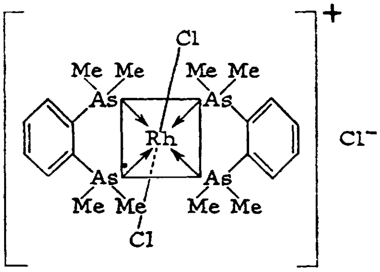
173. *Studies in Co-ordination Chemistry. Part IV. Complexes of Rhodic Halides with a Ditertiary Arsine.*

By R. S. Nyholm.

The complexes of tervalent rhodium halides with a chelating ditertiary arsine, *o*-phenylenebisdimethylarsine, have been prepared and studied. A series of salts have been isolated in which the univalent cation contains two molecules of the chelate group co-ordinated to the rhodium atom, two halogen atoms completing the octahedral configuration. All attempts to obtain complexes in which a halogen bridge connected two rhodium atoms were unsuccessful and it is concluded that such bridges, if formed, are unstable. The properties of the complexes are discussed.

In view of the ease with which bivalent rhodium formed binuclear halogen bridged complexes with tertiary arsines (Dwyer and Nyholm, *J. Proc. Roy. Soc. N.S.W.*, 1941, **75**, 127), the preparation of similar complexes of tervalent rhodium has been attempted. With tertiary arsines, bivalent rhodium halides gave rise to binuclear halogen bridged complexes of the type $[Rh(Hal)_2,3AsR_3]_2$ very readily and it was hoped that favourable circumstances for bridge formation with tervalent rhodium would be provided by the use of a suitable ditertiary arsine chelating group. Earlier work with diphenylmethylarsine (Dwyer and Nyholm, *ibid.*, p. 140) had shown that non-electrolytes of the formula $Rh(Hal)_3,3AsR_3$ could be isolated, but the use of a ditertiary arsine chelating group forces the rhodium either to bridge or to form a salt to complete a co-ordination number of six. It has been found, however, that the only complexes which could be isolated were salts containing two molecules of the chelate group to each rhodium atom and in which only part of the halogen was ionised. Variations in the method of preparation, such as changing the ratio of the reactants or refluxing the rhodium bisdiarsine salt with excess rhodic halide, failed to give the dimer. If formed, this dimer should be easily isolated, for binuclear complexes are usually much less soluble than the monomers from which they are derived. Most Group VIII metals, particularly those of the palladium and the platinum triad, have a tendency to form non-electrolytes with tertiary arsines rather than salts, and the formation of a salt in this case suggests that halogen bridges between tervalent rhodium atoms, if formed, are weaker than those between bivalent rhodium atoms.

The compounds isolated had the general formula $Rh(Hal)_3,2C_6H_4(AsMe_2)_2$; the chloride was investigated more than the *bromide* or the *iodide* because of its higher solubility in water, but the other two salts had similar properties. The compounds were formed in solution by heating the diarsine under reflux with the appropriate rhodic salt and were precipitated by addition of the corresponding acid. Since only part of the halogen was ionised, a salt-like structure for the complexes was presumed; then if a co-ordination number of six for the rhodium is assumed, the structure $[Rh(Hal)_2,2C_6H_4(AsMe_2)_2]Hal$ was expected. In the case of the chloride, this is as inset, the rhodium atom being octahedrally co-ordinated and the compound is *dichlorodi-(*o*-phenylenebisdimethylarsine)-rhodium*(III) *chloride*. This formulation has been confirmed by conductivity measurements and potentiometric titration with silver nitrate, a silver electrode being used. The molecular conductivity at a dilution of 1024 litres was 94 mhos; this figure is of the order expected for a strong electrolyte which forms two ions per molecule. The M/1024-solution was then titrated with silver nitrate in the presence of acetone and barium nitrate; the acetone was used to increase the sensitivity, and the barium nitrate the conductivity. The end-point of the titration occurred after only one of the three chlorine atoms had been precipitated (see figure), showing that only one chlorine atom was ionised. The small divergence from the calculated value is attributed to slight hydrolysis of the two covalently bound halogen atoms. In view of the dilution, the smallness of this hydrolysis is remarkable and indicates a very stable cation.



There is no evidence as to whether the two covalently bound chlorine atoms in the complex cation are *cis-* or *trans-*, but the latter is considered the more likely. This could be decided by attempts at optical resolution, for the *cis*-dichloro-compound should be capable of being resolved, but the *trans*-complex is inactive for it has a plane of symmetry. Complexes of tervalent cobalt and nickel in which similar cations are present will be described in Parts V and VI of this series.

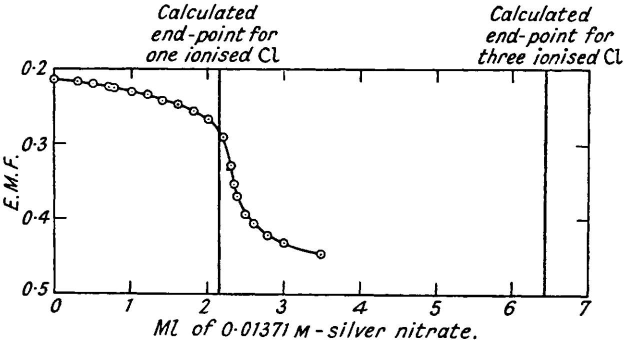
EXPERIMENTAL.

o-*Phenylenebisdimethylarsine*.—This was prepared as described in Part III (preceding paper).

Dichlorodi-(o-*phenylenebisdimethylarsine*)*rhodium*(III) *Monochloride*.—Sodium hexachlororhodate (0·65 g.), dissolved in distilled water (10 ml.), was treated with *o*-phenylenebisdimethylarsine (0·45 g.) in alcohol (70 ml.) containing hydrochloric acid (10N.; 5 ml.). (The ratio Rh : arsine was 1 : 1 in an attempt to obtain the bridged complex.) When the solution was heated, all the arsine dissolved, and after a few minutes the colour changed from red to light yellow, the complex salt being formed in solution. (An atmosphere of hydrogen, used initially, was later found unnecessary.) The solution was then heated under reflux for many hours in an attempt to effect bridging, but the only reaction was partial reduction to rhodium. The solution was filtered, and the filtrate concentrated to about 10 ml. and treated with concentrated hydrochloric acid. A yellow precipitate was obtained immediately and after cooling in ice this was filtered off and washed quickly with ice-cold dilute alcoholic hydrochloric acid and finally with small quantities of ice-cold water. It was then dried in the vacuum desiccator giving a yield of 0·4 g. The *compound*, recrystallised from aqueous alcohol containing a little hydrochloric acid, decomposed above 300° without melting (Found: C, 30·4; H, 4·2; Cl, 13·6; Rh, 13·1. $C_{20}H_{32}Cl_3As_4Rh$ requires C, 30·7; H, 4·1; Cl, 13·6; Rh, 13·1%). It was completely insoluble in benzene, chloroform, or light petroleum but dissolved readily in acetone or alcohol and was moderately soluble in warm water.

During the above preparation one occasionally obtained a heavy brown precipitate after a few seconds' refluxing which gradually re-dissolved on further heating. It was quite insoluble in all solvents and was probably the complex *salt* $[RhCl_2,2C_6H_4(AsMe_2)_2]_3[RhCl_6]$ (Found: Rh, 16·0. $C_{60}H_{96}Cl_{12}As_{12}Rh_4$ requires Rh, 16·2%). This compound appears to arise from the temporary coexistence of the two necessary ions, and it is significant that it is formed most readily in the presence of excess of sodium hexachlororhodate.

Potentiometric titration of M/1024-$[RhCl_2,2C_6H_4(AsMe_2)_2]Cl$, *with silver–silver chloride electrode.*



Dibromodi-(o-*phenylenebisdimethylarsine*)*rhodium*(III) *Bromide*.—Sodium hexachlororhodate (1·0 g.), dissolved in distilled water (13 ml.), was added to *o*-phenylenebisdimethylarsine (1·45 g.) in alcohol (60 ml.) containing concentrated hydrobromic acid (5 ml.); 30% hypophosphorous acid (2 ml.) was added to prevent the formation of bromine; it caused very little reduction of the rhodium salt. The solution was heated, and after a few minutes a brown sandy powder was precipitated which gradually dissolved on further refluxing to form an orange solution. After several hours' refluxing the solution was filtered from a very small amount of precipitate and concentrated to a small bulk on the water-bath. On cooling the residue (about 15 ml.) in ice, a yellowish-brown powder crystallised out. This was filtered off and washed with ice-cold alcohol and finally with ice-cold distilled water. It was dried in a vacuum desiccator. The *compound* (Found: C, 27·0; H, 3·8; Rh, 11·4. $C_{20}H_{32}Br_3As_4Rh$ requires C, 26·2; H, 3·5; Rh, 11·25%) did not melt but decomposed above 300°. It may be recrystallised from alcohol containing a little hydrobromic acid. An alcoholic solution precipitated only part of the bromine on treatment with silver nitrate.

Di-iododi-(o-*phenylenebisdimethylarsine*)*rhodium*(III) *Iodide*.—Sodium hexachlororhodate (2·0 g.), dissolved in water (25 ml.), was added to *o*-phenylenebisdimethylarsine (2·9 g.) in alcohol (125 ml.) containing hydriodic acid (57%; 10 ml.) just decolorised with hypophosphorous acid. To the mixture was added hypophosphorous acid (4 ml.), and on heating, the arsine quickly dissolved and a brownish-red powder was precipitated. This gradually dissolved on further refluxing and after 2 hours the solution was filtered and heated on the water-bath until the volume was about 50 ml. On cooling, beautiful crimson crystals were precipitated which were filtered off and washed many times with alcohol and finally with water. The *iodide* was much less soluble than the chloride or bromide and the addition of hydriodic acid when recrystallising from alcohol was not necessary. Two recrystallisations from alcohol gave an analytically pure specimen (Found: C, 23·0; H, 3·2; I, 36·2; Rh, 9·8. $C_{20}H_{32}I_3As_4Rh$ requires C, 22·7; H, 3·0; I, 36·2; Rh, 9·75%). The compound was completely insoluble in all organic solvents except alcohol and was insoluble in water. An alcoholic solution gave an immediate precipitate with silver nitrate, more silver iodide being formed on boiling owing, apparently, to rupture of the cation.

Conductivity of the Chloride Complex.—Measurements were carried out in a pipette-type cell of volume about 15 ml. and constant 0·0508 cm.$^{-1}$. The resistance of an M/1024-solution of the salt in this cell at 25° was 532 ohms. The conductivity of the water used was $3{\cdot}5 \times 10^{-6}$ mho/cm.^{3}. From these data the molecular conductance at a dilution of 1024 litres is 94 mhos.

Potentiometric Titration.—30 Ml. of the M/1024-solution of the chloride complex were treated with AnalaR acetone (100 ml.) and barium nitrate (1 g.), and the solution titrated with 0·01371M-silver nitrate from a microburette, the solution being stirred vigorously throughout the titration. A silver–silver chloride electrode was immersed in the solution, and a reference electrode consisting of a silver–silver chloride electrode in saturated potassium chloride connected to the solution through an ammonium nitrate bridge. The result (see figure) shows clearly that only one of the three chlorine atoms is ionised.

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Sir William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

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