625. *Complexes of Iridium*(III) *Halides with Tertiary Phosphines and Tertiary Arsines.*

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New complexes of iridium(III) halides with tertiary phosphines and tertiary arsines are described. They include mononuclear complexes of the type $[IrX_3(MR_3)_3]$ (X = halogen, MR_3 = phosphine or arsine), salts of the type $[PHR_3][IrCl_4(PR_3)_2]$, and a chloro-bridged complex $[Ir_2Cl_6(PEt_3)_4]$.

SOME new complexes of tertiary phosphines and tertiary arsines with iridium(III) halides were required when continuing our work on the reactions of alcohols with transition-metal complexes to give hydrido- and/or carbonyl complexes.[1] This paper describes their preparation and properties.

Chloroiridic acid is a convenient starting material. It was reduced to an iridium(III) chloro-complex with boiling ethanol in the presence of hydrochloric acid, and then the tertiary phosphine or tertiary arsine was added. When triethylphosphine was added, prolonged boiling (20 hr.) led to a mixture of three complexes, a yellow trichloro-complex $[IrCl_3(PEt_3)_3]$, a small quantity of an isomeric colourless complex $[IrCl_3(PEt_3)_3]$, and a pink salt $[PHEt_3][IrCl_4(PEt_3)_2]$. The dipole moment ($\mu$ = 6·9 D) of the yellow isomer indicates the configuration (I; L = PEt_3, X = Cl).

Unfortunately, the white isomer was too insoluble in benzene for its dipole moment to be measured, but its colour, low solubility in non-polar solvents, and high melting point and the formation of a non-conducting solution in nitrobenzene strongly favour the other possible configuration (II). For convenience in this paper the configurations (I) and (II) are referred to as the *trans*- and the *cis*-configuration, respectively, because in (I) two sets

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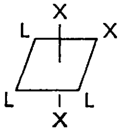
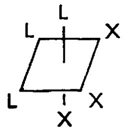
[1] Chatt and Shaw, *Chem. and Ind.*, 1961, 290.

of identical ligands are in *trans*-positions whereas in (II) all identical ligands are in *cis*-positions. The pink salt $[PHEt_3][IrCl_4(PEt_3)_2]$ is a univalent-univalent electrolyte in nitrobenzene and the corresponding pink tetraphenylarsonium salt was easily obtained from it. The phosphonium salt $[PHEt_3][IrCl_4(PEt_3)_2]$, on prolonged boiling in ethanol, gave the yellow *trans*-isomer $[IrCl_3(PEt_3)_3]$ and is a possible intermediate in its production.

(I)





(II)

A pink electrolyte was also prepared by Dwyer and Nyholm [2] from methyldiphenylarsine and formulated as $H[IrCl_4(AsMePh_2)_2]$. This was prepared by boiling iridium trichloride with methyldiphenylarsine in ethanol in the presence of a large amount of concentrated hydrochloric acid. Dwyer and Nyholm suggested that, as first obtained, this pink acid was probably contaminated with the arsonium salt, $[AsHMePh_2][IrCl_4(AsMePh_2)_2]$, but repeated precipitation by addition of water to an alcohol solution containing hydrochloric acid gave the pure acid. We carried out this reaction with diethylphenylphosphine and obtained a pink diethylphenylphosphonium salt rather than the free acid, because diethylphenylphosphine is a much stronger base than methyldiphenylarsine. Reduction of chloroiridic acid in ethanol followed by prolonged boiling with diethylphenylphosphine gave a similar mixture of complexes, *viz.*, *trans*- and *cis*-$[IrCl_3(PEt_2Ph)_3]$ and the pink salt $[PHEt_2Ph][IrCl_4(PEt_2Ph)_2]$.

A much more convenient route to complexes of the type *trans*-$[IrCl_3(MR_3)_3]$ (M = P or As, R = alkyl or aryl) is provided by the use of the higher-boiling 2-methoxyethanol (b. p. 124°) as solvent, excellent yields being obtained more quickly: the complex *trans*-$[IrCl_3(PEt_2Ph)_3]$ was prepared in 94% yield with a reaction time of only 25 min.

Corresponding tribromoiridium(III) complexes cannot be obtained analogously to the chlorides as they are reduced to hydrido-complexes by alcohols. However, by treating sodium bromoiridite in aqueous ethyl methyl ketone with diethylphenylphosphine the complex *trans*-$[IrBr_3(PEt_2Ph)_3]$ was prepared in good yield.

A chloro-bridged compound $[Ir_2Cl_6(PEt_3)_4]$ was obtained by reaction of chloroiridic acid with 2-methoxyethanol followed by addition of triethylphosphine (two moles per iridium g.-atom) and heating under reflux for 50 min. The molecular weight, measured ebullioscopically in chloroform, and the formation of a non-conducting solution in nitrobenzene, favour the binuclear bridged structure for this compound; corresponding bridged compounds of rhodium $[Rh_2Cl_6(MR_3)_4]$ (M = P or As, R = alkyl) have also been prepared.[3] The iridium compound was too insoluble in non-polar solvents such as benzene for its dipole moment to be determined.

EXPERIMENTAL

M. p.s were determined on a Kofler hot stage and have been corrected. Operations involving tertiary phosphines and tertiary arsines were carried out in an atmosphere of nitrogen.

Action of Triethylphosphine on Chloroiridic Acid in Ethanol.—Chloroiridic acid (8·17 g.) was boiled with ethanol (60 c.c.) and concentrated hydrochloric acid (1 c.c.) until the purple solution became brownish-green. Triethylphosphine (11·04 g.) was next added, and the mixture heated under reflux for 20 hr., then evaporated to half its bulk and cooled. Yellow crystals separated, which on recrystallisation from ethanol or light petroleum (b. p. 80—100°) gave trans-*trichlorotristriethylphosphineiridium*(III) as lemon-yellow prisms (7·24 g.), m. p. 116—117° (Found: C, 33·3; H, 7·05. $C_{18}H_{45}Cl_3IrP_3$ requires C, 33·1; H, 6·95%). The mother-liquors from the

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[2] Dwyer and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1945, **99**, 121.

[3] Chatt and Shaw, unpublished work.

preparative mixture were evaporated to dryness and the residue extracted with light petroleum (b. p. 80—100°). The extract, on cooling, gave a further quantity (3·05 g.) of *trans*-trichlorotristriethylphosphineiridium(III). The insoluble residue, recrystallised from methanol, gave *triethylphosphonium tetrachlorobistriethylphosphineiridate*(III) (1·1 g.) as pink prisms, m. p. 155—167° (decomp.) (Found: C, 31·45; H, 6·75. $C_{18}H_{46}Cl_4IrP_3$ requires C, 31·35; H, 6·7%), whose molar conductivity in nitrobenzene at 23° was 19·2 mho. Treatment of this pink salt (0·2 g.) in ethanol solution with an ethanolic solution of tetraphenylarsonium chloride (0·25 g.) gave *tetraphenylarsonium tetrachlorobistriethylphosphineiridate*(III) as pink needles (0·25 g.), m. p. 245—249° (Found: C, 44·9; H, 5·3. $C_{36}H_{50}As_4Cl_4IrP_2$ requires C, 45·3; H, 5·3%). cis-*Trichlorotristriethylphosphineiridium*(III) was obtained when *trans*-trichlorotristriethylphosphineiridium (10 g.) was recrystallised from ethanol; this gave the pure *trans*-isomer (8·4 g.), but the mother-liquors, on storage for six weeks at room temperature, deposited a mixture of colourless and yellow crystals. These were washed with ether to leave a residue of the *cis*-complex as colourless prisms (0·48 g.), m. p. 261—264° (Found: C, 33·2; H, 6·9%).

Action of Diethylphenylphosphine on Chloroiridic Acid in Ethanol.—A solution of chloroiridic acid (6·6 g.) in ethanol (80 c.c.) was boiled until the solution became brownish-green. Diethylphenylphosphine (10·1 g.) and concentrated hydrochloric acid (1 c.c.) in ethanol (10 c.c.) were then added, the mixture heated under reflux for 6 hr. and evaporated to dryness, and the residue extracted with boiling benzene. The benzene extract was evaporated and the residue recrystallised from ethyl methyl ketone to give trans-*trichlorotris*(*diethylphenylphosphine*)-*iridium*(III) as yellow needles (4·39 g.), m. p. 235—241° (decomp.) (Found: C, 44·9; H, 5·9%; *M*, ebullioscopically in 0·64% benzene solution, 829. $C_{30}H_{45}Cl_3IrP_3$ requires C, 45·2; H, 5·7%; *M*, 797). The ethyl methyl ketone mother-liquors, on storage, deposited cis-*trichlorotris*(*diethylphenylphosphine*)*iridium*(III) as colourless prisms (1·4 g.), m. p. 255—265°, which were recrystallised from nitrobenzene (Found: C, 45·05; H, 5·9; Cl, 13·25. $C_{30}H_{45}Cl_3IrP_3$ requires Cl, 13·35%). The residue insoluble in benzene (see above) was recrystallised from ethanol to give *diethylphenylphosphonium tetrachlorobis*(*diethylphenylphosphine*)*iridate*(III) as pink prisms (1·01 g.), m. p. 227—240° (decomp.) (Found: C, 43·25; H, 5·6. $C_{30}H_{46}Cl_4IrP_3$ requires C, 43·2; H, 5·55%). In nitrobenzene solution at 23° this pink salt had a molar conductivity of 26 mho. A solution of the pink salt (0·25 g.) in ethanol containing a little concentrated hydrochloric acid was treated with a solution of tetraphenylarsonium chloride (0·3 g.) in ethanol; pink needles (0·3 g.) of *tetraphenylarsonium tetrachlorobis*(*diethylphenylphosphine*)*iridate*(III) separated (Found: C, 50·1; H, 4·95. $C_{44}H_{50}AsCl_4IrP_2$ requires C, 50·35; H, 4·8%).

General Preparation of Complexes of the Type trans-$[IrCl_3(MR_3)_3]$ (M = P or As).—These were prepared by reducing chloroiridic acid to the tervalent state by heating it with an alcohol containing a little hydrochloric acid, then adding the tertiary phosphine or tertiary arsine (3·3 mol.), and heating the whole under reflux (for times shown in each case below). The product separated on cooling or was isolated after evaporation, and was purified by recrystallisation. The preparation of *trans*-trichlorotristriethylphosphineiridium(III) is given as typical.

trans-*Trichlorotristriethylphosphineiridium*(III). A solution of chloroiridic acid (4·1 g.) in 2-methoxyethanol (50 c.c.) containing concentrated hydrochloric acid (0·5 c.c.) was heated on a steam-bath until greenish-brown. Triethylphosphine (5·50 g.) was then added and the mixture heated under reflux for 30 min. On cooling, *trans*-trichlorotristriethylphosphineiridium(III) (5·16 g.) separated as yellow prisms, m. p. 113—115°.

trans-*Trichlorotris*(*tri*-n-*propylphosphine*)*iridium*(III) was prepared in 58% yield in ethanol (6 hr.) and formed yellow prisms, m. p. 236—242°, from ethanol (Found: C, 41·8; H, 8·25. $C_{27}H_{63}Cl_3IrP_3$ requires C, 41·6; H, 8·15%).

trans-Trichlorotris(diethylphenylphosphine)iridium(III) was prepared in 94% yield in 2-methoxyethanol (25 min.).

trans-*Trichlorotris*(*di-n-propylphenylphosphine*)*iridium*(III) was prepared in 32% yield in ethanol (6 hr.) and formed yellow needles, m. p. 230—236°, from ethanol (Found: C, 49·2; H, 6·6. $C_{36}H_{57}Cl_3IrP_3$ requires C, 49·05; H, 6·5%).

trans-*Trichlorotris*(*di-n-butylphenylphosphine*)*iridium*(III) was prepared in 42% yield in ethanol (5 hr.) and formed yellow prisms, m. p. 155—158°, from methanol (Found: C, 51·95; H, 7·15. $C_{42}H_{69}Cl_3IrP_3$ requires C, 52·25; H, 7·2%).

trans-*Trichlorotris*(*diethyl*-p-*methoxyphenylphosphine*)*iridium*(III) was prepared in 82% yield in 2-methoxyethanol (15 min.) and formed yellow prisms, m. p. 235—240°, from ethanol (Found: C, 44·6; H, 5·85. $C_{33}H_{51}Cl_3IrO_3P_3$ requires C, 44·6; H, 5·8%).

trans-*Trichlorotristriethylarsineiridium*(III) was prepared in 50% yield in ethanol (24 hr.) and formed orange prisms, m. p. 110—111·5°, from methanol (Found: C, 27·5; H, 5·7. $C_{18}H_{45}As_3Cl_3Ir$ requires C, 27·55; H, 5·8%).

trans-*Trichlorotris*(*diethylphenylarsine*)*iridium*(III) was prepared in 89% yield in 2-methoxyethanol (25 min.) and formed orange prisms from ethyl methyl ketone (Found: C, 38·9; H, 5·0. $C_{30}H_{45}As_3Cl_3Ir$ requires C, 38·8; H, 4·9%).

trans-*Tribromotris*(*diethylphenylphosphine*)*iridium*(III).—Diethylphenylphosphine (2·48 g.) was added to a solution of sodium bromoiridite dodecahydrate (5·0 g.) in water (10 c.c.) and ethyl methyl ketone (20 c.c.). The mixture was heated under reflux for 70 min., then cooled, and the orange precipitate recrystallised from ethyl methyl ketone, to give the *product* as orange prisms (1·85 g.), m. p. 235—250° (decomp.) (Found: C, 38·6; H, 4·8. $C_{30}H_{45}Br_3IrP_3$ requires C, 38·7; H, 4·8%).

Di-μ-chlorotetrachlorotetrakistriethylphosphinedi-iridum(III) $[Ir_2Cl_6(PEt_3)_4]$.—A solution of chloroiridic acid (6·0 g.) in 2-methoxyethanol (25 c.c.) and concentrated hydrochloric acid (1 c.c.) was heated at 95° until the purple colour had disappeared. Triethylphosphine (3·88 g,. 2·1 mol.) was then added and the mixture heated under reflux for 50 min. On cooling, the bridged *complex* separated. Recrystallisation from methylene chloride–methanol gave yellow-orange prisms (1·54 g.), m. p. 235—275° (decomp.) (Found: C, 26·75; H, 5·7%; *M*, ebullioscopically in 2·31% $CHCl_3$ solution, 1027. $C_{24}H_{60}Cl_6Ir_2P_4$ requires C, 26·95; H, 5·65%; *M*, 1070). The compound was non-conducting in nitrobenzene solution.

Dipole moments of iridium(III) complexes in benzene at 25°.

$10^3\omega$	$\Delta\varepsilon/\omega$	$\Delta v/\omega$	$_{T}P$	$_{E}P$	$_{O}P$	μ (D)
trans-$[IrCl_3(PEt_3)_3]$						
4·738	8·295					
5·202	8·187					
5·134		0·527				
6·251		0·512	1136	(153)	960 *	6·85 *
trans-$[IrCl_3(PEt_2Ph)_3]$						
3·728	7·200					
4·881	7·201	(0·52)	1231 *	(198)	1003 *	7·0 *
trans-$[IrCl_3(AsEt_3)_3]$						
5·242	6·680					
8·691	6·693	(0·52)	1135 *	(184)	924 *	6·7 *

* Calc. from $\Delta\varepsilon/\omega$ by using estimated values of densities and refractivities; estimated values are given in parentheses.[4]

Determination of Dipole Moments.—The method of determination and meanings of the symbols are as described previously.[4] The results are tabulated.

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[4] Chatt and Shaw, *J.*, 1959, 705, 4020.