

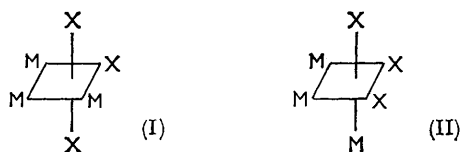
481. *The Preparation of Rhodium(III) Halide Complexes with Tertiary Phosphines and Tertiary Arsines.*

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New complexes of rhodium(III) halides are described. These include mononuclear complexes of the type $[\text{RhX}_3(\text{MR}_3)_3]$ ($\text{X} = \text{halogen}$, $\text{MR}_3 = \text{phosphine or arsine}$) and two types of binuclear halo-bridged complex, $[\text{Rh}_2\text{X}_6(\text{MR}_3)_3]$ and $[\text{Rh}_2\text{X}_6(\text{MR}_3)_4]$. Dipole-moment data are given, and some reactions of the complexes are described.

COMPLEXES of rhodium(III) halides with methyldiphenylarsine and methyldi-*p*-tolylarsine of the type $[\text{RhX}_3(\text{AsMeR}_2)_3]$ are known,^{1,2} but their configurations have not been determined; analogous complexes with tertiary phosphines have not hitherto been described. In our study of alkyl, hydrido, and carbonyl derivatives of transition metals stabilised by tertiary phosphines and tertiary arsines we required a series of rhodium(III) halide complexes of the type $[\text{RhX}_3(\text{MR}_3)_3]$ ($\text{X} = \text{halogen}$; $\text{M} = \text{P, As}$; $\text{R} = \text{alkyl or aryl group}$), and in this Paper we describe their preparation and properties. We also describe two types of binuclear complex, $[\text{Rh}_2\text{X}_6(\text{MR}_3)_3]$ and $[\text{Rh}_2\text{X}_6(\text{MR}_3)_4]$.

Preparation of Mononuclear Complexes.—Addition of a tertiary phosphine or tertiary arsine (3 mol.) to a hot alcoholic solution of rhodium trichloride gave an orange solution from which orange crystals of a complex of formula $[\text{RhCl}_3(\text{MR}_3)_3]$ separated on cooling, or could be isolated by evaporation and extraction with a suitable solvent. The complexes were monomeric and presumably octahedral and could therefore have either of the configurations (I) or (II) ($\text{M} = \text{P, As}$; $\text{X} = \text{Cl}$).



Bistertiary phosphine (and arsine) complexes of platinous chloride of *cis*-configuration, e.g., *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$, have dipole moments of *ca.* 10.5 D,³ indicating a moment of *ca.* 7 D along the direction of the P–Pt–Cl vector. Thus complexes of the type $[\text{RhCl}_3(\text{MR}_3)_3]$ of configuration (I) should have moments of *ca.* 7 D and compounds of configuration (II) should have moments of greater than 11 D. The dipole moments of the complexes $[\text{RhCl}_3(\text{MR}_3)_3]$ are *ca.* 7 D, clearly indicating configuration (I) which we shall call the *trans*-configuration. Chloro-complexes of this type were prepared from triethyl, tri-*n*-propyl-, tri-*n*-butyl-, dimethylphenyl-, diethylphenyl-, and ethyldiphenyl-phosphine, and triethyl-, tri-*n*-butyl-, and dimethylphenyl-arsine. In addition to these complexes, small quantities of yellow monomeric complexes which analysed as $[\text{RhCl}_3(\text{MR}_3)_3]$ were isolated from triethylphosphine and triethyl- and dimethylphenyl-arsine. These were too insoluble in

¹ Dwyer and Nyholm, *Proc. Roy. Soc. N.S.W.*, 1941, **75**, 140.

² Lewis, Nyholm, and Reddy, *Chem. and Ind.*, 1960, 1386.

³ Jensen, *Z. anorg. Chem.*, 1936, **229**, 250.

benzene for dipole-moment measurements and are probably the *cis*-isomers [configuration (II)].

Although the chloro-complex $[\text{RhCl}_3(\text{PPr}^n_3)_3]$, with lithium bromide in acetone, readily gave the bromo-complex, $[\text{RhBr}_3(\text{PPr}^n_3)_3]$, attempts to make corresponding iodo-, thio-cyanato-, and nitro-complexes by metathetical replacement gave impure products.

Attempts to prepare organo-complexes by replacing the chloro-groups with alkyl or aryl groups were unsuccessful. On treatment of complexes of the type *trans*- $[\text{RhCl}_3(\text{PR}_3)_3]$ with methylmagnesium chloride, *o*-tolyl-lithium, or mesitylmagnesium bromide, there was evidence of reaction (colour change), but attempts to isolate the products failed. Recently, $[\text{RhBr}(\text{1-naphthyl})_2(\text{PPr}^n_3)_3]$ has been obtained in poor yield by treatment of $[\text{RhCl}_3(\text{PPr}^n_3)_3]$ with 1-naphthylmagnesium bromide, but attempts to prepare analogous methyl, phenyl, *o*-tolyl, and mesityl derivatives failed.⁴ Attempts to replace chlorine by hydrogen were also unsuccessful. Reduction of rhodium(III) complexes of the type *trans*- $[\text{RhCl}_3(\text{PR}_3)_3]$ with sodium borohydride or lithium aluminium hydride gave dark solutions from which we were unable to isolate any crystalline material; possibly a rhodium hydrido-complex or a complex in a low valency state was formed. During attempted reduction with hydrazine, it displaced the phosphine from *trans*- $[\text{RhCl}_3(\text{PR}_3)_3]$ to give a hydrazine complex; the same complex was obtained by treating rhodium trichloride with hydrazine and was not investigated further. Treatment of *trans*- $[\text{RhCl}_3(\text{PR}_3)_3]$ with hydrazine hydrochloride readily gave complexes of formula $[\text{Rh}_2\text{Cl}_6(\text{N}_2\text{H}_4)(\text{PR}_3)_4]$, in which the hydrazine has displaced two phosphine molecules and is apparently acting as a bridging group between two rhodium atoms, since the tri-*n*-pentylphosphine compound is dimeric. The lower homologues were too insoluble for molecular-weight determinations. Treatment of *trans*- $[\text{RhCl}_3(\text{PR}_3)_3]$ with phenylhydrazine hydrochloride or pyridine hydrochloride gave complexes of the type $[\text{RhCl}_3\text{L}(\text{PR}_3)_2]$ (L = phenylhydrazine or pyridine), again with displacement of phosphine.

Preparation of Binuclear Complexes.—By analogy with other Group VIII metals, one would expect rhodium(III) halides to form halo-bridged polynuclear complexes with tertiary phosphines and arsines. Thus palladium(II) and platinum(II) halides form complexes of the type $[\text{M}_2\text{X}_4\text{L}_2]$ (M = Pd, Pt; X = Cl, Br, I; L = $\text{PR}_3, \text{AsR}_3$) containing two bridging halogen atoms,⁵⁻⁷ and ruthenium(II) and osmium(II) form complexes of type $[\text{M}_2\text{X}_3\text{L}_6]^+$ (M = Ru, Os; X = Cl, Br; L = PR_3) containing three bridging halogen atoms;⁸ the halo-bridged complex of iridium(III) $[\text{Ir}_2\text{Cl}_6(\text{PET}_3)_4]$, with two bridging halogen atoms, is also known.⁹ We find that rhodium(III) halides form similar compounds. On treating rhodium trichloride in ethanol with triethylphosphine (2 mol.) the binuclear complex $[\text{Rh}_2\text{Cl}_6(\text{PET}_3)_4]$ was readily obtained. It was also obtained by treating *trans*- $[\text{RhCl}_3(\text{PET}_3)_3]$ with rhodium trichloride ($\frac{1}{2}$ mol.) in hot ethanol. Analogous binuclear species of the type $[\text{Rh}_2\text{Cl}_6(\text{MR}_3)_4]$ (M = P, As) were prepared by using tri-*n*-propyl-, tri-*n*-butyl-, and tri-*n*-pentyl-phosphine, and triethylarsine. Treatment of the chloro-complex $[\text{Rh}_2\text{Cl}_6(\text{P}^n\text{Bu}^n_3)_4]$ with lithium bromide in acetone gave the bromo-analogue, but attempts to prepare corresponding iodo-complexes gave mixtures. We consider these binuclear complexes to have two bridging halo-atoms, so that each rhodium atom is octahedrally co-ordinated. The dipole moments of these complexes are very high (*ca.* 11.5 D), but these do not determine the configurations since several isomers of formula $[\text{Rh}_2\text{X}_6(\text{MR}_3)_4]$ having large dipole moments are possible. The chloro-bridged complexes reacted rapidly with free ligand to give mononuclear complexes $[\text{RhCl}_3(\text{MR}_3)_3]$ (M = P, As), but attempts to prepare mixed complexes of the type $[\text{RhCl}_3(\text{C}_5\text{H}_5\text{N})(\text{MR}_3)_2]$ by treating the bridged complexes with pyridine (2 mol.) gave mixtures.

⁴ Chatt and Underhill, *J.*, 1963, 2088.

⁵ Mann, *Ann. Reports*, 1938, 35, 148.

⁶ Mann and Wells, *J.*, 1938, 702.

⁷ Chatt, *J.*, 1951, 652.

⁸ Chatt and Hayter, *J.*, 1961, 896.

⁹ Chatt, Field, and Shaw, *J.*, 1963, 3371.

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We have also prepared binuclear complexes of the type $[\text{Rh}_2\text{Cl}_6(\text{MEt}_3)_3]$ ($\text{M} = \text{P, As}$) by treating rhodium trichloride with triethyl-phosphine or -arsine ($1\frac{1}{2}$ mol. per rhodium atom). These complexes were very stable thermally. The triethylarsine chloro-complex $[\text{Rh}_2\text{Cl}_6(\text{AsEt}_3)_3]$ gave, with triethylarsine (1 mol.), the binuclear complex $[\text{Rh}_2\text{Cl}_6(\text{AsEt}_3)_4]$, described above, and, with lithium bromide in acetone, the bromo-complex $[\text{Rh}_2\text{Br}_6(\text{AsEt}_3)_3]$. Presumably these complexes have three halogen atoms bridging two octahedrally co-ordinated rhodium atoms, but the dipole moment (8.6 D) of the complex $[\text{Rh}_2\text{Cl}_6(\text{AsEt}_3)_3]$ does not determine its stereochemistry since several structures of the right order of polarity can be written for a complex of this formula. Rhodium(III) is unusual in forming both two- and three-atom halogen bridges in otherwise very similar complexes. It is intermediate in behaviour between ruthenium(II) which forms only three-atom bridges, which cannot be split to two-atom bridges by 1 mol. of the phosphine, and palladium(II) which forms only two-atom bridged complexes.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus, and are corrected. Operations involving free tertiary phosphines or arsines were carried out in an atmosphere of nitrogen.

Action of Triethylphosphine (3.5 mol.) on Rhodium Trichloride.—Triethylphosphine (10.41 g.) was added to a solution of rhodium trichloride trihydrate (6.54 g.) in methanol (130 c.c.), and after 10 min. the red solution was evaporated to dryness and the residue extracted with benzene. The benzene extract was evaporated to dryness and the residue recrystallised from methanol to give *trans-trichlorotris(triethylphosphine)rhodium(III)* as orange-red prisms (3.55 g.), m. p. 114–117° (Found: C, 38.4; H, 8.1. $\text{C}_{18}\text{H}_{45}\text{Cl}_3\text{P}_3\text{Rh}$ requires C, 38.35; H, 8.05%). The benzene-insoluble residue was dissolved in methylene chloride, ether was added, and the resultant precipitate was recrystallised from methylene chloride-ethanol to give di- μ -chlorotetrachlorotetrakis(triethylphosphine)dirhodium(III) (0.67 g.) (Found: C, 32.55; H, 7.0) (see below). The methylene chloride-ether mother-liquors, on evaporation, gave a mixture of orange-red prisms and yellow needles. On adding methanol, the orange-red prisms of *trans-trichlorotris(triethylphosphine)rhodium(III)* dissolved leaving the *cis-isomer* as yellow needles (0.43 g.), m. p. 169–174° (decomp.) (Found: C, 38.6; H, 8.0%). This *cis-isomer* partly isomerised to the *trans-isomer* on attempted recrystallisation.

trans-Trichlorotris(tri-n-propylphosphine)rhodium(III), $[\text{RhCl}_3(\text{PPr}^n)_3]$.—Tri-n-propylphosphine (5.00 g., 4.1 mol.) was added to a solution of rhodium trichloride trihydrate (2.0 g.) in ethanol (50 c.c.). The solution was then boiled, and on cooling the required complex separated. Recrystallisation gave orange prisms (3.7 g.), m. p. 179–186° (decomp.) (from ethanol) (Found: C, 46.9; H, 9.2. $\text{C}_{27}\text{H}_{63}\text{Cl}_3\text{P}_3\text{Rh}$ requires C, 47.0; H, 9.2%).

trans-Trichlorotris(tri-n-butylphosphine)rhodium(III), $[\text{RhCl}_3(\text{PBu}^n)_3]$.—This was similarly prepared (40% yield) as orange-red prisms, m. p. 139–142° (decomp.) [from light petroleum (b. p. 60–80°)] (Found: C, 52.8; H, 10.0. $\text{C}_{36}\text{H}_{81}\text{Cl}_3\text{P}_3\text{Rh}$ requires C, 52.95; H, 10.0%).

trans-Trichlorotris(dimethylphenylphosphine)rhodium(III), $[\text{RhCl}_3(\text{PMe}_2\text{Ph})_3]$.—Dimethylphenylphosphine (4.72 g., 3.3 mol.) was added to a solution of rhodium trichloride trihydrate (2.75 g.) in methanol (100 c.c.). The solution was boiled for 5 min. and cooled, when the *product* (4.00 g.) separated. This gave orange prisms, m. p. 218–224° (decomp.) (from ethanol) (Found: C, 46.15; H, 5.35. $\text{C}_{24}\text{H}_{33}\text{Cl}_3\text{P}_3\text{Rh}$ requires C, 46.2; H, 5.35%).

trans-Trichlorotris(diethylphenylphosphine)rhodium(III), $[\text{RhCl}_3(\text{PEt}_2\text{Ph})_3]$.—Diethylphenylphosphine (15.26 g., 3.3 mol.) was added to a solution of rhodium trichloride trihydrate (7.16 g.) in ethanol (100 c.c.). The mixture was then heated to boiling, and on cooling, the *product* separated as orange prisms (19.3 g.), m. p. 183–196° (decomp.) [from ethanol, n-propanol, or benzene-light petroleum (b. p. 80–100°)] (Found: C, 50.9; H, 6.45. $\text{C}_{30}\text{H}_{45}\text{Cl}_3\text{P}_3\text{Rh}$ requires C, 50.9; H, 6.4%).

trans-Trichlorotris(ethylidiphenylphosphine)rhodium(III), $[\text{RhCl}_3(\text{PEtPh}_2)_3]$.—Ethylidiphenylphosphine (6.42 g., 3.3 mol.) was added to a solution of rhodium trichloride trihydrate (2.40 g.) in ethanol (60 c.c.) and the mixture heated to boiling. On cooling, the *product* separated as orange prisms (4.3 g.) which decomposed above 200° without melting (Found: C, 59.0; H, 5.45. $\text{C}_{42}\text{H}_{45}\text{Cl}_3\text{P}_3\text{Rh}$ requires C, 59.2; H, 5.3%).

cis- and trans-Trichlorotris(triethylarsine)rhodium(III), $[\text{RhCl}_3(\text{AsEt}_3)_3]$.—Triethylarsine

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(6.75 g., 3.3 mol.) was added to a solution of rhodium trichloride trihydrate (3.3 g.) in ethanol (100 c.c.), and the mixture heated to boiling. The yellow prisms (0.74 g.) which separated on cooling were recrystallised from methylene chloride-methanol to give the *cis-isomer* as yellow needles, m. p. 166—173° (decomp.) [Found: C, 31.3; H, 6.45%; *M* (ebullioscopically in 1.7% CHCl₃ solution), 719. C₁₈H₄₅As₃Cl₃Rh requires C, 31.1; H, 6.5%; *M*, 696]. The mother-liquors from the original reaction mixture were evaporated to ca. 25 c.c. and cooled, giving a mixture of red and yellow crystals. This mixture was extracted with cold benzene, leaving the small amount of yellow crystalline material undissolved. The benzene extract was evaporated to dryness and the residue recrystallised from methanol to give the *trans-isomer* as red prisms (2.4 g.), m. p. 111—112.5° (Found: C, 31.15; H, 6.5%).

trans-Trichlorotris(tri-n-butylarsine)rhodium(III), [RhCl₃(AsBu₃)₃].—Tri-*n*-butylarsine (3.32 g., 3.2 mol.) was added to a solution of rhodium trichloride trihydrate (1.19 g.) in ethanol (20 c.c.). The mixture was heated to boiling and cooled, when the required product (2.02 g.) separated. It formed red *prisms*, m. p. 110—122° (decomp.) (from methanol) (Found: C, 45.9; H, 8.65. C₃₆H₈₁As₃Cl₃Rh requires C, 45.6; H, 8.6%).

cis- and trans-Trichlorotris(dimethylphenylarsine)rhodium(III), [RhCl₃(AsMe₂Ph)₃].—Dimethylphenylarsine (5.63 g., 3.3 mol.) was added to a solution of rhodium trichloride trihydrate (2.45 g.) in ethanol. The mixture was boiled for ca. 1 min., and the yellow precipitate was filtered off from the hot solution and washed with ethanol. This yellow precipitate gave the *cis-isomer* as bright yellow prisms (0.14 g.), m. p. 198—206° (decomp.) (from methanol-methylene chloride) (Found: C, 38.25; H, 4.55. C₂₄H₃₃As₃Cl₃Rh requires C, 38.15; H, 4.4%). The hot mother-liquors, on cooling, deposited orange crystals (3.65 g.) which, on slow recrystallisation from ethanol, gave the *trans-isomer* as orange-red prisms, m. p. 190—194 (decomp.) (Found: C, 38.2; H, 4.55%).

trans-Tribromotris(tri-n-propylphosphine)rhodium(III), [RhBr₃(PPR₃)₃].—The trichloro-complex (0.50 g.) and lithium bromide (2 g.) were heated under reflux in acetone (30 c.c.) for 5 min. The mixture was evaporated to dryness, and the residue was washed with water, dried, and recrystallised from benzene-light petroleum (b. p. 80—100°), giving red *prisms* (0.465 g.), m. p. 160—163° (Found: C, 39.45; H, 7.75. C₂₇H₆₃Br₃P₃Rh requires C, 39.4; H, 7.7%).

Action of Phenylhydrazine Hydrochloride on Trichlorotris(triethylphosphine)rhodium(III).—Phenylhydrazine hydrochloride (0.24 g.) was added to a solution of *trans*-trichlorotris(triethylphosphine)rhodium(III) (0.22 g.) in methanol (10 c.c.). The mixture was then boiled for 5 min., cooled, water was added, and the resultant precipitate recrystallised from ethanol to give *trichloro(phenylhydrazine)bis(triethylphosphine)rhodium(III)* as orange needles (0.203 g.), m. p. 151—155° (decomp.) (Found: C, 38.9; H, 7.1; N, 5.5. C₁₈H₃₃Cl₃N₂P₂Rh requires C, 39.05; H, 6.9; N, 5.05%), ν_{\max} (in Nujol) 3368, 3233 cm⁻¹ (N-H stretch).

Action of Phenylhydrazine Hydrochloride on Trichlorotris(tri-n-butylphosphine)rhodium(III).—Similar treatment of trichlorotris(tri-*n*-butylphosphine)rhodium (0.5 g.) with phenylhydrazine hydrochloride (0.4 g.) in methanol (20 c.c.) gave *trichloro(phenylhydrazine)bis(tri-n-butylphosphine)rhodium(III)* as bright orange plates (0.42 g.), m. p. 142—146° (decomp.) [from light petroleum (b. p. 80—100°)] (Found: C, 49.6; H, 8.8; N, 4.2. C₃₀H₆₂Cl₃N₂P₂Rh requires C, 49.9; H, 8.65; N, 3.9%), ν_{\max} (in Nujol) 3287, 3260, 3221 cm⁻¹ (N-H stretch).

Action of Hydrazine Hydrochloride on Di- μ -chloro-tetrachlorotetrakis(tri-n-pentylphosphine)dirhodium(III).—A solution of the bridged compound (0.22 g.) in methanol (40 c.c.) was boiled with hydrazine hydrochloride (0.50 g.) for 2 min., then cooled, and water added. The resultant precipitate gave *hexachloro(hydrazine)tetrakis(tri-n-pentylphosphine)dirhodium(III)* as orange prisms (1.38 g.), m. p. 111—114° (from methanol) [Found: C, 50.3; H, 9.7; N, 2.15%; *M* (ebullioscopically in benzene), 1364, 1366, 1372]. C₆₀H₁₃₆Cl₆N₂P₄Rh₂ requires C, 50.5; H, 9.6; N, 1.95%; *M*, 1427), ν_{\max} (in hexane) 3257, 3195, and 3129 cm⁻¹ (N-H stretch).

Action of Hydrazine Hydrochloride on trans-Trichlorotris(triethylphosphine)rhodium(III).—Hydrazine hydrochloride (0.20 g.) was added to a solution of *trans*-trichlorotris(triethylphosphine)rhodium(III) (0.40 g.) in methanol (10 c.c.). The mixture was then boiled for 1 min. and cooled. The resultant orange precipitate gave *hexachloro(hydrazine)tetrakis(triethylphosphine)dirhodium(III)* as orange plates (0.29 g.), m. p. 223—231° (decomp.) (from acetic acid) (Found: C, 31.3; H, 7.05; N, 3.55. C₂₄H₆₄Cl₆N₂P₄Rh₂ requires C, 31.2; H, 7.0; N, 3.05%).

Action of Hydrazine Hydrochloride on trans-Trichlorotris(tri-n-butylphosphine)rhodium(III).—A solution of *trans*-trichlorotris(tri-*n*-butylphosphine)rhodium(III) (1.05 g.) in methanol (10 c.c.) was boiled with hydrazine hydrochloride (0.5 g.) for 1 min., then cooled, and water added. The

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resultant precipitate gave *hexachloro(hydrazine)tetrakis(tri-n-butylphosphine)dirhodium(III)* as orange prisms (0.73 g.), m. p. 179—182° [from methanol, then from light petroleum (b. p. 80—100°)] (Found: C, 45.65; H, 8.9; N, 2.6. $C_{48}H_{112}Cl_6N_2P_4Rh_2$ requires C, 45.75; H, 8.95; N, 2.2%).

Action of Pyridine Hydrochloride on trans-Trichlorotris(tri-n-propylphosphine)rhodium(III).—Pyridine hydrochloride (0.60 g.) was added to the *trans*-isomer (0.50 g.) in methanol (5 c.c.) and the mixture heated to boiling, then cooled, and water added. The resultant precipitate gave *trichloro(pyridine)bis(tri-n-propylphosphine)rhodium(III)* as orange prisms (0.50 g.), m. p. 173—186° (decomp.) (from ethanol) (Found: C, 45.15; H, 7.85; N, 2.3. $C_{23}H_{47}Cl_3NP_2Rh$ requires C, 45.35; H, 7.8; N, 2.3%).

Preparation of Halogen-bridged Complexes.—(1) *Di-μ-chloro-tetrachlorotetrakis(triethylphosphine)dirhodium(III)*, $[Rh_2Cl_6(PEt_3)_4]$. (a) Triethylphosphine (3.13 g., 2.3 mol.) was added to a solution of rhodium trichloride trihydrate (3.0 g.) in ethanol (50 c.c.) and the mixture shaken at 20° for 45 min. The resultant brown precipitate (2.7 g.) gave *di-μ-chloro-tetrachlorotetrakis(triethylphosphine)dirhodium(III)* as reddish purple prisms, m. p. 248—261° (decomp.) (from chloroform-ethanol) (Found: C, 32.45; H, 6.8. $C_{24}H_{60}Cl_6P_4Rh_2$ requires C, 32.55; H, 6.8%).

(b) A mixture of *trans*-trichlorotris(triethylphosphine)rhodium(III) (1.5 g.) and rhodium trichloride trihydrate (0.38 g., 0.55 mol.) was heated in ethanol (50 c.c.) for 5 min. On cooling, *di-μ-chloro-tetrachlorotetrakis(triethylphosphine)dirhodium(III)* separated as reddish purple prisms (0.67 g.), m. p. 248—258° (decomp.).

(2) *Di-μ-chloro-tetrachlorotetrakis(tri-n-propylphosphine)dirhodium(III)*, $[Rh_2Cl_6(PPr^i)_4]$. Tri-n-propylphosphine (1.77 g.) was added to a solution of rhodium trichloride trihydrate (1.40 g.) in ethanol (25 c.c.) and the mixture heated on a water-bath for 15 min. and then cooled. The product gave orange-brown *prisms* (1.11 g.), m. p. 180—192° (from methanol-methylene chloride) (Found: C, 39.85; H, 7.95. $C_{36}H_{84}Cl_6P_4Rh_2$ requires C, 40.8; H, 8.0%).

(3) *Di-μ-chloro-tetrachlorotetrakis(tri-n-butylphosphine)dirhodium(III)*, $[Rh_2Cl_6(PBu^i)_4]$. Tri-n-butylphosphine (5.12 g., 2.0 mol.) was added to a solution of rhodium trichloride trihydrate (3.35 g.) in methanol (50 c.c.), and the mixture heated to 60° and then cooled. The resultant orange-brown precipitate (3.91 g.) gave, on recrystallisation from light petroleum (b. p. 80—100°) and then from acetone, red-brown *prisms*, m. p. 172—180° (decomp.) [Found: C, 47.2; H, 9.0%; *M* (ebullioscopically in benzene), 1163 (0.686% solution), 1305 (1.584% solution). $C_{48}H_{108}Cl_6P_4Rh_2$ requires C, 46.95; H, 8.85%; *M*, 1228].

(4) *Di-μ-chloro-tetrachlorotetrakis(tri-n-pentylphosphine)dirhodium(III)*, $[Rh_2Cl_6[P(n-C_5H_{11})_3]_4]$. Tri-n-pentylphosphine (5.23 g., 3.0 mol.) was added to a solution of rhodium trichloride trihydrate (1.88 g.) in methanol (40 c.c.). The solution was boiled and then evaporated to dryness. The viscous residue gave brown *plates* (1.2 g.), m. p. 146—150° (from methanol) (Found: C, 51.65; H, 9.6. $C_{60}H_{132}Cl_6P_4Rh_2$ requires C, 51.6; H, 9.55%).

(5) *Di-μ-bromo-tetrabromotetrakis(tri-n-butylphosphine)dirhodium(III)*, $[Rh_2Br_6(PBu^i)_4]$. A mixture of the corresponding bridged chloro-complex (0.35 g.), lithium bromide (3 g.), and acetone (20 c.c.) was heated under reflux for 90 min. and then evaporated to dryness. The residue was washed with water and gave red-brown *prisms* (0.33 g.), m. p. 168—171° (from acetone) (Found: C, 38.6; H, 7.35. $C_{48}H_{108}Br_6P_4Rh_2$ requires C, 38.55; H, 7.3%).

(6) *Di-μ-chloro-tetrachlorotetrakis(triethylarsine)dirhodium(III)*, $[Rh_2Cl_6(AsEt_3)_4]$. A solution of rhodium trichloride trihydrate (1.29 g.) in ethanol (10 c.c.) was added to a solution of triethylarsine (1.66 g.) in ethanol (10 c.c.). The mixture was heated to boiling and cooled, when the required product separated. It formed orange-brown *prisms* (0.71 g.), m. p. 240—256° (decomp.) (from methanol-methylene chloride) (Found: C, 27.0; H, 5.55; Cl, 20.25. $C_{24}H_{60}As_4Cl_6Rh_2$ requires C, 27.0; H, 5.65; Cl, 19.95%). The product was non-conducting in nitrobenzene solution.

(7) *Tri-μ-chloro-trichlorotris(triethylphosphine)dirhodium(III)*, $[Rh_2Cl_6(PEt_3)_3]$. Triethylphosphine (2.89 g., 1.5 mol.) was added to a solution of rhodium trichloride trihydrate (4.30 g.) in ethanol (75 c.c.), and the solution boiled for 5 min. and cooled. The resultant brown precipitate (5.18 g.) gave brown *prisms*, m. p. 260—270° (decomp.) (from methanol-methylene chloride) (Found: C, 27.8; H, 5.9. $C_{18}H_{45}Cl_6P_3Rh_2$ requires C, 27.95; H, 5.85%).

(8) *Tri-μ-chloro-trichlorotris(triethylarsine)dirhodium(III)*, $[Rh_2Cl_6(AsEt_3)_3]$. Triethylarsine (5.42 g.) was added to a solution of rhodium trichloride trihydrate (6.43 g.) in ethanol (100 c.c.). The solution was heated to boiling and cooled, and the resultant brown precipitate (6.37 g.) gave

brown *needles*, m. p. 260—265° (decomp.) (from methanol–methylene chloride) [Found: C, 24.1; H, 5.05; Cl, 23.25%; *M* (ebullioscopically in 1.17% benzene solution), 861. $C_{18}H_{45}As_3Cl_6Rh_2$ requires C, 23.9; H, 5.0; Cl, 23.5%; *M*, 905.] The compound was diamagnetic.

(9) *Action of triethylarsine on tri- μ -chloro-trichlorotris(triethylarsine)dirhodium(III).* A solution of triethylarsine (0.023 g.) in dichloromethane (5.28 c.c.) was added to a solution of tri- μ -chloro-trichlorotris(triethylarsine)dirhodium(III) (0.905 g.) in dichloromethane (10 c.c.). After the solution had been standing for 19 hr., the product (0.65 g.) was precipitated with methanol. Recrystallisation from methanol–methylene chloride gave di- μ -chloro-tetrachloro-tetrakis(triethylarsine)dirhodium(III) as orange-brown prisms identical with a sample prepared above (Found: C, 27.05; H, 5.65. Calc. for $C_{24}H_{60}As_4Cl_6Rh_2$: C, 27.0; H, 5.65%).

(10) *Tri- μ -bromo-tribromotris(triethylarsine)dirhodium(III),* $[Rh_2Br_6(AsEt_3)_3]$. A solution of lithium bromide (3.5 g.) in acetone (25 c.c.) was added to a solution of tri- μ -chloro-trichloro-tris(triethylarsine)dirhodium(III) (1.0 g.) in ethyl methyl ketone (75 c.c.). The mixture was kept at 20° for 1 hr., and then evaporated to dryness. The residue was washed with water and extracted with benzene. The benzene solution was dried ($MgSO_4$) and evaporated to dryness. The residue gave red-brown *needles* (0.19 g.), m. p. 248—255° (decomp.) (from ethyl methyl ketone (Found: C, 18.55; H, 3.85. $C_{18}H_{45}As_3Br_6Rh_2$ requires C, 18.45; H, 3.85%).

Dipole Moments.—These are given in the Table; the method of determination and the meaning of the symbols are as described previously.¹⁰

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

	$10^3\omega$	$\Delta\epsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	T^P	E^P	O^P	μ (D)
<i>trans</i> - $[RhCl_3(PEt_3)_3]$	3.795	10.16	—	—	—	—	—	—
	5.431	10.06	—	(0.47)	1188 *	(158)	1006 *	7.0 *
<i>trans</i> - $[RhCl_3(PPr^i)_3]$	3.844	8.268	—	—	—	—	—	—
	5.348	8.265	—	(0.47)	1214 *	(193)	993 *	6.95 *
<i>trans</i> - $[RhCl_3(PEt_2Ph)_3]$	4.507	8.851	—	—	—	—	—	—
	5.060	8.899	—	(0.47)	1327 *	(203)	1094 *	7.3 *
<i>trans</i> - $[RhBr_3(PPr^i)_3]$	4.434	7.702	—	(0.53)	1426 *	(201)	1195 *	7.6 *
<i>trans</i> - $[RhCl_3(AsMe_2Ph)_3]$	2.577	8.367	—	—	—	—	—	—
	2.890	8.328	—	(0.47)	1340 *	(229)	1077 *	7.25 *
$[Rh_2Cl_6(PBu^i)_4]$	5.561	13.02	—	—	—	—	—	—
	8.498	13.04	—	—	—	—	—	—
	16.51	—	5.95	—	—	—	—	—
	25.77	—	6.08	—	—	—	—	—
	13.642	—	—	0.345	—	—	—	—
	9.042	—	—	0.321	3143	469	2674	11.5
$[Rh_2Cl_6(AsEt_3)_4]$	1.408	13.94	—	—	—	—	—	—
	2.027	14.19	—	(0.49)	3035	(374)	2605 *	11.3 *
$[Rh_2Cl_6(AsEt_3)_3]$	1.439	9.023	—	—	—	—	—	—
	1.515	9.031	—	(0.43)	1727	(339)	1337	8.1 *

Estimated values are in parentheses.

* Calc. by using estimated values of densities and refractivities.

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¹⁰ Chatt and Shaw, *J.*, 1959, 705, 4020.