; the *trans*-compound dissolved to an orange solution which slowly charred. This difference in reactivity is similar to that observed for the *cis*- and *trans*-planar complexes of bivalent platinum.

Some interesting facts on *cis–trans*-isomerism were noticed. Jensen (*Z. anorg. Chem.*, 1936, **229**, 225) observed that stability of *cis*-isomers of the type $Pt(Hal)_2,2AsEt_3$ increased in passing from the iodide to the chloride; the *cis*-di-iodo-complexes had to be made indirectly and soon reverted to the *trans*-forms on heating. This behaviour has also been observed with the diphenylmethylarsine anologues; the iodide forms a complex which is readily soluble in benzene and is undoubtedly the *trans*-form, but the much less soluble *cis*-form is favoured by the chloride and bromide. The equilibrium between *cis*- and *trans*-forms appeared to be much affected by both solvent and temperature in the cases of the chloride and bromide, which made the preparation of pure isomers difficult. The tetrabromo- and tetrachloro-platinum complexes of this arsine favoured the *cis*-form. An interesting difference was observed between the stabilities of the *cis*- and the *trans*-form of $PtCl_2,2AsEt_3$ and the corresponding tetrachlorides. The white *cis*-platinous complex required heating in solution for many days to convert it into the more soluble, yellow *trans*-isomer. However, the corresponding *cis*-tetrachloro-complex formed a considerable amount of the darker yellow *trans*-isomer on being left in the sunlight for a few hours. In these circumstances the *cis*-platinous complex was stable indefinitely. It appears to be well established that the stability of the *cis*-forms, both of bivalent and of quadrivalent platinum, increases with increasing electronegativity of the attached halogen, but steric factors depending on the particular arsine used are also important.

As expected for octahedrally co-ordinated quadrivalent complexes using d^2sp^3 bonds, the complexes are diamagnetic and the specific susceptibility of the compound $PtBr_4,2AsMePh_2$ ($\chi = -0{\cdot}41 \times 10^{-6}$) is of the order found by Asmussen (Doctorial Thesis, Copenhagen, 1941) for a large number of quadrivalent platinum complexes.

Apart from two complexes involving the $[PtCl_6]^{2-}$ ion, no salt-like complexes with tertiary arsines were isolated, and all attempts to obtain tertiary arsine complexes corresponding to ammines such as $[Pt(NH_3)_5Cl]Cl_3$ or $[Pt(NH_3)_4Cl_2]Cl_2$ were unsuccessful. Also, no halogen-bridged quadrivalent complexes were isolated. It is concluded from a study of these very stable complexes that combination of a tertiary arsine with a metal in a high oxidation state does not lead to instability provided that strong covalent bonds are formed between the metal and the arsenic atom.

EXPERIMENTAL.

Complexes of Triethylarsine.—Bivalent compounds. These were all prepared by Jensen's method (*Z. anorg. Chem.*, 1936, **229**, 225). The colour and m. p.s (Jensen's m. p.s in parentheses) were: *cis*-$PtCl_2,2AsEt_3$, white, m. p. 142° (142—142·5°); *trans*-$PtCl_2,2AsEt_3$, yellow, m. p. 119° (120—121°); *trans*-$PtBr_2,2AsEt_3$, deep yellow, m. p. 120° (120—121°); *trans*-$PtI_2,2AsEt_3$, orange, m. p. 92° (94°). The yield of *trans*-$PtCl_2,2AsEt_3$ was very much smaller than that of the *cis*-isomer produced simultaneously. The *cis*- was converted into the *trans*-form by refluxing in chloroform solution for several days, the isomerisation being very slow.

Jensen (*loc. cit.*) assigned the *cis*- and *trans*-configurations to the above compounds on the basis of their electric dipole moments in benzene, that of the *trans*-forms being zero and that of the *cis*- being in the vicinity of 10 Debye units. He pointed out that the *trans*-isomers differed from the *cis*- in several of their physical properties, and foremost amongst these were their colours and solubilities in benzene. The *trans*-forms were deeper in colour and were much more soluble in benzene than the *cis*-isomers. Special consideration has been given to these properties in the assignment of the *cis*- or *trans*-configuration to the various platinous complexes described here.

Bistriethylarsinetetrachloroplatinum(IV). (i) *trans*-Isomer. *trans*-Bistriethylarsinedichloroplatinum(II) (1·1 g.), dissolved in cold chloroform (25 ml.), was treated with gaseous chlorine until no further absorption occurred. The solution became warm and changed colour from deep yellow to orange red. The chloroform was then removed at the pump at room temperature, and the orange residue recrystallised from alcohol. The *compound* was obtained as short, stumpy, dark yellow crystals, m. p. 155° (Found: C, 21·7; H, 4·6; Pt, 19·5; *M*, cryoscopic in 2·58% solution in benzene, 630. $C_{12}H_{30}Cl_4As_2Pt$ requires C, 21·75; H, 4·5; Pt, 19·5%; *M*, 661). It dissolved readily in benzene and other organic solvents except light petroleum. An acetone solution gave no reaction with silver nitrate unless heated and left for some time. After many months' standing the compound became oily.

(ii) *cis*-Isomer. *cis*-Bistriethylarsinedichloroplatinum(II) (1·2 g.), dissolved in chloroform (15 ml.), was treated with gaseous chlorine as above, the solution becoming warm and acquiring a bright yellow colour. After removal of the chloroform at room temperature at the pump, the yellow residue was recrystallised from alcohol. The *compound* was obtained as yellow needles which formed a characteristic mat; it was much lighter in colour than the *trans*-isomer and melted at 125° (Found: C, 21·9; H, 4·7; Pt, 19·5%). It was moderately soluble in alcohol and acetone but practically insoluble in benzene even when boiling. If heated under reflux for a long time with benzene it gradually dissolved to a yellow solution of the *trans*-isomer. This change also occurred on standing in sunlight, a behaviour in marked contrast with that of the bivalent *cis*-compound which on standing shows no tendency at all to change into the *trans*-isomer. An acetone solution gives an immediate copious precipitate with silver nitrate solution, a reaction in which it differs from the *trans*-isomer. When treated with concentrated sulphuric acid, the *cis*-isomer reacted immediately with effervescence with the evolution of hydrogen chloride; when similarly treated, the *trans*-isomer dissolved to an orange solution and slow charring then took place.

trans-*Bistriethylarsinetetrabromoplatinum*(IV). *trans*-Bistriethylarsinedibromoplatinum(II) (1·40 g.), dissolved in benzene (15 ml.) (yellow solution), was treated with bromine (0·34 g.) in carbon tetrachloride (4 ml.) and the solution immediately became deep red. Evaporation at the pump at ordinary temperatures yielded beautiful scarlet crystals m. p. 172° raised by recrystallisation from alcohol to 173°. The *compound* crystallised as flat rhombs (Found: Pt, 23·2; *M*, cryoscopic in 1·33% solution in benzene, 775. $C_{12}H_{30}Br_4As_2Pt$ requires Pt, 23·3%; *M*, 839). It dissolved readily in organic solvents, particularly benzene and chloroform. An acetone solution slowly precipitated silver chloride on treatment with silver nitrate.

trans-*Bistriethylarsinetetraiodoplatinum*(IV).—*trans*-Bistriethylarsinedi-iodoplatinum(II) (1·2 g.), dissolved in chloroform (30 ml.), was treated with iodine (0·4 g.) dissolved in chloroform (40 ml.), the light orange solution turning to a dark wine-red colour. After evaporation of the chloroform at the pump, the residue was recrystallised from alcohol. The *compound* was obtained as purplish black, flat rectangular crystals, m. p. 144° (Found : Pt, 18·9. $C_{12}H_{30}I_4As_2Pt$ requires Pt, 19·0%); it was readily soluble in benzene and chloroform to a red solution but less soluble than either the chloride or the bromide.

Complexes of Triphenylarsine.—*cis*-Bistriphenylarsinedichloroplatinum (II) was prepared according to Jensen (*loc. cit.*). It decomposed above 300° on heating (Found : Pt, 22·0. Calc. for $C_{36}H_{30}Cl_2As_2Pt$: Pt, 22·0%).

trans-Bistriphenylarsinedichloroplatinum(II) was prepared from the *cis*-isomer by Jensen's method (*loc. cit.*). He recommended refluxing in chloroform for 15 minutes, but in this experiment the *cis*-isomer (0·65 g.) was refluxed with chloroform (36 ml.) for 1½ hours, the almost colourless solution turning deep yellow. Removal of the chloroform gave a compound slightly more yellow than the starting material. This was dissolved in benzene (50 ml.) by refluxing, cooled, and treated with chlorine (0·05 g.) in carbon tetrachloride (2 ml.). The solution became bright yellow and on concentration it afforded yellow crystals which can be recrystallised from benzene with difficulty in small quantities; m. p. 290° (Found : Pt, 20·7. $C_{36}H_{30}Cl_4As_2Pt$ requires Pt, 20·6%). Owing to the low solubility of complexes of this *tetrachloroarsine*, no other complexes were prepared.

Complexes of Diphenylmethyarsine.—*Bisdiphenylmethylarsinedichloroplatinum*(II). This compound was isolated in two forms; one is an almost white, crystalline substance, m. p. 223°, practically insoluble in organic solvents, and the other is light yellow and slightly more soluble, and on heating softens first at 207° and then melts at 214°. On standing or heating, the form of m. p. 214° changes over into that of m. p. 223°, which is no doubt the *cis*-isomer. Unfortunately, low solubility in cold benzene prevented confirmation of this by electric-dipole measurements. Burrows and Parker (*J. Proc. Roy. Soc. N.S.W.*, 1934, **68**, 39) obtained these compounds, one as yellow prisms, m. p. 207° readily soluble in toluene, and the other as yellow needles, m. p. 218°, much less soluble in toluene.

Low-melting form. Diphenylmethylarsine (1·5 g.), dissolved in alcohol (50 ml.), was added to hexahydrated chloroplatinic acid (1·0 g.) dissolved in alcohol (150 ml.), and the solution heated on the water-bath for one hour. Yellow crystals began to form, and on cooling an almost quantitative yield (1·4 g.) was obtained (Found : C, 41·3; H, 3·4; Cl, 9·3; Pt, 25·9. Calc. for $C_{26}H_{26}Cl_2As_2Pt$: C, 41·3; H, 3·4; Cl, 9·4; Pt, 25·8%). The compound was washed many times with alcohol, recrystallisation being difficult without change into the other form taking place. It was readily soluble in chloroform, fairly soluble in acetone but less soluble in cold benzene, from which it crystallised as the other form.

High-melting form. This preparation is commenced as for the other isomer but more concentrated solutions are used. Diphenylmethylarsine (7 g.), dissolved in alcohol (250 ml.), was added to hexahydrated hexachloroplatinic acid (5 g.) dissolved in alcohol (250 ml.). After a few seconds' heating an orange-yellow precipitate appeared which decomposed on further heating, forming a yellow, horny mass and a white powder. The mixture was heated for about an hour, the mass being occasionally broken up, and was then filtered and the residue extracted with chloroform. Removal of chloroform from the almost colourless solution gave a white compound, m. p. 223°, which was less soluble than the other isomer in all solvents (Found : C, 41·4; H, 3·5; Pt, 25·8%).

Two by-products were isolated during a study of the above reaction. When the arsine and chloroplatinic acid reacted in cold alcoholic solution, a yellow precipitate was obtained after about 20 seconds. This substance was insoluble in all solvents, and heating caused decomposition in all solvents tried. The composition varied slightly (C, 39·2—39·8; H, 3·0—3·4; Cl, 13·6; Pt, 23·9—24·7%), but agreed fairly well with $[Pt(AsMePh_2)_4][PtCl_6]$ which requires C, 39·5; H, 3·29; Cl, 13·65; Pt, 24·75%. Its insolubility supports the above formulation and it may be similar to salts of the type $[Pt(AsR_3)_4][PtCl_4]$ isolated by Jensen using trialkylarsines. It is suggested that the platinichloride, rather than the platinochloride, was formed here because reduction with diphenylmethylarsine proceeds more slowly than with trialkylarsines and the temporary co-existence of $[Pt(AsR_3)_4]^{2+}$ and $[PtCl_6]^{2-}$ ions is feasible. From the filtrate of this preparation large orange crystals were obtained after standing for 24 hours. These had m. p. 224° (decomp.) and were insoluble in all solvents. The compound was decomposed by heating with dilute sodium hydroxide solution. The analysis (Found : C, 34·4; H, 3·1; Cl, 23·8; Pt, 21·2%) suggests a formulation as the *salt* $[HAsMePh_2]_2[PtCl_6]$, which requires C, 34·7; H, 3·12; Cl, 23·7; Pt, 21·7%. This substance appears to be one of the few cases where addition of a proton to a tertiary arsine takes place.

Bisdiphenylmethylarsinedibromoplatinum(II).—Diphenylmethylarsine (1·5 g.), dissolved in alcohol (125 ml.), was added to a solution of sodium bromide (5 g.) in distilled water (25 ml.), and the solution added to hexahydrated chloroplatinic acid (1·0 g.) dissolved in alcohol (25 ml.). The buff-coloured precipitate first formed gradually dissolved on heating on the water-bath and the solution lightened in colour. The bright yellow crystals which were slowly precipitated were filtered off after about 2 hours and well washed with alcohol. After recrystallisation from acetone the compound melted at 201° (Found : C, 37·5; H, 3·1; Pt, 23·1. Calc. for $C_{26}H_{26}Br_2As_2Pt$: C, 37·0; H, 3·1; Pt, 23·1%). Burrows and Parker (*loc. cit.*) first described this compound and reported m. p. 196°. It is only very slightly soluble in cold benzene but dissolves on heating; the low solubility in benzene in comparison with that of the iodide indicates that the compound is almost certainly the *cis*-form.

Bisdiphenylmethylarsinedi-iodoplatinum(II).—Diphenylmethylarsine (1·5 g.) and potassium iodide (5 g.), dissolved in a mixture of water (30 ml.) and alcohol (150 ml.), were added to hexahydrated hexachloroplatinic acid (1·0 g.) dissolved in alcohol (20 ml.). The pale pink precipitate which formed at once gradually darkened on heating on the water-bath and after about 3 hours was replaced by a pinkish-orange crystalline powder in a colourless solution. This precipitate was then filtered off, washed many times with alcohol, and recrystallised from benzene and light petroleum; m. p. 229° (Found : C, 33·3; H, 2·8; Pt. 20·6. $C_{26}H_{26}I_2As_2Pt$ requires C, 33·3; H, 2·8; Pt, 20·8%). The *compound* dissolved very readily in chloroform and cold benzene and was fairly soluble in acetone. From its ready solubility in benzene it is undoubtedly the *trans*-isomer.

Bisdiphenylmethylarsinetetrachloroplatinum(IV). This *compound* had to be prepared in benzene solution for it was obtained from chloroform–carbon tetrachloride as a low-melting, difficultly crystallisable substance containing solvent which was very difficult to remove. Bisdiphenylmethylarsinedichloroplatinum (II) (m. p. 223°) (0·75 g.) was dissolved in benzene (75 ml.) by heating under reflux, and chlorine (0·075 g.) in carbon tetrachloride (10 ml.) was added to the warm solution. The light yellow solution deepened in colour and after removal of about half of the solvent the compound crystallised as deep yellow microcrystalline rods (0·6 g.) which were filtered off and washed with benzene, in which they are only very slightly soluble. It may be recrystallised from benzene, the m. p. varying from 205° to 215°, the lower m. p. form gradually increasing on standing (Found, for form of m. p. 205° : C, 37·4; H, 3·1; Pt, 23·9. Found, for form of m. p. 215° : C, 37·8; H, 3·1; Cl, 17·3; Pt, 23·7. $C_{26}H_{26}Cl_4As_2Pt$ requires C, 37·8; H, 3·1; Cl, 17·4; Pt, 23·7%). The substance appears to be an equilibrium mixture of *cis*- and *trans*-forms, but attempts to separate them were not successful. Owing to the low solubility even in bromoform the molecular weight could not be determined.

Bisdiphenylmethylarsinetetrabromoplatinum(IV). Bisdiphenylmethylarsinedibromoplatinum(II) (m. p. 201°) (3·05 g.), dissolved in chloroform (35 ml.), was treated with bromine (0·58 g.) dissolved in carbon tetrachloride (9 ml.) at room temperature. The yellow solution immediately became orange-red in colour and was concentrated at room temperature at the pump to about 10 ml. Orange crystals of the *tetrabromo*-compound (3·1 g.) crystallised out, and were recrystallised from chloroform–carbon tetrachloride. The m. p. varied from 212° to 218°, but after standing for some weeks the compound melted at 214° (Found : C, 31·5; H, 2·7; Pt, 19·3%). The first preparation melted at 227° (Found : C, 30·6; H, 2·9; Br, 31·9; Pt, 19·1%; *M*, cryoscopic in 0·737% solution in bromoform, 967. $C_{26}H_{26}Br_4As_2Pt$ requires C, 31·1; H, 2·6; Br, 31·9; Pt, 19·4%; *M*, 1003) and was more soluble in organic solvents, but heating, recrystallisation, or standing caused a gradual fall in the m. p. to that of the less soluble form. The compound (m. p. 214°) is soluble in chloroform, slightly soluble in benzene, but practically insoluble in alcohol or acetone, and is quite insoluble in ether or light petroleum; it is too insoluble both in freezing bromoform and in boiling benzene for the molecular weight to be determined. The form of m. p. 227° is probably *trans*-, and the other an equilibrium mixture of *cis*- and *trans*-isomers.

Bisdiphenylmethylarsinetetraiodoplatinum(IV). Bisdiphenylmethylarsinedi-iodoplatinum(II) (*trans*) (1·76 g.), dissolved in chloroform (25 ml.), was treated with iodine (0·45 g.) dissolved in chloroform–carbon tetrachloride (10 ml.; 1 : 1). After a few seconds the light orange solution became dark wine-red in colour and glistening purplish-black crystals were precipitated. The solution was concentrated to about 15 ml. at room temperatures at the pump, and a yield of 1·9 g. of the *tetraiodide* was obtained which melted at 193° after recrystallisation from chloroform and carbon tetrachloride. The compound is fairly soluble in chloroform and bromoform but not very soluble in benzene. Its properties indicate that it is the *trans*-isomer (Found : C, 25·8; H, 2·4; I, 42·6; Pt, 16·2%; *M*, cryoscopic in 0·507% solution in bromoform, 1100. $C_{26}H_{26}I_4As_2Pt$ requires C, 26·2; H, 2·2; I, 42·8; Pt, 16·4%; *M*, 1191).

Bisdiphenylmethylarsinedichlorodibromoplatinum(IV). Oxidation of *cis*-$PtCl_2,2AsMePh_2$ with bromine or of *cis*-$PtBr_2,2AsMePh_2$ with chlorine gave the same product (m. p. and mixed m. p.) : it may be an equilibrium mixture.

The dibromo-compound (m. p. 201°) (0·84 g.) in chloroform (25 ml.) was treated with chlorine (0·071 g.) in carbon tetrachloride (5 ml.) and the yellow solution turned orange. Carbon tetrachloride (10 ml.) was added, and the solution concentrated to half bulk, filtered from a small amount of sticky material, and then evaporated to dryness, and the residue was recrystallised from carbon tetrachloride-chloroform. The *compound* was obtained as a microcrystalline powder, m. p. 203° (Found : C, 34·3; H, 2·9; Pt, 21·1. $C_{26}H_{26}Cl_2Br_2As_2Pt$ requires C, 34·1; H, 2·8; Pt, 21·3%). It was also prepared by the action of bromine (0·09 g.) in carbon tetrachloride (1·5 ml.) on the chloro-compound (m. p. 223°) (0·4 g.) dissolved in benzene (60 ml.) by heating. After evaporation of the bulk of the solvent, the orange complex was obtained; m. p. 203°. Solubilities are low, suggesting that the two arsine groups are *cis*-, but the configuration of the halogens is unknown.

Bisdiphenylmethylarsinedichlorodi-iodoplatinum(IV). This compound was prepared by two methods. (*a*) Bisdiphenylmethylarsinedi-iodoplatinum(II) (m. p. 229°, *trans*-) (1·9 g.) was dissolved in chloroform (30 ml.), and chlorine (0·142 g.) in carbon tetrachloride (10 ml.) added. The solution was kept cold and changed colour from pink to dark wine-red. Concentration at the pump at room temperature precipitated a brownish powder, m. p. 163°. The compound crystallised as brown rods; it was not recrystallised for fear of disproportionation.

(*b*) Bisdiphenylmethylarsinedichloroplatinum(II) (m. p. 214°) (0·75 g.) was dissolved in cold chloroform (30 ml.), and iodine (0·25 g.) in carbon tetrachloride–chloroform (10 ml.; 1 : 1) added. The very pale yellow turned to a dark red colour, and evaporation at room temperature at the pump to a volume of 10 ml. precipitated light brown crystals of the required complex, m. p. 163° (Found : C, 31·2; H, 2·6; Pt, 19·3. $C_{26}H_{26}Cl_2I_2As_2Pt$ requires C, 30·9; H, 2·6; Pt, 19·3%).

From its method of preparation this compound is clearly a trans-*dichloro*-trans-*di-iodobisarsine* complex. Attempts to obtain an analytically pure specimen of the *cis*-dichloro-*trans*-di-iodo-complex were unsuccessful because disproportionation occurred so rapidly that the first fraction crystallising from the reaction mixture was contaminated with the tetraiodo-compound.

Reduction of Bisdiphenylmethylarsinedichlorodi-iodoplatinum(IV). The above *trans*-compound (0·5 g.), freshly prepared by the action of chlorine on the *trans*-di-iodo-compound, was dissolved in cold chloroform (25 ml.), and sulphur dioxide bubbled through the dark red solution. The colour faded during the first 15 minutes and after about an hour had become light orange, and was then apparently unaltered. The solution was filtered, the chloroform removed at the pump, and the pinkish-brown residue recrystallised twice from benzene and light petroleum, pink needles being obtained, m. p. (and mixed m. p. with a pure specimen of *trans*-di-iodo-compound) 229°. Attempts to reduce the tetrahalogeno-compound by boiling with acetone, the method used by Mann and Purdie (*loc. cit.*) for the auric complexes, were not successful.

Bisdiphenylmethylarsinedibromodi-iodoplatinum(IV). Bisdiphenylmethylarsinedibromoplatinum(II) (m. p. 201°) (0·84 g.), dissolved in chloroform (30 ml.), was treated with iodine (0·25 g.) dissolved in carbon tetrachloride–chloroform (30 ml.; 1 : 1) and the yellow orange solution immediately turned dark red. Removal of most of the solvent at room temperatures at the pump gave glistening black crystals which disproportionated when attempts were made to carry out recrystallisation. The *compound* melts at 185°, and from the analysis (Found: C, 27·6; H, 2·5; Pt, 17·5. $C_{26}H_{26}Br_2I_2As_2Pt$ requires C, 28·3; H, 2·4; Pt, 17·8%) appears to contain traces of the tetraiodide. In view of their instability these complexes were not further investigated.

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