

### 188. Some Complexes of Tertiary Phosphines with Ruthenium(II) and Osmium(II).

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The reactions of  $\text{RuCl}_3$  and  $(\text{NH}_4)_2\text{OsCl}_6$  with a variety of mono- and di-tertiary phosphines are described. The properties, reactions, and structures of the resulting complexes,  $[\text{M}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ;  $\text{PR}_3 = \text{PMe}_2\text{Ph}$ ,  $\text{PEt}_2\text{Ph}$ ,  $\text{PMePh}_2$ , or  $\text{PEtPh}_2$ ), and *cis*- and *trans*- $[\text{MX}_2(\text{chelate})_2]$  [chelate =  $\text{C}_2\text{H}_4(\text{PR}_2)_2$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ , or  $\text{Ph}$ ),  $\text{CH}_2(\text{PPh}_2)_2$ , and  $o\text{-C}_6\text{H}_4(\text{PEt}_2)_2$ ;  $\text{X} =$  halogen,  $\text{SCN}$ ], are discussed.

In this laboratory we have recently prepared a number of planar organo- and hydrido-complexes of platinum and nickel having the metal-carbon and metal-hydrogen bonds stabilised by tertiary phosphines.<sup>1</sup> As a preliminary to the preparation of analogous octahedral complexes of ruthenium and osmium it was necessary to obtain octahedral complexes of tertiary phosphines with osmium and ruthenium halides. These were unknown, and in this paper we describe their preparation. The complexes of the chelating diphosphines proved most useful for our purpose and were most extensively studied; those of the monophosphines were investigated mainly as intermediates in the preparation of the chelate complexes.

It was expected that tertiary phosphines, with their tendency to form spin-paired complexes, would give octahedral complexes of  $\text{Ru}(\text{II})$  and  $\text{Os}(\text{II})$  in which the metals are in the stable  $d_6$  electronic state. Complexes of this type are known;<sup>2</sup> e.g.,  $[\text{MCl}_2(\text{AsMePh}_2)_4]$ ,  $[\text{OsI}_2(\text{AsMePh}_2)_3]_2$ ,  $[\text{MCl}_2\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ). We have found, in general, that ruthenium and osmium give similar complexes, minor differences being attributed to the greater relative size of osmium(II), to its greater susceptibility to oxidation, and to the lower rates of reaction of its complexes.

*Complexes of Ditertiary Phosphines.*—These were prepared as follows from the ditertiary phosphines,  $\text{C}_2\text{H}_4(\text{PR}_2)_2$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{Ph}$ ),  $\text{CH}_2(\text{PPh}_2)_2$ , and  $o\text{-C}_6\text{H}_4(\text{PEt}_2)_2$ , and were all of the type  $[\text{MCl}_2(\text{ditertiary phosphine})_2]$ .

*Method 1. trans- $[\text{MCl}_2(\text{ditertiary phosphine})_2]$ .* The *trans*-dichloro-complexes were prepared by refluxing a slight excess (ca. 10%) of the ditertiary phosphine with ruthenium trichloride or  $(\text{NH}_4)_2\text{OsCl}_6$  in aqueous ethanol. All the ditertiary phosphines gave complexes of this type in reasonable yield (30–80%) as yellow or orange crystals. The *trans*-octahedral structures were confirmed by measurement of molecular weight (monomeric), conductivity (non-electrolytes), and dipole moment ( $<1.5$  D).

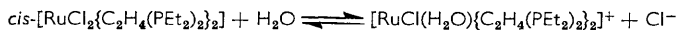
*Method 2. cis- $[\text{MCl}_2(\text{ditertiary phosphine})_2]$ .* The *cis*-dichloro-isomers were prepared in high yields by reaction of the ditertiary phosphines with the monotertriary phosphine complexes [e.g.,  $\text{I}$ ;  $\text{X} = \text{Cl}$ ] at 150–200° in the absence of solvent. Only  $\text{C}_2\text{H}_4(\text{PPh}_2)_2$  in the ruthenium(II) series did not yield the *cis*-isomer in this manner, but a high yield of the *trans*-isomer was obtained instead. A model of *cis*- $[\text{RuCl}_2\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}_2]$  showed strain between the phenyl groups and this may be sufficient to cause isomerisation to the *trans*-form. However, the strain cannot be great because both *cis*- $[\text{RuCl}_2\{\text{CH}_2(\text{PPh}_2)_2\}_2]$ , in which the steric requirements of the ligand are slightly less, and *cis*- $[\text{OsCl}_2\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}_2]$ , in which the strain is relieved by a larger metal atom, have been prepared. In the preparation of the *cis*-osmium complex, the *trans*-isomer was also obtained in 60% yield.

The *cis*-octahedral structures were confirmed by measurement of molecular weight (monomeric in benzene), conductivity (non-electrolytes in nitrobenzene), and dipole

<sup>1</sup> Chatt and Shaw, *J.*, 1959, 705, 4020; 1960, 1718; Chatt, Duncanson, and Shaw, *Proc. Chem. Soc.*, 1957, 343.

<sup>2</sup> Dwyer, Humpoletz, and Nyholm, *Proc. Roy. Soc., N.S.W.*, 1946, 80, 217; Dwyer, Nyholm, and Tyson, *ibid.*, 1947, 81, 272; Nyholm and Sutton, *J.*, 1958, 567, 572.

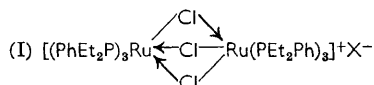
moment (8—11 D). The complexes  $cis\text{-}[\text{MCl}_2\{\text{C}_2\text{H}_4(\text{PR}_2)_2\}_2]$  (R = Me, Et) and  $cis\text{-}[\text{RuCl}_2\{o\text{-C}_6\text{H}_4(\text{PEt}_2)_2\}_2]$  also give conducting solutions in water, in which they are probably aquated, *e.g.*,



Of the complexes prepared during the present study, only those of the type  $cis\text{-}[\text{OsX}_2(\text{chelate})_2]$  were appreciably oxidised in air. Oxidation was particularly noticeable when the chelate was  $\text{C}_2\text{H}_4(\text{PR}_2)_2$  (R = Me or Et) and when the complexes were slightly impure; dark green or blue materials were formed.

*Method 3.*  $cis\text{-}$  and  $trans\text{-}[\text{MX}_2(\text{ditertiary phosphine})_2]$  (X = Br, I, SCN, CN, OAc). Complexes of this type were prepared from the corresponding  $cis\text{-}$  or  $trans\text{-}$  dichloro-complex by metathetical reaction with the appropriate metal salt (*e.g.*, LiBr) in solution. Most of the  $trans\text{-}$  complexes reacted only slowly in alcohol or tetrahydrofuran and some not at all. The products were best separated by chromatography (method 3a). The  $cis\text{-}$  complexes of ruthenium(II) were readily obtained in aqueous or aqueous-ethanolic solution. However,  $cis\text{-}[\text{OsCl}_2\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$  was relatively slow to react with lithium iodide in acetone, about 16 hours' refluxing being required for complete reaction (method 3b). In neither case (3a or 3b) was any stereochemical inversion observed, and in both series reaction was slower with the bulkier ligands  $[\text{CH}_2]_n(\text{PPh}_2)_2$  ( $n = 1$  or  $2$ ). The great difference in reaction rates between the  $trans\text{-}$  and  $cis\text{-}$  isomers which is also observed in planar complexes, *e.g.*,  $trans\text{-}$  and  $cis\text{-}[\text{PtCl}_2(\text{PR}_3)_2]$ , may be attributed to the high  $trans\text{-}$  effect of the tertiary phosphine.

*Method 4.*  $cis\text{-}[\text{RuCl}_2\{\text{C}_2\text{H}_4(\text{PR}_2)_2\}_2]$  (R = Me, Et). The complexes  $trans\text{-}[\text{RuCl}_2\{\text{C}_2\text{H}_4(\text{PR}_2)_2\}_2]$  (R = Me or Et) react with an excess of aluminium trialkyls  $\text{AlR}'_3$  (R' = Me, Et, or Pr<sup>n</sup>) at 60—80° in absence of solvent to give dark red oils of unknown composition. After the product has been washed with light petroleum, treatment with ethanol causes a vigorous reaction with gas evolution and formation of the corresponding  $cis\text{-}$  dichloro-complexes, identical with those obtained by method 2.  $cis\text{-}$  and  $trans\text{-}[\text{MCl}_2\{(\text{CH}_2)_n(\text{PPh}_2)_2\}_2]$  ( $n = 1$  or  $2$ ) give complex chloro-alkyls, on similar treatment,<sup>3</sup> while  $trans\text{-}[\text{OsCl}_2\{\text{C}_2\text{H}_4(\text{PR}_2)_2\}_2]$  (R = Me or Et) do not yield crystalline products.



*Complexes of Monotertiary Phosphines.*—Mixed alkylarylphosphines react with aqueous-ethanolic ruthenium trichloride or ammonium hexachloro-osmate(IV) to give yellow or orange crystalline complexes,  $[\text{M}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}$  ( $\text{PR}_3 = \text{PMe}_2\text{Ph}$ ,  $\text{PEt}_2\text{Ph}$ ,  $\text{PMePh}_2$ , or  $\text{PEtPh}_2$ ), to which we assign a symmetrical bridged structure of the type (I; X = Cl). The complexes are stable in air, can be recrystallised from alcohol or acetone, and are obtained even in the presence of a large excess of the tertiary phosphine, which might have been expected to split the bridge. The complex  $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$  is typical and was found to be almost completely dissociated into its constituent ions in boiling acetone, and to be a uni-univalent electrolyte in nitrobenzene and diamagnetic in the solid state. Derivatives could be prepared by replacement of the chloride anion and were found to be of the type [I; X =  $\text{ClO}_4$ ,  $\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ ,  $\text{BPh}_4$ , or  $\text{SCN}$ ] consistent with the presence of a unique chloride ion in the parent complex. These observations are not consistent with the possible alternative structures  $[\text{Ru}(\text{PEt}_2\text{Ph})_6][\text{RuCl}_4]$  or  $[\text{Ru}(\text{PEt}_2\text{Ph})_4][\text{RuCl}_4(\text{PEt}_2\text{Ph})_2]$ . The three-membered chloro-bridge is suggested in order to retain octahedral ruthenium(II). The corresponding complexes of osmium(II) were assigned a structure similar to (I) on the basis of molecular-weight and conductivity measurements.

<sup>3</sup> Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153.

The compound (I; X = SCN) is stable in the solid state but disproportionates in chloroform solution into (I; X = Cl) and an insoluble, possibly polymeric compound, which appears to contain both bridging and terminal thiocyanate groups, from the evidence of its infrared spectrum.<sup>4</sup>

*Reactions of Monotertiary Phosphine Complexes.*—The triple chloro-bridge in  $[\text{Ru}_2\text{Cl}_3(\text{PR}_2\text{Ph})_6]\text{Cl}$  (III; R = Me, Et) is not split by *p*-toluidine or hydrazine. Ditertiary phosphines, 1,1'-bipyridyl, and 1,10-phenanthroline slowly react with the complex (III; R = Et) in ethanol, displacing the monotertiary phosphine to give complexes of the type *cis*- $[\text{RuCl}_2(\text{ditertiary phosphine})_2]$ , *cis*- $[\text{RuCl}_2(\text{PET}_2\text{Ph})_2(\text{bipy})]$  and *cis*- $[\text{RuCl}_2(\text{PET}_2\text{Ph})(1,10\text{-phen})]$  respectively.

The complexes  $[\text{Ru}_2\text{Cl}_3(\text{PRPh}_2)_6]\text{Cl}$  (R = Me or Et) are less stable than those derived from  $\text{PR}_2\text{Ph}$  and react also with hydrazine, giving unstable red materials, probably of the type  $[\text{RuCl}_2(\text{PRPh}_2)_2(\text{N}_2\text{H}_4)]$ .

$[\text{Os}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}$  reacts similarly with ditertiary phosphines to give *cis*- $[\text{OsCl}_2(\text{ditertiary phosphine})_2]$  and with cyclo-octa-1,5-diene to give  $[\text{OsCl}_2(\text{C}_8\text{H}_{12})(\text{PEtPh}_2)_2]$ .

#### EXPERIMENTAL

Microanalyses are by the Microanalytical Department of these Laboratories. M. p.s were determined on a Kofler hot-stage and are corrected. Alumina for chromatography was Spence's grade H, 100—200 mesh. The light petroleum had b. p. 60—80°. Molar conductivities were determined in nitrobenzene at 20°. The ruthenium trichloride and ammonium chloro-osmate were commercial products used without further purification.

The diphosphines  $\text{C}_2\text{H}_4(\text{PR}_2)_2$  (R = Et or Ph) and *o*- $\text{C}_6\text{H}_4(\text{PET}_2)_2$  were prepared as described by Chatt and Hart<sup>5</sup> and by Hart.<sup>6</sup> Bisdiphenylphosphinomethane was obtained by Dr. H. R. Watson by a method similar to that of Issleib and Müller,<sup>7</sup> and bisdimethylphosphinoethane as follows:<sup>8</sup>

All operations were carried out under nitrogen at *ca.* -70° with good stirring. Sodium (23.0 g.) was dissolved in liquid ammonia (*ca.* 500 c.c.), and dry phosphine (from zinc phosphide and hydrochloric acid) passed through the solution until the blue colour had been replaced by the yellow-green of monosodium phosphide  $\text{NaPH}_2$ . The colour was then just discharged by addition of methyl iodide (*ca.* 142 g.) in dry ether (50 c.c.) during  $\frac{3}{4}$  hr. To the colourless solution was added a suspension of sodamide prepared from sodium (23 g.) in liquid ammonia (500 c.c.) to which had been added hydrated ferric nitrate (0.1—0.2 g.) as catalyst. The bright green colour of  $\text{NaPHMe}$  appeared and the solution was stirred for 1½ hr. to ensure completion of the reaction. The green colour was just discharged (to grey) by another addition of methyl iodide in ether, and dark red  $\text{NaPMe}_2$  was formed by addition of sodamide as previously. 1,2-Dichloroethane (*ca.* 49.5 g.) in ether (40 c.c.) was then added slowly (20—25 min.), discharging the red colour through orange and green to dark grey. The final addition was made cautiously to avoid excess. The reactants were next allowed to warm to room temperature with slow stirring and complete evaporation of the ammonia (overnight). Boiled-out water was added at room temperature to dissolve the salts, and the diphosphine extracted with ether (500 c.c.) and worked up in the same way as one of the lower aliphatic monophosphines; this gave a 35—40% yield (26—30 g.) of a colourless liquid, b. p. 81—82°/26 mm. (Parshall<sup>9</sup> records 104°/60 mm.), characterised as its diquatery salt  $[\text{Me}_2\text{P}(\text{C}_2\text{H}_4)_2\text{PMe}_2]\text{Br}_2$  formed by reaction with ethylene dibromide in warm ethanol and recrystallised from aqueous ethanol (Found: C, 28.65; H, 6.0.  $\text{C}_8\text{H}_{20}\text{Br}_2\text{P}_2$  requires C, 28.4; H, 6.0%).

*o*-Phenylenebisdimethylarsine was prepared as described by Chatt and Mann.<sup>10</sup>

*Ditertiary Phosphine and Other Chelate Complexes.*—*Method 1, trans*- $[\text{MCl}_2(\text{ditertiary phosphine})_2]$ . *trans*-Dichlorodi- $[\text{1,2-bis}(\text{diethylphosphino})\text{ethane}]\text{ruthenium(II)}$ . Ruthenium trichloride (0.60 g., 2.88 mmoles) in water (15 ml.) was added to 1,2-bis(diethylphosphino)ethane

<sup>4</sup> Chatt, Duncanson, Hart, and Owston, *Nature*, 1958, **181**, 43, and references therein.

<sup>5</sup> Chatt and Hart, *J.*, 1960, 1378.

<sup>6</sup> Hart, *J.*, 1960, 3324.

<sup>7</sup> Issleib and Müller, *Chem. Ber.*, 1959, **92**, 3175.

<sup>8</sup> Cf. Wymore and Bailar, *J. Inorg. Nucl. Chem.*, 1960, **14**, 42.

<sup>9</sup> Parshall, *J. Inorg. Nucl. Chem.*, 1960, **14**, 291.

<sup>10</sup> Chatt and Mann, *J.*, 1939, 610.

(1.48 g., 7.20 mmoles) in ethanol (120 ml.) under nitrogen, and the solution refluxed for 2 hr. The black solution gradually became dark green and finally cleared to brown. Dilution with water (100 ml.) gave a yellow precipitate which, after crystallisation from aqueous ethanol, afforded the pure *complex* (0.64 g., 38%) as bright yellow rhombs, m. p. 241—242°, subliming at 200° [Found: C, 41.15; H, 8.3%; *M* (ebullioscopically in 0.5% benzene solution), 629.  $C_{20}H_{48}Cl_2P_4Ru$  requires C, 41.1; H, 8.3%; *M*, 585]. This compound was a non-electrolyte and was also prepared in 83% yield by reaction between  $[Ru(NH_3)_6]Cl_2$  and 1,2-bis(diethylphosphino)ethane at 200° in the absence of solvent or by a similar reaction between the ditertiary phosphine and *trans*- $[RuCl_2(AsMe_2Ph)_2]$ . It was identified in both cases by mixed m. p.

The following complexes were similarly prepared.

*trans*-Dichlorodi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II), bright yellow prisms (55% yield) (from ethanol), m. p. 294°, subliming at 245° (Found: C, 30.4; H, 6.9.  $C_{12}H_{32}Cl_2P_4Ru$  requires C, 30.5; H, 6.8%).

*trans*-Dichlorodi-[1,2-bis(diphenylphosphino)ethane]ruthenium(II), orange plates (from chloroform) (66% yield), which rapidly effloresced in air to a pale yellow powder, m. p. 284—285° (decomp.) (Found: C, 64.4; H, 5.2.  $C_{52}H_{48}Cl_2P_4Ru$  requires C, 64.5; H, 5.0%); this compound was also obtained in almost quantitative yield by method 2 and in 25% yield by reaction between ruthenium trichloride and 1,2-bis(diphenylphosphino)ethane (2.5 mol.) at 230° for 24 hr.

*trans*-Dichlorodi-[1,2-bis(diphenylphosphino)methane]ruthenium(II), orange prisms (from chloroform), which lost solvent on drying in a vacuum at 80°, leaving a pale orange powder (75% yield), m. p. 276.5—278° (decomp.) (Found: C, 63.6; H, 4.9.  $C_{50}H_{44}Cl_2P_4Ru$  requires C, 63.8; H, 4.7%). *trans*-Dichlorodi-[*o*-phenylenebis(diethylphosphino)]ruthenium(II), yellow needles (from ethyl acetate) (38% yield), m. p. 241—242° (decomp.) (Found: C, 49.2; H, 7.1.  $C_{23}H_{48}Cl_2P_4Ru$  requires C, 49.4; H, 7.1%).

*trans*-Di-iododi-[1,2-bis(diethylphosphino)ethane]ruthenium(II) was prepared by a modification of method 1, the aqueous solution of ruthenium trichloride being treated with a 30-fold excess of aqueous sodium iodide, before addition of the diphosphine. After refluxing for 6½ hr., the brown precipitated product was filtered off and repeated crystallisation from benzene afforded the pure *complex* as orange-brown needles (8% yield), m. p. 267—270° (decomp.), subliming at 200° (Found: C, 31.6; H, 6.3; I, 33.9.  $C_{20}H_{48}I_2P_4Ru$  requires C, 31.3; H, 6.3; I, 33.1%). A considerable quantity of a golden-yellow complex, probably containing mixed halides, was also obtained.

*trans*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]osmium(II). Bisdiethylphosphinoethane (2.86 g., 13.8 mmoles) in ethanol (200 ml.) and ammonium hexachloro-osmate(IV) (2.01 g., 4.6 mmoles) in water (200 ml.) were refluxed together for several hours, a clear red solution, probably containing Os(IV), being obtained. The reduction was completed by a few drops of hydrazine hydrate, and the resulting clear yellow solution was concentrated by distillation. Cooling gave yellow crystals, which afforded the pure *complex* from methanol as pale yellow irregular prisms (28%), m. p. 247—250° (decomp.) (Found: C, 35.75; H, 7.3.  $C_{20}H_{48}Cl_2OsP_4$  requires C, 35.7; H, 7.2%).

*trans*-Dichlorodi-[1,2-bis(dimethylphosphino)ethane]osmium(II) was similarly prepared and was purified by chromatography on alumina, being eluted as a purple band (yellow solution) by 1:9 ether-benzene. Crystallisation from methylcyclohexane afforded the pure complex as yellow prisms (30%), m. p. 298—300° (decomp.), subliming at 200° (Found: C, 26.0; H, 5.7.  $C_{12}H_{32}Cl_2OsP_4$  requires C, 25.7; H, 5.75%). The following complexes were similarly prepared, except that the treatment with hydrazine hydrate was not necessary.

*trans*-Dichlorodi-[1,2-bis(diphenylphosphino)ethane]osmium(II), in 80% yield from chloroform, as large orange prisms, efflorescing to yellow crystals, m. p. 293—296° (decomp.); this compound was identical with the major product obtained by reaction between  $C_2H_4(PPh_2)_2$  and  $[Os_2Cl_3(PEt_2Ph)_6]Cl$ , and analysis indicates that it crystallises with  $\frac{1}{3}CHCl_3$  (Found: C, 57.4; H, 4.5; Cl, 8.8.  $C_{52}H_{48}Cl_2OsP_4 \cdot \frac{1}{3}CHCl_3$  requires C, 57.3; H, 4.4; Cl, 9.7%). *trans*-Dichlorodi-[1,2-bis(diphenylphosphino)methane]osmium(II), from dimethylformamide solution by precipitation with methanol (70% yield), as golden-yellow needles, m. p. >350° (Found: C, 58.7; H, 4.5; Cl, 6.8.  $C_{50}H_{44}Cl_2OsP_4$  requires C, 58.3; H, 4.3; Cl, 6.9%).

*Method 2, cis*- $[MCl_2(\text{ditertiary phosphine})_2]$ . *cis*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]ruthenium(II). Tri-*μ*-chlorohexakis(diethylphosphino)diruthenium(II) chloride (0.39 g., 0.29 mmole) and 1,2-bis(diethylphosphino)ethane (0.25 g., 1.20 mmoles) were heated together

under nitrogen in the absence of solvent. At 145° reaction occurred with effervescence and the formation of a homogeneous pale yellow liquid. The temperature was raised to 200° to complete the reaction and, on cooling, the liquid partially solidified and was washed with light petroleum to remove the displaced diethylphenylphosphine. Crystallisation of the solid residue from ethyl acetate afforded the pure complex as lemon-yellow plates (0.25 g., 76%), m. p. 214—214.5° [Found: C, 40.9; H, 8.1%; *M* (ebullioscopically in benzene), 627 (0.45% solution); 610 (1.65%). C<sub>20</sub>H<sub>48</sub>Cl<sub>2</sub>P<sub>4</sub>Ru requires C, 41.1; H, 8.3%; *M*, 585]. This compound is a non-electrolyte in nitrobenzene and has a molar conductivity in water of 92 ohm<sup>-1</sup> (8.57 × 10<sup>-3</sup>M; 25°). The following complexes were similarly prepared.

*cis*-Dichlorodi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II), pale yellow prisms (from benzene) (85% yield), m. p. 263—264°, subliming at 230° [Found: C, 30.3; H, 6.8; Cl, 14.7%; *M* (ebullioscopically in methanol), 292 (0.68% solution), 289 (1.3%), 303 (2.2%). C<sub>12</sub>H<sub>32</sub>Cl<sub>2</sub>P<sub>4</sub>Ru requires C, 30.5; H, 6.8; Cl, 15.0%; *M*, 1472]. This compound is a non-electrolyte in nitrobenzene, and has a molar conductivity in water of 142 ohm<sup>-1</sup> (5.34 × 10<sup>-3</sup>M; 25°).

*cis*-Dichlorodi-[1,2-bis(diphenylphosphino)methane]ruthenium(II), canary-yellow rhombs (from chloroform) (80% yield), m. p. 273—273.5° (decomp.) (Found: C, 63.9; H, 4.7. C<sub>50</sub>H<sub>44</sub>Cl<sub>2</sub>P<sub>4</sub>Ru requires C, 63.8; H, 4.7%).

*cis*-Dichlorodi-[*o*-phenylenebis(diethylphosphine)]ruthenium(II), yellow needles (from ethyl methyl ketone) (35% yield), m. p. 233—234.5° (decomp.) (Found: C, 49.4; H, 7.15. C<sub>28</sub>H<sub>48</sub>Cl<sub>2</sub>P<sub>4</sub>Ru requires C, 49.4; H, 7.1%).

*cis*-Dichlorodi-[*o*-phenylenebis(dimethylarsine)]ruthenium(II), yellow prisms (from methanol) (87% yield), subliming above 300°, but not melting below 350° (Found: C, 32.4; H, 4.5. C<sub>20</sub>H<sub>32</sub>As<sub>2</sub>Cl<sub>2</sub>Ru requires C, 32.3; H, 4.3%).

*cis*-Dichlorobis(diethylphenylphosphine)-1,1'-bipyridylruthenium(II), black needles (reddish-brown when crushed) (from benzene) (85% yield), m. p. >350° (Found: C, 54.8; H, 5.8; N, 4.3. C<sub>30</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Ru requires C, 54.5; H, 5.8; N, 4.2%). This compound is a non-electrolyte and does not react with 1,1'-bipyridyl (1 mole) at 230°.

*cis*-Dichlorobis(diethylphenylphosphine)-1,10-phenanthroline-ruthenium(II), as black needles (dark red when crushed) (from ethanol) (85% yield), m. p. >350° (Found: C, 56.3; H, 5.8; N, 4.6. C<sub>32</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Ru requires C, 56.1; H, 5.6; N, 4.1%).

Similarly prepared from [Os<sub>2</sub>Cl<sub>3</sub>(PEtPh<sub>2</sub>)<sub>6</sub>]Cl, 2H<sub>2</sub>O and chelate ligands were: *cis*-dichlorodi-[1,2-bis(diethylphosphino)ethane]osmium(II), from methylcyclohexane in 80% yield as colourless needles, m. p. 208—211° (Found: C, 35.6; H, 7.1. C<sub>20</sub>H<sub>48</sub>Cl<sub>2</sub>OsP<sub>4</sub> requires C, 35.7; H, 7.2%). *cis*-Dichlorodi-[1,2-bis(dimethylphosphino)ethane]osmium(II), in 65% yield by sublimation at 260° *in vacuo* as colourless crystals, m. p. 295—305° (decomp.) (Found: C, 26.0; H, 5.75. C<sub>12</sub>H<sub>32</sub>Cl<sub>2</sub>OsP<sub>4</sub> requires C, 25.7; H, 5.7%).

*cis*-Dichlorodi-[1,2-bis(diphenylphosphino)ethane]osmium(II) was obtained in 40% yield by reaction between C<sub>2</sub>H<sub>5</sub>(PPh<sub>2</sub>)<sub>2</sub> and [Os<sub>2</sub>Cl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>6</sub>]Cl: extraction of the crude product with tetrahydrofuran gave a pink solution and evaporation and crystallisation from ethyl acetate afforded the pure complex as pale yellow prisms, m. p. 290—291° (decomp.) (Found: C, 59.0; H, 5.0. C<sub>52</sub>H<sub>48</sub>Cl<sub>2</sub>OsP<sub>4</sub> requires C, 59.0; H, 4.6%). The tetrahydrofuran-insoluble portion of the crude product (60% of total) consisted mainly of *trans*-[OsCl<sub>2</sub>{C<sub>2</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>]<sub>2</sub>, which was obtained from chloroform in the solvated form (Found: C, 57.3, 56.9; H, 4.55, 4.4%). Crystallisation from dimethylformamide-methanol gave the unsolvated complex as pale yellow plates, m. p. 295—297° (decomp.) (Found: C, 59.4; H, 4.7; Cl, 6.6. C<sub>52</sub>H<sub>48</sub>Cl<sub>2</sub>OsP<sub>4</sub> requires C, 59.0; H, 4.6; Cl, 6.7%).

*cis*-Dichlorodi-[1,2-bis(diphenylphosphino)methane]osmium(II), pale yellow feathery needles (from nitrobenzene-methanol) (85% yield), m. p. >350° (Found: C, 58.2; H, 4.45. C<sub>50</sub>H<sub>44</sub>Cl<sub>2</sub>OsP<sub>4</sub> requires C, 58.3; H, 4.3%). This compound is solvated on crystallisation from chloroform (Found: C, 52.8; H, 4.1. C<sub>50</sub>H<sub>44</sub>Cl<sub>2</sub>OsP<sub>4</sub>.CHCl<sub>3</sub> requires C, 53.3; H, 3.95%); the solvent was only partially removed after 10 hr. *in vacuo* at 80° (Found: C, 53.8; H, 4.2%).

*cis*-Dichlorodi-[*o*-phenylenebis(diethylphosphine)]osmium(II), solvated pale yellow rhombs (80% yield) (from benzene), m. p. 258—270° (decomp.) (Found: C, 48.3; H, 6.4. C<sub>28</sub>H<sub>48</sub>Cl<sub>2</sub>OsP<sub>4</sub>.C<sub>6</sub>H<sub>6</sub> requires C, 48.2; H, 6.4%).

Dichlorocyclo-octa-1,5-dienedi(ethyl)diphenylphosphine]osmium(II), khaki-coloured (30% yield) (from light petroleum), m. p. 135—142° (decomp.) (Found: C, 54.1; H, 5.3. C<sub>36</sub>H<sub>42</sub>Cl<sub>2</sub>OsP<sub>2</sub> requires C, 54.2; H, 5.3%).

*Method 3.* (a) *trans-Isomers, trans-[MX<sub>2</sub>(ditertiary phosphine)<sub>2</sub>]* (X = Br, I, CN, OAc). *trans-Dibromodi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II)*. *trans-Dichlorodi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II)* (0.50 g.) was refluxed in ethanol with lithium bromide (4.6 g., 30-fold excess) for 2 days, the solution slowly changing in colour from yellow to orange. The solvent was removed at 12 mm., and the water-insoluble residue dissolved in benzene (10 ml.) and chromatographed on alumina. Elution with benzene containing 20% of light petroleum gave the pure *complex*, which crystallised from acetone as orange prisms (37%), m. p. 286.5—289° (decomp.), subliming at 200° (Found: C, 25.4; H, 5.8. C<sub>12</sub>H<sub>32</sub>Br<sub>2</sub>P<sub>4</sub>Ru requires C, 25.7; H, 5.75%). Elution with methanol gave unchanged dichloro-complex (0.26 g.).

The following complexes were similarly prepared.

*trans-Di-iododi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II)* was eluted with benzene and crystallised from ethyl methyl ketone as brick-red prisms (35% yield), m. p. 302.5—304° (decomp.), subliming at 250° (Found: C, 22.1; H, 4.9. C<sub>12</sub>H<sub>32</sub>I<sub>2</sub>P<sub>4</sub>Ru requires C, 22.0; H, 4.9%).

*trans-Dibromodi-[1,2-bis(diethylphosphino)ethane]ruthenium(II)* was eluted with benzene containing 20% of light petroleum and crystallised from 50% benzene–light petroleum as pale orange needles (25% yield), m. p. 264.5—266° subliming at 220° (Found: C, 35.9; H, 7.2. C<sub>20</sub>H<sub>48</sub>Br<sub>2</sub>P<sub>4</sub>Ru requires C, 35.7; H, 7.2%).

*trans-Dicyanodi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II) monohydrate* was eluted with 1 : 19 methanol–benzene and crystallised from acetone as colourless needles (48% yield), m. p. >350°, subliming at 300° (Found: C, 35.6; H, 7.5; N, 6.2. C<sub>14</sub>H<sub>34</sub>N<sub>2</sub>OP<sub>4</sub>Ru requires C, 35.7; H, 7.3; N, 5.9%). Water of hydration was not removed after heating in a vacuum at 100° for 16 hr. The infrared spectrum (Nujol mull) showed a strong band at 2064 cm.<sup>-1</sup> attributed to  $\nu_{C\equiv N}$ .

*trans-Diacetatodi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II) monohydrate* was obtained from acetone as colourless prisms (70% yield), m. p. 245—260° (decomp.), subliming at 180° (Found: C, 35.7; H, 7.6. C<sub>16</sub>H<sub>38</sub>O<sub>5</sub>P<sub>4</sub>Ru.H<sub>2</sub>O requires C, 35.75; H, 7.5%); this compound decomposed on attempted chromatography; its infrared spectrum (hexachlorobutadiene mull) shows two strong doublet bands at 1603, 1570, and 1433, 1395 cm.<sup>-1</sup>, both due to the unidentate acetate groups.

*trans-Di-iododi-[1,2-bis(diethylphosphino)ethane]osmium(II)*, from dimethylformamide in 55% yield as light orange needles, m. p. 272—274° (decomp.), subliming at 220° (Found: C, 28.5; H, 5.8. C<sub>20</sub>H<sub>48</sub>I<sub>2</sub>OsP<sub>4</sub> requires C, 28.05; H, 5.65%).

(b) *cis-Isomers, cis-[MX<sub>2</sub>(ditertiary phosphine)<sub>2</sub>]* (X = Br, I, SCN). *cis-Dibromodi-[1,2-bis(diethylphosphino)ethane]ruthenium(II)*. *cis-Dichlorodi-[1,2-bis(diethylphosphino)ethane]ruthenium(II)* (0.50 g.) was dissolved in hot water (40 ml.), and the solution was filtered, and added to a solution of potassium bromide (1.0 g.) in water (3 ml.). The yellow precipitate was filtered off and washed with water; crystallisation from ethanol afforded the pure *complex* as yellow plates (88% yield), m. p. 191° (Found: C, 35.9; H, 7.2. C<sub>20</sub>H<sub>48</sub>Br<sub>2</sub>P<sub>4</sub>Ru requires C, 35.7; H, 7.2%).

The following complexes were similarly prepared.

*cis-Di-iododi-[1,2-bis(diethylphosphino)ethane]ruthenium(II)*, obtained from chloroform as orange-brown prisms (90% yield), had m. p. 263—264° (decomp.), subliming at 260° (Found: C, 31.4; H, 6.3; I, 32.6. C<sub>20</sub>H<sub>48</sub>I<sub>2</sub>P<sub>4</sub>Ru requires C, 31.3; H, 6.3; I, 33.1%).

*cis-Dithiocyanatodi-[1,2-bis(diethylphosphino)ethane]ruthenium(II)* formed, from aqueous acetone, colourless prisms (74% yield), m. p. 325—326.5° (decomp.), subliming at 300° (Found: C, 41.75; H, 7.55; N, 4.6. C<sub>22</sub>H<sub>46</sub>N<sub>2</sub>P<sub>4</sub>RuS<sub>2</sub> requires C, 42.0; H, 7.7; N, 4.45%); the infrared spectrum (Nujol mull) shows a strong doublet band at 2110, 2105 cm.<sup>-1</sup> due to  $\nu_{C\equiv N}$ .

*cis-Dibromodi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II)*, yellow prisms (from ethanol) (50% yield), m. p. 242—243° (decomp.) (Found: C, 26.05; H, 5.7. C<sub>12</sub>H<sub>32</sub>Br<sub>2</sub>P<sub>4</sub>Ru requires C, 25.7; H, 5.75%).

*cis-Di-iododi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II)*, golden-yellow prisms (from ethanol) (55% yield), m. p. 289—291° (decomp.) (Found: C, 22.2; H, 4.9; I, 38.3. C<sub>12</sub>H<sub>32</sub>I<sub>2</sub>P<sub>4</sub>Ru requires C, 22.0; H, 4.9; I, 38.7%).

*cis-Dithiocyanatodi-[1,2-bis(dimethylphosphino)ethane]ruthenium(II)*, colourless plates (from acetone) (75% yield), decomp. 328° (Found: C, 32.9; H, 6.5; N, 5.1. C<sub>14</sub>H<sub>32</sub>N<sub>2</sub>P<sub>4</sub>RuS<sub>2</sub>

requires C, 32.5; H, 6.2; N, 5.4%); the infrared spectrum (Nujol mull) has a strong doublet band at 2108, 2102  $\text{cm}^{-1}$  due to  $\nu_{\text{C}\equiv\text{N}}$ .

*cis*-Di-iododi-[*o*-phenylenebis(diethylphosphine)]ruthenium(II), golden-yellow prisms (from ethyl methyl ketone) (65% yield), m. p. 247—248° (decomp.) (Found: C, 40.1; H, 5.8.  $\text{C}_{28}\text{H}_{48}\text{I}_2\text{P}_4\text{Ru}$ ,  $\frac{1}{2}\text{C}_4\text{H}_8\text{O}$  requires C, 40.1; H, 5.8%); the solvent of crystallisation was not removed after 6 hr. in a vacuum at 100°.

*cis*-Di-iododi-[1,2-bis(diethylphosphino)ethane]osmium(II). *cis*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]osmium(II) (0.25 g.) and lithium iodide (1.0 g.) were dissolved in acetone and heated under reflux for 16 hr. to give a white precipitate and a pale yellow solution. Solvent was removed at 15 mm., and the water-insoluble residue crystallised from ethanol in a nitrogen atmosphere to give the pure complex (80% yield) as pale yellow needles, m. p. 221.5—222.5° (slight decomp.); recrystallisation occurs above 225° and the m. p. is then 260—266° (decomp.) (Found: C, 28.3; H, 5.8.  $\text{C}_{20}\text{H}_{48}\text{I}_2\text{OsP}_4$  requires C, 28.05; H, 5.65%).

*Method 4*, *cis*- $[\text{RuCl}_2\{\text{C}_2\text{H}_4(\text{PR}_2)_2\}]_2$  (R = Me, Et). *cis*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]ruthenium(II). *trans*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]ruthenium(II) (0.20 g.) was warmed with triethylaluminium (0.25 ml.) under nitrogen at 60—80° to give a dark red oil. After about 5 min., the oil was well washed with light petroleum to remove excess of triethylaluminium; it was then suspended in light petroleum, and ethanol was added dropwise. A vigorous reaction with effervescence occurred and the oil dissolved to give a pale yellow solution, which deposited crystals on cooling; these were filtered off and crystallisation from benzene containing 50% of light petroleum afford the pure *cis*-isomer (0.15 g., 75%), m. p. 210—213° (Found: C, 40.9; H, 8.2.  $\text{C}_{20}\text{H}_{48}\text{Cl}_2\text{P}_4\text{Ru}$  requires C, 41.1; H, 8.3%). The dimethylphosphino-analogue was similarly prepared in 50% yield.

*Monotertiary Phosphine Complexes*.—*Tri-μ-chlorohexakis(diethylphenylphosphine)diruthenium(II) chloride*. Ruthenium trichloride (12.9 g., 0.062 mole) in water (400 ml.) and diethylphenylphosphine (46.1 g., 0.28 mole) in methanol (1200 ml.) were refluxed together under nitrogen for 24 hr., the colour of the solution changing from black through dark green to clear orange-yellow. When the yellow colour was obtained, the solution was concentrated to about half its original volume and, on cooling, deposited yellow crystals. This product was filtered off and, after being washed with methanol, was sufficiently pure for use as raw material for the preparation of the ditertiary phosphine complexes (yield 32.2 g., 75%). The pure complex was obtained from methanol as canary-yellow needles, m. p. 150—152° [Found: C, 53.4; H, 6.9%; *M* (ebullioscopically in acetone), 822 (0.23% solution), 753 (3.25%).  $\text{C}_{60}\text{H}_{90}\text{Cl}_4\text{P}_6\text{Ru}_2$  requires C, 53.7; H, 6.8%; *M*, 1341]. This compound is diamagnetic in the solid state and has a molar conductivity in nitrobenzene of 23.5  $\text{ohm}^{-1}$  ( $4.6 \times 10^{-3}\text{M}$ ) and in acetone of 116  $\text{ohm}^{-1}$  ( $2.66 \times 10^{-3}\text{M}$ ).

The following complexes were similarly prepared.

*Tri-μ-chlorohexakis(dimethylphenylphosphine)diruthenium(II) chloride dihydrate* separated in 80% yield from methanol as bright yellow crystals, m. p. 118—120° [Found: C, 47.7; H, 5.7%; *M* (ebullioscopically in acetone), 464 (1.04% solution), 484 (1.52%).  $\text{C}_{48}\text{H}_{66}\text{Cl}_4\text{P}_6\text{Ru}_2 \cdot 2\text{H}_2\text{O}$  requires C, 47.7; H, 5.8%; *M*, 1209]. Molar conductivity 26.2  $\text{ohm}^{-1}$  ( $2.04 \times 10^{-3}\text{M}$ ).

*Tri-μ-chlorohexakis(ethylidiphenylphosphine)diruthenium(II) chloride trihydrate* was obtained from methanol as orange crystals (55% yield), m. p. 134.5—135° (decomp.) [Found: C, 59.9; H, 5.7%; *M* (ebullioscopically in acetone), 645 (1.41% solution), 710 (2.21%).  $\text{C}_{84}\text{H}_{90}\text{Cl}_4\text{P}_6\text{Ru}_2 \cdot 3\text{H}_2\text{O}$  requires C, 59.9; H, 5.75%; *M*, 1683.5]. Molar conductivity 17.5  $\text{ohm}^{-1}$  ( $1.72 \times 10^{-3}\text{M}$ ).

*Tri-μ-chlorohexakis(methyldiphenylphosphine)diruthenium(II) chloride trihydrate* separated from ethanol (65% yield) as orange crystals, m. p. 175—178° (decomp.) (Found: C, 58.75; H, 5.4.  $\text{C}_{78}\text{H}_{78}\text{Cl}_4\text{P}_6\text{Ru}_2 \cdot 3\text{H}_2\text{O}$  requires C, 58.6; H, 5.3%). Molar conductivity 21.2  $\text{ohm}^{-1}$  ( $2.82 \times 10^{-3}\text{M}$ ).

*Tri-μ-chlorohexakis(diethylphenylphosphine)diruthenium(II) picrate* was precipitated on treating an ethanolic solution of (I; X = Cl) with aqueous sodium picrate. The complex was filtered off, washed with water, and crystallised twice from aqueous acetone, forming lemon-yellow plates, m. p. 153.5—155° (decomp.) (Found: C, 51.9; H, 6.3; N, 2.8.  $\text{C}_{66}\text{H}_{92}\text{Cl}_3\text{N}_3\text{O}_7\text{P}_6\text{Ru}_2$  requires C, 51.7; H, 6.0; N, 2.75%). Molar conductivity 19.3  $\text{ohm}^{-1}$  ( $1.93 \times 10^{-3}\text{M}$ ). *Tri-μ-chlorohexakis(diethylphenylphosphine)diruthenium(II) perchlorate monohydrate* was precipitated by treating an ethanolic solution of (I; X = Cl) with an excess of

20% perchloric acid; recrystallisation from ethanol afforded the pure complex as yellow needles (70% yield), m. p. 149.5–151° (decomp.) (Found: C, 50.6; H, 6.3.  $C_{60}H_{90}Cl_4O_4Ru_2H_2O$  requires C, 50.6; H, 6.5%). Molar conductivity 24.6  $\text{ohm}^{-1}$  ( $1.9 \times 10^{-3}M$ ).

*Tri-μ-chlorohexakis(diethylphenylphosphine)diruthenium(II) tetraphenylborate* was precipitated on treating an ethanolic solution of (I; X = Cl) in ethanol with 100% excess of ethanolic sodium tetraphenylborate. The precipitate was filtered off and washed with water and ethanol; three crystallisations from acetone afforded the pure complex as yellow microcrystals,

*Dipole moments.*

	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	$\tau^P$	$\epsilon^P$	$\sigma^P$	$\mu$ (D)
<i>trans</i> -[RuCl <sub>2</sub> {C <sub>2</sub> H <sub>4</sub> (PEt <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> ]	3.726	0.521						
	4.671	0.565						
	7.822	0.539		(0.53)	167 *	(133)	14 *	0.85 *
<i>cis</i> -[RuCl <sub>2</sub> {C <sub>2</sub> H <sub>4</sub> (PEt <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> ]	3.090	18.186						
	3.621	17.978						
	4.067	17.985						
	12.33		7.90					
	20.32		9.09					
	4.545			0.572				
	5.277			0.493	2097	132.9	1944	9.75
<i>cis</i> -[RuI <sub>2</sub> {C <sub>2</sub> H <sub>4</sub> (PEt <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> ]	1.873	15.581						
	4.224	15.591						
	7.457		8.24					
	9.600		8.04					
	9.126			0.559	2388	167	2196	10.35
<i>trans</i> -[RuCl <sub>2</sub> {C <sub>2</sub> H <sub>4</sub> (PMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> ]	4.627	0.536						
	7.223	0.543						
	6.492			0.493				
	19.82		7.94					
	25.57		8.37		140	112	11	0.75
<i>trans</i> -[RuCl <sub>2</sub> { <i>o</i> -C <sub>6</sub> H <sub>4</sub> (PEt <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> ]	6.282	0.723						
				(0.35)	217 *	(181)	9.6 *	0.7
<i>cis</i> -[RuCl <sub>2</sub> {CH <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> ]	3.655	11.47						
	5.220	10.88						
				(0.53)	2154 *	(266)	1848 *	9.5 *
<i>cis</i> -[RuCl <sub>2</sub> (PEt <sub>2</sub> Ph) <sub>2</sub> (1,1'-bipyridyl)]	0.982	20.52						
	0.9975	20.77						
				(0.53)	2691 *	(177)	2487 *	11.0 *
<i>cis</i> -[OsCl <sub>2</sub> {C <sub>2</sub> H <sub>4</sub> (PEt <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> ]	1.186	14.44						
	2.398	14.24						
	34.17		7.71					
	44.62		8.06					
	4.296			0.535	1942	150	1770	9.3
<i>cis</i> -[OsCl <sub>2</sub> {C <sub>2</sub> H <sub>4</sub> (PPh <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> ]	1.319	7.649						
	1.441	7.638						
				(0.53)	1716 *	(269)	1407 *	8.3 *

Estimated values are in parentheses. \* Calc. by using estimated values of densities and refractivities.

m. p. 156–159° (decomp.) (Found: C, 1.9; H, 7.15.  $C_{84}H_{110}BCl_3P_6Ru_2$  requires C, 62.1; H, 6.8%).

*Tri-μ-chlorohexakis(diethylphenylphosphine)diruthenium(II) thiocyanate* was precipitated as pale yellow plates (m. p. 160–161°) by mixing cold filtered solutions of (I; X = Cl) in ethanol and potassium thiocyanate (10-fold excess) in water. The complex was filtered off, washed successively with water and ethanol, and dried *in vacuo* (Found: C, 53.45; H, 6.6; N, 1.2.



$C_{61}H_{90}Cl_3NP_6Ru_2S$  requires C, 53.7; H, 6.65; N, 1.0%. Molar conductivity  $27.7 \text{ ohm}^{-1}$  ( $2.04 \times 10^{-3}M$ -solution). The infrared spectrum (Nujol mull) shows a strong band at  $2053 \text{ cm}^{-1}$  attributed to  $\nu_{C\equiv N}$  of the thiocyanate anion. This complex was insoluble in most organic solvents but, in chloroform, it rapidly disproportionated into  $[Ru_2Cl_3(PEt_2Ph)_6]Cl$  (identified by mixed m. p. with an authentic specimen) and an insoluble, unidentified, pale yellow compound (m. p.  $>350^\circ$ , blackening at  $260^\circ$ ) (Found: C, 51.9; H, 6.3; N, 3.1%). Molar conductivity  $3.6 \text{ ohm}^{-1}$  ( $6.9 \times 10^{-4}M$ , for  $M \approx 1450$ ). Its infrared spectrum (Nujol mull) contains bands at  $2117 \text{ cm}^{-1}$  (strong) and at  $2145 \text{ cm}^{-1}$  (medium) attributed to terminal and bridging  $\nu_{C\equiv N}$  respectively.

*Tri- $\mu$ -chlorohexakis(ethylidiphenylphosphine)diosmium(II) chloride dihydrate.* Ethyldiphenylphosphine (7.53 g., 35.0 mmoles) in ethanol (400 ml.) was refluxed with ammonium hexachlorosmate(IV) (3.84 g., 8.75 mmoles) in water (100 ml.) for 6 hr. A dark red precipitate was first obtained, which slowly dissolved to give a greenish-yellow colour and finally a clear orange-yellow solution. Cooling gave yellow crystals (7.51 g., 95%) of crude product, which was obtained pure from ethanol as yellow-orange plates, m. p.  $180$ — $182^\circ$  (decomp.) [Found: C, 54.7; H, 5.2%;  $M$  (ebullioscopically in acetone), 980 (1.07% solution), 955 (1.80%).  $C_{84}H_{94}Cl_4O_2Os_2P_6$  requires C, 54.7; H, 5.1%;  $M$ , 1844]. Molar conductivity  $21.6 \text{ ohm}^{-1}$  ( $2.8 \times 10^{-3}M$ ).

The following compounds were similarly prepared.

*Tri- $\mu$ -chlorohexakis(methyldiphenylphosphine)diosmium(II) chloride* separated in 40% yield from ethanol as bright yellow crystals, m. p.  $185$ — $186^\circ$  (decomp.) (Found: C, 54.2; H, 4.7.  $C_{78}H_{78}Cl_2Os_2P_6$  requires C, 54.4; H, 4.6%). Molar conductivity  $24.4 \text{ ohm}^{-1}$  ( $2.0 \times 10^{-3}M$ ). *Tri- $\mu$ -chlorohexakis(diethylphenylphosphine)diosmium(II) chloride* was isolated in 85% yield from methanol as lemon-yellow needles, m. p.  $178.5$ — $180^\circ$  (decomp.) (Found: C, 47.3; H, 5.9.  $C_{60}H_{90}Cl_4Os_2P_6$  requires C, 47.4; H, 6.0%). Molar conductivity  $20.4 \text{ ohm}^{-1}$  ( $3.8 \times 10^{-3}M$ ).

*Ditertiary Phosphine Complexes of Ruthenium(III).*—*trans-Dichlorodi-[1,2-bis(diethylphosphino)ethane]ruthenium(III) perchlorate.* *trans*-Dichlorodi-[1,2-bis(diethylphosphino)ethane]-ruthenium(III) (0.10 g.) in ethanol (5 ml.) was treated with 20% perchloric acid (2 ml.) to give, on warming, a clear dark green solution. On cooling, dark green crystals separated, which, after crystallisation from ethanol containing a little perchloric acid, afforded the pure *complex* as dark green needles (60%), m. p.  $172$ — $173.5^\circ$  (decomp.) (Found: C, 35.0; H, 7.1; Cl, 15.7.  $C_{20}H_{48}Cl_2O_4P_4Ru$  requires C, 35.1; H, 7.1; Cl, 15.55%). *cis-Dichlorodi-[1,2-bis(diethylphosphino)ethane]ruthenium(III) perchlorate* was similarly prepared in 70% yield from the *cis*-dichloro-isomer as dark green needles, m. p.  $167.5$ — $169.5^\circ$  (decomp.) (Found: C, 34.9; H, 7.1; Cl, 15.7%).

*Dipole Moments.*—These (see Table) were determined as described in ref. 1, where the meanings of the symbols are also given.

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