

**788.** *Complex Compounds of Tertiary Phosphines and a Tertiary Arsine with Rhenium(v), Rhenium(III), and Rhenium(II).*

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The reactions of various tertiary organic phosphines with sodium perhenate or rhenium heptoxide, in the presence of halogen acids and alcohols, are shown to form mainly oxo- and oxoalkoxy-complexes of the types  $[\text{ReOX}_3(\text{PR}_3)_2]$  and  $[\text{ReO}(\text{OR}')\text{X}_2(\text{PR}_3)_2]$  ( $\text{X} = \text{halogen}$ ,  $\text{R} = \text{an organic group}$ ), respectively. A few members of these two series were known but had been incorrectly formulated as  $[\text{ReX}_3(\text{PR}_3)_2]$  and  $[\text{ReX}_2(\text{PR}_3)_2]$ . The above reactions also yield a new type of compound,  $[\text{ReCl}_3(\text{PEt}_2\text{Ph})_2]$ ; and in the presence of hydrazine dihydrochloride, a compound of a further new type,  $[\text{ReCl}_2(\text{PPh}_3)_2]$ , is formed. Preparations involving diethylphenylphosphine and triphenylphosphine are examined in detail. Complexes of other phosphines, including ditertiary phosphines, and of diethylphenylarsine, are briefly examined for comparison, and also a few complexes of rhenium trichloride.

Rhenium(v), like osmium in its higher-valent states, has a pronounced tendency to form multiple bonds to oxygen and, as shown by the preparation of a stable phenylimido-complex,  $[\text{Re}(\text{NPh})\text{Cl}_3(\text{PEt}_2\text{Ph})_2]$ , also to nitrogen. In these oxo- and phenylimido-complexes the Re-O and Re-N bonds both appear to have a bond order greater than 2.

To advance general investigations of low-valent states, and of the hydrido- and organo-complexes of transition metals stabilised by tertiary phosphines, we required a number of complexes of tertiary phosphines with rhenium halides. Little has been published on this subject,<sup>1,2</sup> and when we attempted to repeat what was published it became evident that much of it was in error. This earlier work all concerned complexes of triarylphosphines, mainly triphenylphosphine, which give rather poorly soluble complexes. We have, therefore, made a complete re-investigation of the complexes of tertiary phosphines with rhenium in its common valency states, using as our model diethylphenylphosphine which gives better-crystalline complexes of convenient solubility. In this paper we shall describe the elementary chemistry of the common complexes of diethylphenylphosphine with rhenium(v), rhenium(III), and rhenium(II), and compare it with that of the triphenylphosphine derivatives, which have been re-formulated where necessary, and with that

<sup>1</sup> Freni and Valenti, 17th Internat. Congress Pure Appl. Chem., Munich, 1959, Abs. A1057; *J. Inorg. Nuclear Chem.*, 1961, **16**, 240.

<sup>2</sup> Colton, Levitus, and Wilkinson, *J.*, 1960, 4121.

of tertiary aliphatic phosphine derivatives. We shall also describe analogous complexes derived from diethylphenylarsine and some complexes derived from ditertiary phosphines, *e.g.*,  $\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2$ .

The earlier workers who had investigated the triarylphosphine complexes, where they were in error, had failed to find oxygen in them. It occurs as oxo- and ethoxy-groups attached to rhenium and in one case as triphenylphosphine oxide.<sup>3,4</sup> We detected the oxygen because of the consistently low carbon and hydrogen analyses of our supposed halogeno-complexes, *e.g.*,  $[\text{ReCl}_3(\text{PEt}_2\text{Ph})_2]$  which was found to be  $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ ; in this case carbon was low by about 0.8%. The existence of oxygen was corroborated by oxygen analyses and infrared spectra. Oxygen analysis of compounds containing phosphorus tends, with the present technique, to give high results,<sup>5</sup> but in our experience they are consistently high and can be used to determine beyond doubt the number of oxygen atoms. In the complexes where alkoxy-groups are also present further corroboration was provided by Zeisel analysis.

The infrared spectra have been investigated by Dr. D. M. Adams who finds that complexes containing the Re:O bond have strong absorption in the region 958—985  $\text{cm}^{-1}$ , half-band width 10  $\text{cm}^{-1}$ . This falls within the range (900—1100  $\text{cm}^{-1}$ ) characteristic of metal-oxygen double-bond stretching frequencies.<sup>6</sup> In the complexes containing the group Re:O(OR) where R is methyl, ethyl, methoxyethyl, or benzyl, the Re:O absorption band appears some 20—30  $\text{cm}^{-1}$  lower, in the region 930—958  $\text{cm}^{-1}$ , and there is an additional strong band, half-width  $\sim 30$   $\text{cm}^{-1}$ , in the region 906—917  $\text{cm}^{-1}$ , except in the spectrum of the oxomethoxy-complexes, *e.g.*,  $[\text{ReO}(\text{OMe})\text{Cl}_2(\text{PEt}_2\text{Ph})_2]$ . This additional band may be associated with the  $\text{CH}_2$  part of the OR grouping, probably the  $\text{CH}_2$  rocking mode which occurs in the region 700—1100  $\text{cm}^{-1}$  and is usually intense. Its closeness to  $\nu(\text{Re:O})$  and its absence from the methoxy-complexes renders its previous assignment<sup>3</sup> to a Re—O vibration impossible. Indeed the complex  $[\text{ReO}(\text{OMe})\text{Cl}_2\{\text{P}(\text{CH}_2\text{Cl})_3\}_2]$ , which is particularly clear in the 400—600  $\text{cm}^{-1}$  region, has a band at 500  $\text{cm}^{-1}$  which is very probably caused by the Re—O stretching vibration.

Previous workers have used the following four methods to obtain triphenylphosphine complexes of rhenium and in each case we give one example of the type of complex they claimed to have obtained. (1) Interaction of alkali per-rhenate or rhenium heptoxide with the tertiary phosphine in concentrated hydrochloric acid and ethanol:  $[\text{ReCl}_3(\text{PPh}_3)_2]$ .<sup>1</sup> (2) Interaction of rhenium heptoxide, the tertiary phosphine, and hydrazine dihydrochloride in ethanol:  $[\text{ReCl}_2(\text{PPh}_3)_2]$ .<sup>1</sup> (3) Interaction of rhenium trichloride with the tertiary phosphine in ethanol or acetone:  $[\text{ReCl}_3(\text{PPh}_3)]$ .<sup>1,2</sup> (4) Interaction of  $[\text{ReCl}_3(\text{PPh}_3)]$  in acetone with chlorine in presence of an excess of the phosphine:  $[\text{ReCl}_3(\text{PPh}_3)_2]$ .<sup>2</sup> We have applied these methods, but only method (3) gave products of the type stated, except that a new red complex,  $[\text{ReCl}_2(\text{PPh}_3)_2]$ , was obtained by method (2) under anhydrous conditions only. We obtained no crystalline product by method (4), the product of which has recently been re-formulated<sup>3</sup> as  $[\text{ReCl}_3(\text{OPPh}_3)_2]$ . Reactions (1) and (2) generally yield oxo- and oxoethoxy-complexes of types  $[\text{ReOX}_3(\text{PPh}_3)_2]$  and  $[\text{ReO}(\text{OEt})\text{X}_2(\text{PPh}_3)_2]$  (X = halogen), depending on the reaction conditions.<sup>4</sup>

*Complexes of Diethylphenylphosphine.*—The reactions to be discussed below are somewhat complex and are summarised in Scheme 1, where the letter on each arrow refers to the headed sections below and the figure to the numbered reactions above.

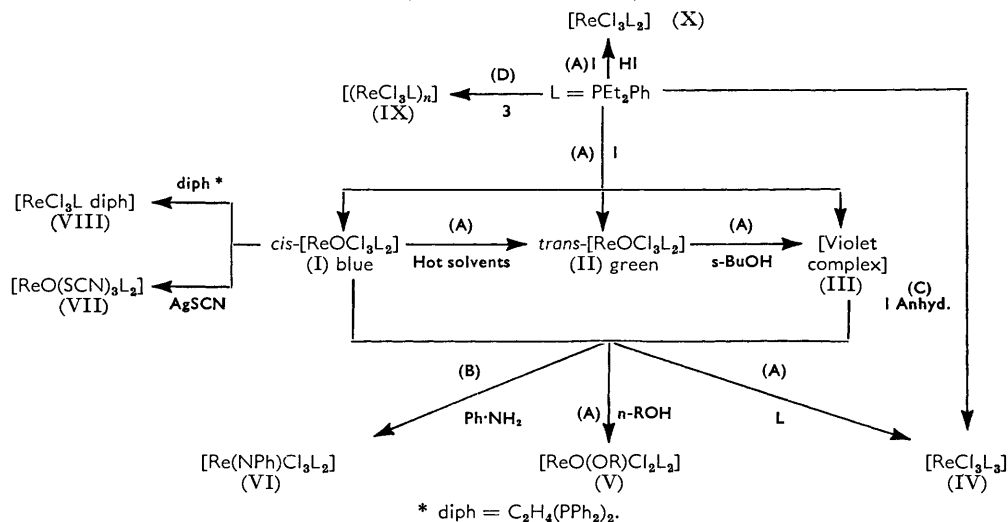
A. *Reaction 1.* With refluxing for several hours this yields a mixture of three complexes, a blue (I), a green (II), and a violet one (III). These have analyses and molecular weights which indicate the formula  $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ . Three octahedral

<sup>3</sup> Lock and Wilkinson, *Chem. and Ind.*, 1962, 40.

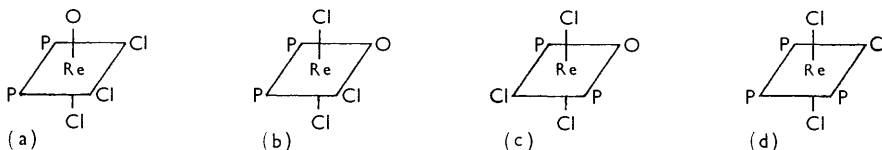
<sup>4</sup> Chatt and Rowe, *Chem. and Ind.*, 1962, 92.

<sup>5</sup> F. H. Oliver, in "Comprehensive Analytical Chemistry," ed. Wilson and Wilson, Elsevier, New York, Vol. IB, 1960, p. 577.

<sup>6</sup> Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

Scheme 1. Preparation and reactions of diethylphenylphosphine complexes.  
(For A,B,1,2 etc., see text.)

isomers (a, b, c) of this formula, are possible: two *cis*-isomers of high dipole moment, and a *trans*-isomer of low moment. The blue complex (I) is a *cis*-isomer of [ReOCl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>2</sub>], as shown by its dipole moment of 10.8 D. The green complex (II) (moment 1.7 D) is the *trans*-isomer (c), and this has been confirmed by complete X-ray structure determination.<sup>7</sup> The violet complex (III) has too low a dipole moment (3.0 D) to be the other *cis*-isomer, and, unlike the blue and the green complex, the solid is paramagnetic ( $\mu_{\text{eff}}$ . 1.92 B.M.).



The best formula appears to be *trans*-[Re(OH)Cl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>2</sub>] because preliminary X-ray results<sup>7</sup> indicate a structure almost identical with that of (II), but there is a strong element of doubt because the infrared spectrum shows a possible Re=O band and no OH absorption. This complex (III) is a non-electrolyte in nitrobenzene.

Complexes (I), (II), and (III) have almost identical infrared spectra. The relative proportions obtained in the preparative reaction are very dependent on the reaction conditions, and the compounds are not reversibly interconvertible. However, the blue *cis*-isomer (I) is readily converted into the green *trans*-isomer (II) in hot solvents and this into the violet complex (III) in boiling butan-2-ol. All three give the same product [ReCl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>3</sub>] (IV) when boiled in ethanolic solution with an excess of the phosphine; the time for completion of this reaction depends on the complex, as follows: blue, 20 min., green, 5 min., violet, 5 hr. All three complexes also react with boiling ethanol, to give a diamagnetic product of the formula [ReO(OR)Cl<sub>2</sub>(PEt<sub>2</sub>Ph)<sub>2</sub>] (V; R = Et); this reaction is general and corresponding compounds were obtained from methyl, benzyl, and 2-methoxyethyl alcohol. The oxoethoxy-product from (II) is a mixture of isomers which have not yet been fully characterised, and the reactions of these substances are still under investigation.

<sup>7</sup> Ehrlich and Owston, personal communication.

When hydriodic acid is used in place of hydrochloric acid in reaction 1, only *cis*-[ReOI<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>2</sub>] (X) is obtained, with no evidence of other isomers.

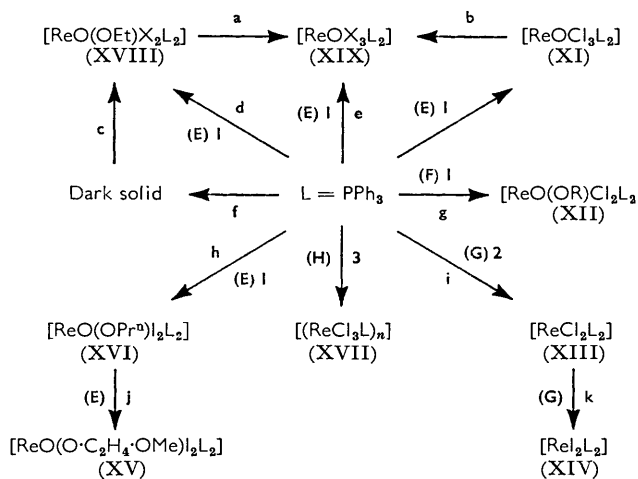
B. An attempt to obtain similar oxophenylamido-complexes by treating each of the three compounds, (I), (II), and (III), with aniline in benzene produced instead a phenylimido-complex [Re(NPh)Cl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>2</sub>] (VI). It seems that the tendency of rhenium to form double bonds to first-row elements is not limited to oxygen, and that rhenium, like its neighbour osmium, forms multiple bonds to nitrogen rather easily.

C. *Reaction 1*. Under anhydrous conditions this reaction yields complex (IV). From its dipole moment (6.3 D) this must have configuration (d).

D. *Reaction 3*. In ethanol, this gave material [{ReCl<sub>3</sub>(PEt<sub>2</sub>Ph)}<sub>n</sub>], poorly soluble in all solvents and probably a polymer linked through chlorine bridges.

*Complexes of Triphenylphosphine.*—The formation of the complexes of this phosphine and some of their reactions are summarised in Scheme 2. This phosphine differs from diethylphenylphosphine in forming no stable isomeric complexes or anything corresponding to the violet complex discussed above; nor were we able to obtain a product [ReCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>], analogous to (IV), by reaction 1. On the other hand, we have obtained by this reaction two members of a new series of complexes [ReX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (X = Cl or I).

Scheme 2. Preparation and reactions of triphenylphosphine complexes.  
(For E, F, I, 2, etc., see text.)



(a) HBr, where X = Br. (b) AgSCN, where X = SCN. (c) EtOH-C<sub>6</sub>H<sub>6</sub>. (d) HI (where X = I), HBr (where X = Br). (e) HBr in COMe<sub>2</sub> or AcOH, where X = Br. (f) K<sub>2</sub>ReI<sub>6</sub>, COMe<sub>2</sub>. (g) Anhyd., where R = Et. (h) Pr<sup>n</sup>OH-HI. (i) Anhyd. (j) MeO-C<sub>2</sub>H<sub>4</sub>-OH. (k) NaI.

E. *Reaction 1*. Reaction as described in paragraph A gave only a yellow complex [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (XI). This has a small dipole moment (2.5 D) and its molecule has a two-fold axis of symmetry (*X*-rays).<sup>8</sup> It must, therefore, be the *trans*-isomer of configuration (c) corresponding to the green complex (II) of diethylphenylphosphine. It is very similar to the yellow substance, m. p. 220° (decomp.), obtained by Freni and Valenti<sup>1</sup> by the same reaction, but they formulated it as [ReCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>]. We have been unable to obtain any oxygen-free complex by this reaction. It seems certain that their complex [ReCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] is identical with our (XI), but incorrectly formulated.

When concentrated hydrobromic or hydriodic acid is used in place of hydrochloric acid

<sup>8</sup> J. M. Rowe, personal communication.

in this reaction, a grey diamagnetic oxoethoxy-complex  $[\text{ReO}(\text{OEt})\text{X}_2(\text{PPh}_3)_2]$  (XVIII; X = Br) results instead of an oxo-compound of type (XI). The iodo-complex (XVIII; X = I) is also obtained, on recrystallisation from benzene-ethanol of the dark product which results when  $\text{K}_2\text{ReI}_6$  reacts with triphenylphosphine in acetone. Freni and Valenti claim to have obtained substances of composition  $[\text{ReX}_2(\text{PPh}_3)_2]$  (X = Br, I) by the above two reactions. When reaction 1 is carried out in propan-1-ol with hydriodic acid, a substance  $[\text{ReO}(\text{OPr}^n)\text{I}_2(\text{PPh}_3)_2]$  (XVI) is obtained and this, like  $[\text{ReO}(\text{OEt})\text{I}_2(\text{PPh}_3)_2]$ , on recrystallisation from 2-methoxyethanol gives  $[\text{ReO}(\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{OMe})\text{I}_2(\text{PPh}_3)_2]$  (XV), showing the very ready exchange of alkoxy-groups.

The oxo-complex *trans*- $[\text{ReOBr}_3(\text{PPh}_3)_2]$  (XIX; X = Br) is obtained in the above reaction when glacial acetic acid or acetone is used as reaction medium in place of ethanol, even at room temperature. It is also obtained by the action of hydrobromic acid on the ethoxy-complex (XVIII; X = Br).

F. *Reaction 1*. Under anhydrous conditions, this gives an oxoethoxy-complex  $[\text{ReO}(\text{OEt})\text{Cl}_2(\text{PPh}_3)_2]$  (XII), and in this contrasts with the reaction of diethylphenylphosphine which gives the oxygen-free complex (IV) under these conditions. The oxoethoxy-complex is more conveniently obtained by treating the oxo-complex  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  (XI) with boiling ethanol. Similarly, by using methyl or benzyl alcohol, the corresponding methoxy- and the benzyloxy-complex are obtained.

G. *Reaction 2*. This gives no complex when water is present, but under anhydrous conditions a red complex  $[\text{ReCl}_2(\text{PPh}_3)_2]$  (XIII) is obtained. Reaction with sodium iodide gives the corresponding iodo-complex,  $[\text{ReI}_2(\text{PPh}_3)_2]$  (XIV). These two compounds differ completely in their physical properties from the compounds to which Freni and Valenti have assigned the compositions  $[\text{ReX}_2(\text{PPh}_3)_2]$  (X = Cl, I).

H. *Reaction 3*. This gives a sparingly soluble, probably polymeric, complex  $\{[\text{ReCl}_3(\text{PPh}_3)]_n\}$  (XVII), identical with that previously described.<sup>1,2</sup>

*Complexes of Other Tertiary Phosphines.*—Trialkylphosphines have been examined in less detail. Triethylphosphine by reaction 1 gives both a blue *cis*- and a green *trans*- $[\text{ReOCl}_3(\text{PR}_3)_2]$  (XX and XXI, respectively; R = Et), the former in very poor yield. The *cis*-isomer of the corresponding tri-*n*-propylphosphine complexes seems to be even less stable, because only the green *trans*-isomer (XXI; R = Pr<sup>n</sup>) has been isolated from the products of reaction 1. Generally, the reactions with the purely aliphatic phosphines are much slower than with diethylphenyl- and triphenyl-phosphine; also the yields are lower. These differences appear to be effects of the electronegativity of the groups attached to the phosphorus since tri(chloromethyl)phosphine reacts much more rapidly than the trialkylphosphines but slower than the triarylphosphines, to give a normal product,  $[\text{ReOCl}_3\{\text{P}(\text{CH}_2\text{Cl})_3\}_2]$  (XXII). Ethyldiphenylphosphine by reaction 1, unlike all the other phosphines studied, gives the oxoethoxy-complex  $[\text{ReO}(\text{OEt})\text{Cl}_2(\text{PEtPh}_2)_2]$  (XXIV) directly. In this it behaves in an analogous manner to triphenylphosphine in reaction 1 with hydrobromic and hydriodic acid. Di-*n*-propylphenylphosphine, by reaction 1 in 2-methoxyethanol, gave the analogous compound  $[\text{ReO}(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OMe})\text{Cl}_2(\text{PPr}^n_2\text{Ph})_2]$  (XXV).

1,2-Bisdiphenylphosphinoethane, by reaction 1 in propanol (which is necessary for solubility) gives the expected oxo-complex  $[\text{ReOCl}_3(\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2)]$  (XXVI) when the diphosphine is in relatively low proportion (1.75 mol.). This must of necessity have a *cis*-configuration of the phosphorus atoms about the metal, and its blue colour corroborates our assignment of *cis*-configurations to the blue isomers of the corresponding complexes of the mono-phosphines. An attempt to obtain this product (XXVI) from *cis*- $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$  by reaction with the diphosphine yielded instead a material  $[\text{ReCl}_3(\text{PEt}_2\text{Ph})(\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2)]$  (VIII) (Scheme 1).

Use of a high molar proportion (6 mol.) of the diphosphine in propanol yields the oxygen-free complex salt  $[\text{ReCl}_2(\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2)_2]\text{Cl}$  (XXVIII) which on reduction with sodium borohydride gives a product  $[\text{ReCl}_2(\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2)_2]$  (XXIX).

TABLE I.

Compound	Number	Colour	M. p. (decomp.)	$\nu(\text{Re}=\text{O})$ ( $\text{cm}^{-1}$ )	$\delta(\text{OCH}_2)$ ( $\text{cm}^{-1}$ )
<i>Oxo-complexes.</i>					
<i>cis</i> - $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ .....	I	Blue	157—160°	977vs	—
<i>trans</i> - $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ .....	II	Green	166—169	978vs	—
<i>trans</i> - $[\text{Re}(\text{OH})\text{Cl}_3(\text{PEt}_2\text{Ph})_2]$ * .....	III	Violet	164—166	978vs *	—
<i>cis</i> - $[\text{ReOI}_3(\text{PEt}_2\text{Ph})_2]$ .....	X	Brown	171.5—174	976vs	—
$[\text{ReO}(\text{SCN})_3(\text{PEt}_2\text{Ph})_2]$ .....	VII	Brown	138—142	964vs	—
<i>trans</i> - $[\text{ReOCl}_3(\text{PPh}_3)_2]$ .....	XI	Yellow	211—214	969s	—
<i>trans</i> - $[\text{ReOBr}_3(\text{PPh}_3)_2]$ .....	XIX; X = Br	Yellow	181—183	980vs	—
$[\text{ReO}(\text{SCN})_3(\text{PPh}_3)_2]$ .....	XIX; X = SCN	Brown	132—136	958vs	—
<i>cis</i> - $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ .....	XX; R = Et	Blue	126—129	982vs	—
<i>trans</i> - $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ .....	XXI; R = Et	Green	164—174	973vs	—
<i>trans</i> - $[\text{ReOCl}_3(\text{PPr}^n)_2]$ .....	XXI; R = Pr <sup>n</sup>	Green	130—134	985vs	—
$[\text{ReOCl}_3\{\text{P}(\text{CH}_2\text{Cl})_3\}_2]$ .....	XXII	Red	156—161	975m	—
$[\text{ReOCl}_3\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}]$ .....	XXVI	Blue	257—262	976vs	—
$[\text{ReOCl}_3\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}]$ .....	XXX	Blue	240—243	984vs	—
$[\text{ReOCl}_3(\text{AsEt}_2\text{Ph})_2]$ .....	XXXI	Turquoise	120—122	978vs	—
<i>Oxoalkoxy-complexes.</i>					
$[\text{ReO}(\text{OMe})\text{Cl}_2(\text{PEt}_2\text{Ph})_2]$ .....	V; R = Me	Violet	132—136	937vs	—
$[\text{ReO}(\text{OEt})\text{Cl}_2(\text{PEt}_2\text{Ph})_2]$ .....	V; R = Et	Violet	135—139	951ms	916vs
$[\text{ReO}(\text{OCH}_2\text{Ph})\text{Cl}_2(\text{PEt}_2\text{Ph})_2]$ ...	V; R = CH <sub>2</sub> Ph	Violet-purple	168—172	935vs	906w-m
$[\text{ReO}(\text{OMe})\text{Cl}_2(\text{PPh}_3)_2]$ .....	XII; R = Me	Grey	200—203	946vs	—
$[\text{ReO}(\text{OEt})\text{Cl}_2(\text{PPh}_3)_2]$ .....	XII; R = Et	Grey	199—203	946ms	909vs
$[\text{ReO}(\text{OCH}_2\text{Ph})\text{Cl}_2(\text{PPh}_3)_2]$ .....	XII; R = CH <sub>2</sub> Ph	Grey	178—182	943vs	909m
$[\text{ReO}(\text{OEt})\text{Br}_2(\text{PPh}_3)_2]$ .....	XVIII; X = Br	Grey-brown	147—149	940m	909vs
$[\text{ReO}(\text{OEt})\text{I}_2(\text{PPh}_3)_2]$ .....	XVIII; X = I	Green	155—165	946ms	909vs
$[\text{ReO}(\text{OPr}^n)\text{I}_2(\text{PPh}_3)_2]$ .....	XVI	Olive green	150—160	921vs †	921vs †
$[\text{ReO}(\text{OC}_2\text{H}_4\text{OMe})\text{I}_2(\text{PPh}_3)_2]$ .....	XV	Olive green	153—159	932vs	918 ‡
$[\text{ReO}(\text{OMe})\text{Cl}_2\{\text{P}(\text{CH}_2\text{Cl})_3\}_2]$ .....	XXIII	Purple	138—142	943vs	—§
$[\text{ReO}(\text{OEt})\text{Cl}_2(\text{PEt}_2\text{Ph})_2]$ .....	XXIV	Purple	163—167	942ms	913vs
$[\text{ReO}(\text{OC}_2\text{H}_4\text{OMe})\text{Cl}_2(\text{PPr}^n)_2]$ .....	XXV	Lilac	159—162	958s	917vs
$[\text{Re}(\text{NPh})\text{Cl}_3(\text{PEt}_2\text{Ph})_2]$ .....	VI	Green	197—200	—	—
<i>Rhenium(III) complexes.</i>					
$\{[\text{ReCl}_3(\text{PEt}_2\text{Ph})]_n\}$ .....	IX	Dull purple	> 350	—	—
$[\text{ReCl}_3(\text{PEt}_2\text{Ph})_2]$ .....	IV	Orange	163—166	—	—
$\{[\text{ReCl}_3(\text{PPh}_3)]_n\}$ .....	XVII	Purple	208—210	—	—
$[\text{ReCl}_3(\text{PEt}_2\text{Ph})\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}]$ ...	VIII	Yellow	194—196	—	—
$[\text{ReCl}_2\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}_2\text{Cl}]$ .....	XXVIII	Yellow	219—220	—	—
<i>Rhenium(II) complexes.</i>					
$[\text{ReCl}_2(\text{PPh}_3)_2]$ .....	XIII	Brick red	219—221	—	—
$[\text{ReI}_2(\text{PPh}_3)_2]$ .....	XIV	Dull reddish brown	178—180	—	—
$[\text{ReCl}_2\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}_2]$ .....	XXIX	Yellow	225	—	—

\* Formula and assignment uncertain (see text). † Broad unsymmetrical band probably including both  $\nu(\text{Re}=\text{O})$  and  $\delta(\text{OCH}_2)$ . ‡ Shoulder on  $\text{Re}=\text{O}$  band. § Band at 500  $\text{cm}^{-1}$  probably  $\nu(\text{Re}=\text{O})$ .

Analogous oxygen-free complexes derived from tertiary arsines have already been described.<sup>9</sup>

1,2-Bisdiethylphosphinoethane undergoes reaction 1 rather slowly, as do the aliphatic monophosphines, and gives a blue oxo-complex,  $[\text{ReOCl}_3(\text{Et}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PEt}_2)]$  (XXX).

*Tertiary Monoarsine Complex.*—Diethylphenylarsine, like its phosphorus analogue, gives an oxo-complex by reaction 1, namely,  $[\text{ReOCl}_3(\text{AsEt}_2\text{Ph})_2]$  (XXXI). This has a turquoise colour and appears to be a mixture of a greenish-blue and a green complex. These are probably *cis*- and *trans*-isomers analogous to the compounds (I) and (II), but attempts at complete separation failed, possibly because the isomers are too labile in solution. Partial separation appears to be possible, because the dipole moment of the

<sup>9</sup> Curtis, Ferguson, and Nyholm, *Chem. and Ind.*, 1958, 625.

complex in benzene solution varies with time. The high final apparent dipole moment (8.0 D) indicates a considerable proportion of the *cis*-isomer in the equilibrium mixture.

*Summary.*—The rhenium complexes prepared in this work have been listed in Table 1, together with characteristic properties, and their dipole moments in Table 2. The thiocyanates, obtained from the corresponding chlorides by reaction with silver thiocyanate, are structurally thiocyanates, as indicated by infrared absorption bands in the region 730  $\text{cm}^{-1}$ , assignable to the carbon sulphur bond.<sup>10</sup>

## DISCUSSION

This work confirms the existence of at least three classes of complex of tertiary monophosphines with rhenium halides, namely,  $[(\text{ReX}_3\text{PR}_3)_n]$  (A),  $[\text{ReX}_3(\text{PR}_3)_3]$  (B), and  $[\text{ReX}_2(\text{PR}_3)_2]$  (C) and provides the first definitely proved examples of types B and C. The series A is the best established and since the known complexes in this series are very poorly soluble they probably exist in the solid as halogen-bridged polymers containing octahedrally co-ordinated rhenium(III). The series B is known by only one member,  $[\text{ReCl}_3(\text{PEt}_2\text{Ph})_3]$ , of configuration (d). The members of series C, having  $\text{X} = \text{Cl}$  and I, are derived from triphenylphosphine. These are diamagnetic solids with poor solubility in organic solvents. Since the monomeric  $[\text{ReX}_2(\text{PPh}_3)_2]$  would probably be paramagnetic the low solubility and diamagnetism suggest some polymeric structure with Re-Re bonds for the solids. In boiling benzene and chloroform solutions they are monomeric, but the solubilities in the cold are too low to allow reliable magnetic measurements on our micro-Faraday balance. In benzene solution they have definite but small dipole moments, suggesting very flattened tetrahedral, almost *trans*-planar structures, or the existence of a slight equilibrium concentration of a *cis*-isomer in the solution of the *trans*. In our experience it is usual for the dipole moments of unsymmetrical halogeno-complexes of Group VIII and related metals, *e.g.*, *cis*- $[\text{PtX}_2(\text{PR}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), to increase on passing from chloride to iodide except when this increase is masked by isomerisation of the iodide to a less dipolar isomer. In the rhenium compounds this appears to be reversed (see Table 2). Thus, the iodide has a flatter molecule than the chloride in solution, or if there is a spontaneous equilibration of the planar rhenium(II) complexes it lies more to the side of the *trans*-isomer in the iodide.

In addition to the above complexes of rhenium halides two new series of oxo- and oxoalkoxy-complexes have been established,  $[\text{ReOX}_3(\text{PR}_3)_2]$  (D) and  $[\text{ReO}(\text{Oalk})\text{X}_2(\text{PR}_3)_2]$  (E). These are new types of tertiary phosphine complexes, and somewhat unexpected in view of the high affinity of phosphorus for oxygen, although the formation of oxo- and hydroxy-complexes of rhenium(v) with less strongly reducing ligands is not uncommon. Thus, ethylenediamine (en) and pyridine (py) form complexes of the types  $[\text{ReO}_2\text{en}_2]\text{Cl}$ ,  $[\text{ReO}(\text{OH})\text{en}_2]\text{Cl}_2$ ,  $[\text{Re}(\text{OH})_2\text{en}_2]\text{Cl}_3$ , and  $[\text{ReO}_2\text{py}_4]\text{Cl}$ .<sup>11</sup> Biguanidine<sup>12</sup> (BigH) forms complexes  $[\text{ReO}(\text{OH})(\text{BigH})_2](\text{OH})_2$  and  $[\text{ReO}_2(\text{BigH})_2]^+$ , and diphenylcarbazone<sup>13</sup> (DpcH),  $[\text{Re}(\text{OH})_2\text{Cl}_2(\text{Dpc})]$ . Oxocyno-complexes of the type  $\text{K}_3[\text{ReO}_2(\text{CN})_4]$  were investigated quite early in the history of rhenium chemistry,<sup>14</sup> and recently some similar thiocyanato-complexes  $\text{K}_3[\text{ReO}_2(\text{SCN})_4]$  have been reported.<sup>15</sup>

The literature contains references to three other classes of tertiary phosphine complex of rhenium halides, represented by two isomers of  $[\text{ReCl}_3(\text{PPh}_3)_2]$ <sup>1,2</sup> and a series of formula  $[\text{ReX}_2(\text{PPh}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), supposedly of *cis*-planar configuration.<sup>1</sup> It has been

<sup>10</sup> Turco and Pecile, *Nature*, 1961, **191**, 66; Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

<sup>11</sup> Lebedinskii and Ivanov-Emin, *Zhur. obshchei Khim.*, 1943, **13**, 253; *Zhur. neorg. Khim.*, 1959, **4**, 1762.

<sup>12</sup> M. M. Ray and P. Ray, *Science and Culture*, 1959, **25**, 384.

<sup>13</sup> Daftary and Haldar, *J. Indian Chem. Soc.*, 1960, **37**, 803.

<sup>14</sup> Klemm and Frischmuth, *Z. anorg. Chem.*, 1937, **230**, 215.

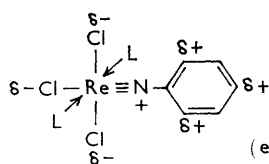
<sup>15</sup> Ryabchikov, Zarinskii, and Nazarenko, *Zhur. neorg. Khim.*, 1961, **6**, 641.

shown beyond doubt that the supposed isomers of  $[\text{ReCl}_3(\text{PPh}_3)_2]$  were incorrectly formulated, one being the rhenium oxo-complex (XI) and the other a phosphine oxide complex.<sup>3</sup>

The substances *cis*- $[\text{ReX}_2(\text{PPh}_3)_2]$  ( $\text{X} = \text{Cl}, \text{I}$ )<sup>1</sup> bear no resemblance to our complexes (XIII and XIV) of those formulæ, and our attempts to repeat Freni and Valenti's preparations of them have given the complexes  $[\text{ReO}(\text{OEt})\text{X}_2(\text{PPh}_3)_2]$ . These oxoethoxy-complexes have physical properties similar to those ascribed by Freni and Valenti to their *cis*- $[\text{ReX}_2(\text{PPh}_3)_2]$ , but it is not certain that the two series are identical. There is one important discrepancy: Freni and Valenti describe their complexes as diamagnetic in the solid state, but paramagnetic ( $\mu = 1.7$  B.M.) in chloroform solution, whereas the oxoethoxy-complexes are diamagnetic in the solid state and in solution. There are other slight but significant discrepancies. Freni and Valenti's compounds cannot, nevertheless, be *cis*-isomers corresponding to our new series  $[\text{ReX}_2(\text{PPh}_3)_2]$  because the dipole moments which they report to be 3.3 D for all three compounds are much too low. Values nearer to 10 D would be expected for such a series of *cis*-isomers. The reported values could point only to tetrahedral configurations, or equilibria of planar *cis*- and *trans*-isomers. Neither of these is compatible with the existence of our new compounds  $[\text{ReX}_2(\text{PPh}_3)_2]$  of essentially *trans*-planar configurations. We conclude that, in spite of the slight discrepancies in reported properties, the compounds  $[\text{ReO}(\text{OEt})\text{X}_2(\text{PPh}_3)_2]$  and Freni and Valenti's *cis*- $[\text{ReX}_2(\text{PPh}_3)_2]$  are probably identical.

Essentially octahedral configurations have been ascribed to the above rhenium(v) and rhenium(III) complexes (classes A, B, D, and E). All are diamagnetic and the rhenium atom contains insufficient electrons to allow any symmetrical filling of the *d*-orbitals by electron pairs. It would be expected, therefore, that, apart from the usual distortion from the ideal octahedral shape owing to the inequality of the ligands, distortions will occur owing to the dissymmetrical filling of the *d*-shell, and distorted rather than regular octahedra are to be expected throughout these series of complexes.

The rhenium complexes afford valuable material for the study of multiple bonding between atoms such as oxygen or nitrogen and a transition metal. In the octahedral rhenium(v) complex, *e.g.*,  $[\text{ReOCl}_3(\text{PR}_3)_2]$ , only one of the three non-bonding *d*-orbitals is needed to accommodate the two paired *d*-electrons and two *d*-orbitals remain for multiple bonding ( $d_\pi-p_\pi$ ) to the oxygen atom. If the Re-O bond defines the *x*-co-ordinate these would be the  $d_{xy}$ - and the  $d_{xz}$ -orbital. Thus the Re-O bond, although written as a formal double bond, may have some triple bond character similar to that of the C=O bond in carbon monoxide. The oxygen in the complexes would thus become less negatively charged than its electronegativity would suggest, owing to mesomeric withdrawal of the  $p_y$  and  $p_z$  lone pairs into the rhenium atom. It may even approach electrical neutrality and the dipole moments of the compounds *trans*- $[\text{ReOCl}_3(\text{PR}_3)_2]$  (c) would be largely due to the Re-Cl bond *trans* to the Re=O bond, *i.e.*, the oxygen would lie at the positive end of the Cl-Re-O dipole. In corresponding phenylimido-complexes  $[\text{ReCl}_3(\text{NPh})(\text{PR}_3)_2]$  the less electronegative nitrogen should donate its electrons even more readily into the



(L =  $\text{PEt}_2\text{Ph}$ )

rhenium atom, and the nitrogen may even become positively charged, so withdrawing electrons from the phenyl group. In this way a small positive charge in the phenyl group could make a disproportionately high contribution to the dipole moment because of its rather great distance from the negative charge on the *trans*-chlorine [see (e)].

This seems the only way to account for the rather high dipole moment of  $[\text{Re}(\text{NPh})\text{Cl}_3(\text{PEt}_2\text{Ph})_2]$  (6.0 D) as compared with  $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$  (1.7 D). A *cis*-arrangement of the tertiary phosphine ligands as in (b; O = NPh) would require a very high moment (8–11 D) and is not a possible alternative explanation. Work is proceeding to find the direction of the bond moments in these compounds and probable orders of Re-O and Re-N bonds.



## EXPERIMENTAL

M. p.s were determined on a Kofler hot-stage and are corrected.

Rhenium trichloride was made from rhenium metal through the pentachloride; <sup>16</sup> potassium hexaiodorhenate, K<sub>2</sub>ReI<sub>6</sub>, was prepared by the method of Briscoe, Robinson, and Rudge.<sup>17</sup> The following reactions are grouped according to the type of compound produced in the reaction and under each type according to the tertiary phosphine, or arsine, in the complex; all the reactions were carried out under nitrogen. The following compounds are in the same order as in Table 1 which provides a key to the Roman numerals.

*Oxo-complexes.*—*cis-Oxotrichlorobisdiethylphenylphosphinerhenium(v)* (I). (a) A mixture of potassium per-rhenate (9.7 g.), diethylphenylphosphine (34.6 g.), concentrated hydrochloric acid (50 c.c.), and ethanol (2.5 l.) was boiled for 3½ hr., evaporated to a quarter of its original volume, and allowed to cool. The solid was removed and washed successively with ethanol, water, and ethanol, then dried *in vacuo*. The product (9.9 g.) was a mixture of a violet and a blue substance from which the violet was extracted by vigorous agitation with cold benzene (200 c.c.) and the blue residue was washed with benzene (200 c.c.). Dilution of the violet filtrates with light petroleum (135 c.c.; b. p. 40–60°) gave a further quantity of the blue compound. The combined blue residues (4.7 g.) recrystallised from chloroform–cyclohexane as needles of *compound* (I) [Found: C, 37.6; H, 4.8; O, 3.0%; *M*, (ebullioscopic in 0.973% chloroform solution) 601, (*X*-ray) 642 ± 6. C<sub>20</sub>H<sub>30</sub>Cl<sub>3</sub>OP<sub>2</sub>Re requires C, 37.5; H, 4.7; O, 2.5%; *M*, 641]. Crystal data: monoclinic prismatic; *a* = 10.00 ± 0.02, *b* = 16.57 ± 0.03, *c* = 15.45 ± 0.03 Å; β = 106.4° ± 0.1°; *U* = 2455 Å<sup>3</sup>; *D*<sub>m</sub> = 1.74 g. cm.<sup>-3</sup> (by flotation); *Z* = 4; space group, *P*2<sub>1</sub>/*c* (*C*<sub>2h</sub><sup>5</sup> No. 14). The molecular weight was determined in chloroform and not in benzene solution, because isomerisation occurred in the latter. The complex was non-conducting in nitrobenzene and the solid was diamagnetic at 20°.

(b) Repetition of the above reaction but with the mixture sodium per-rhenate (9.0 g.), diethylphenylphosphine (36.0 g.), concentrated hydrochloric acid (40 c.c.), and ethanol (500 c.c.), and boiling for 4 hr., then concentrating to one-third of its volume with subsequent cooling, gave a better yield of violet-blue product (11.3 g.), but less of the *cis*-isomer (2.1 g.).

*trans-Oxotrichlorobisdiethylphenylphosphinerhenium(v)* (II). (a) The *cis*-isomer (0.5 g.) was heated to the b. p. in 2-ethoxyethanol (5 c.c.). The resultant green solution, on cooling, deposited green crystals (0.27 g.) of *complex* (II) which were washed with ethanol, dried, and recrystallised from benzene–light petroleum (b. p. 40–60°) [Found: C, 37.7; H, 4.8; O, 2.8%; *M*, (ebullioscopic in 0.534% benzene solution) 619, (in 0.927% benzene solution) 629, (*X*-ray) 651 ± 6.] Crystal data: monoclinic prismatic; *a* = 13.05 ± 0.02, *b* = 7.83 ± 0.01, *c* = 23.90 ± 0.03 Å; β = 91.5 ± 0.1°; *U* = 2441 Å<sup>3</sup>; *D*<sub>m</sub> = 1.77 g. cm.<sup>-3</sup> (by flotation); *Z* = 4; space group, *P*2<sub>1</sub>/*c* (*C*<sub>2h</sub><sup>5</sup> No. 14). The complex was a non-conductor in nitrobenzene, and the solid was diamagnetic at 20°.

(b) The mother-liquors of preparation (b) of the *cis*-isomer (I) were set aside and then filtered from a small amount (0.25 g.) of violet complex (III). Precipitation of the green *trans*-isomer then started and continued for 24 hr. (yield, 4.6 g. of crude product).

*Violet complex* (III). (a) The violet benzene–light petroleum mother-liquor from preparation (a) of the *cis*-isomer (I) was concentrated to one-fifth, and solid was precipitated with an equal volume of light petroleum (b. p. 40–60°). The precipitate (4.9 g.), washed with light petroleum (b. p. 40–60°), dried, and recrystallised from benzene–light petroleum, gave violet needles of *complex* (III) (Found: C, 37.6; H, 4.7; O, 3.5; Cl, 16.4%; *M*, (ebullioscopic in 0.808% benzene solution) 629, (*X*-ray) 647 ± 6]. Crystal data: monoclinic prismatic; *a* = 13.13 ± 0.02, *b* = 7.80 ± 0.01, *c* = 24.13 ± 0.03 Å; β = 91.3 ± 0.1°; *U*, 2470 Å<sup>3</sup>; *D*<sub>m</sub> = 1.74 g. cm.<sup>-3</sup> (by flotation); *Z* = 4; space group, *P*2<sub>1</sub>/*c* (*C*<sub>2h</sub><sup>5</sup> No. 14). The complex was non-conducting in nitrobenzene and the solid was paramagnetic (*μ*<sub>eff</sub> = 1.92 at 20°).

(b) A solution of the *cis*-oxotrichlorobis(diethylphenylphosphine)rhenium(v) (0.3 g.) in butan-2-ol (25 c.c.) was refluxed for 3 hr., during which the blue solution became green and then violet. On cooling, the solution deposited mainly violet, but also some blue, crystals. The soluble violet compound (III) was removed with cold benzene and precipitated (0.2 g.) from the

<sup>16</sup> Hurd and Brimm, *Inorganic Synth.*, 1939, 1, 180, 182.

<sup>17</sup> Briscoe, Robinson, and Rudge, *J.*, 1931, 3218.

benzene solution by addition of light petroleum (b. p. 40–60°) (Found: C, 37.7; H, 4.8; O, 2.75. Calc. for  $C_{20}H_{30}Cl_3OP_2Re$ : C, 37.5; H, 4.7; O, 2.5%). Its identity was shown by its infrared spectrum and by X-ray single-crystal photographs.

*cis-Oxotri-iodobisdiethylphenylphosphinerhenium(v)* (X). Sodium per-rhenate (0.273 g.), diethylphenylphosphine (1.74 g.), and concentrated hydriodic acid (5 c.c.) in ethanol (50 c.c.) were boiled under reflux for 6½ hr., evaporated to ca. 30 c.c., and allowed to cool, so depositing a light brown solid (0.74 g.) which, recrystallised from chloroform–light petroleum (b. p. 60–80°), afforded needles of *compound* (X) (Found: C, 26.1; H, 3.2.  $C_{20}H_{30}I_3OP_2Re$  requires C, 26.2; H, 3.3%).

*Oxotriithiocyanatobisdiethylphenylphosphinerhenium(v)* (VII). *cis*-Oxotrichlorobis(diethylphenylphosphine)rhenium(v) (0.5 g.) and silver thiocyanate (1 g.) in ethanol suspension (25 c.c.) were refluxed for 1½ hr., allowed to cool to ca. 40°, and filtered. Overnight, the filtrate deposited brown crystals which, recrystallised from methanol, gave needles of *compound* (VII),  $\nu(S-C)$  739  $cm^{-1}$  (Found: C, 39.0; H, 4.4; N, 5.8.  $C_{23}H_{30}N_3OP_2ReS_3$  requires C, 39.0; H, 4.3; N, 5.9%).

*trans-Oxotrichlorobistriphenylphosphinerhenium(v)* (XI). Triphenylphosphine (9 g.) in hot ethanol (50 c.c.) was added to a mixture of sodium per-rhenate (1.65 g.), concentrated hydrochloric acid (10 c.c.), and ethanol (50 c.c.) boiling under reflux. A yellow solid was precipitated immediately. The boiling was continued for ½ hr., then the precipitate was removed, washed with ethanol, dried, and recrystallised from benzene–light petroleum (b. p. 100–120°), to give prisms (3.9 g.) of *compound* (XI) [Found: C, 51.75; H, 3.8; O, 2.2%; *M*, (ebullioscopic in 0.912% benzene solution) 867, (X-ray)  $841 \pm 8$ .  $C_{36}H_{30}Cl_3OP_2Re$  requires C, 51.9; H, 3.6; O, 1.9%; *M*, 833.2). Crystal data: monoclinic prismatic;  $a = 24.55 \pm 0.05$ ,  $b = 9.56 \pm 0.02$ ,  $c = 15.80 \pm 0.04$  Å;  $\beta = 117.2^\circ \pm 0.1^\circ$ ;  $U = 3331$  Å<sup>3</sup>;  $D_m = 1.676$ ; space group,  $C2/c$  ( $C_{2h}^6$  No. 15); molecular symmetry 2. It was a non-conductor in nitrobenzene solution and the solid was diamagnetic at 20°.

*Oxotribromobistriphenylphosphinerhenium(v)* (XIX; X = Br). (a) A solution of triphenylphosphine (2.5 g.) in glacial acetic acid (10 c.c.) was added to a hot solution of rhenium heptoxide (0.5 g.) and concentrated hydrobromic acid (1 c.c.) in glacial acetic acid (2.5 c.c.). The mixture was boiled for several minutes and then cooled. A yellow precipitate was formed, which after successive washing with glacial acetic acid, ether, boiling benzene, and boiling methylene chloride, afforded needles (1.96 g.) of *compound* (XIX; X = Br) (Found: C, 44.55; H, 3.3; Br, 24.85.  $C_{36}H_{30}Br_3OP_2Re$  requires C, 44.7; H, 3.1; Br, 24.8%). This *complex* was very slightly soluble in organic solvents, which precluded the determination of dipole moment and ebullioscopic molecular weight. The solid was diamagnetic at 20°.

(b) Rhenium heptoxide (0.5 g.) in acetone (5 c.c.) and concentrated hydrobromic acid (1 c.c.) was boiled for 10 min. under reflux, then allowed to cool. A solution of triphenylphosphine (2.5 g.) in acetone (10 c.c.) was then added and the mixture kept at room temperature. It rapidly became yellow-brown and deposited a yellow solid, which after ½ hr. was removed and purified as under (a). The product (1.83 g.) was shown to be (XIX; X = Br) by its infrared spectrum.

(c) Oxoethoxydibromobistriphenylphosphinerhenium(v) (0.2 g., 1 mol.) in cold dry benzene (5 c.c.) was mixed with dry hydrogen bromide in benzene (6.5 c.c., 0.033N-HBr, 1 mol.). The mixture soon became turbid and deposited yellow crystals (0.11 g.) of *compound* (XIX; X = Br).

*Oxotriithiocyanatobistriphenylphosphinerhenium(v)* (XIX; X = SCN). A mixture of oxotrichlorobistriphenylphosphinerhenium(v) (0.5 g.), silver thiocyanate (1.0 g.), and benzene (22.5 c.c.) was refluxed for 10 min., then evaporated to 5 c.c., diluted with light petroleum (20 c.c.; b. p. 40–60°), and left until crystallisation was complete. The brown product (0.45 g.), recrystallised from benzene–light petroleum (b. p. 40–60°), afforded very small prisms of *complex* (XIX; X = SCN) (Found: C, 52.3; H, 3.45.  $C_{39}H_{30}N_3OP_2ReS_3$  requires C, 52.0; H, 3.4%).

*cis-Oxotrichlorobistriethylphosphinerhenium(v)* (XX; R = Et). A mixture of sodium per-rhenate (2 g.), triethylphosphine (2.4 g.), concentrated hydrochloric acid (10 c.c.), and propan-2-ol (50 c.c.) was refluxed for 40 hr., concentrated until a white precipitate appeared, allowed to cool, and filtered. The filtrate, concentrated to about half its volume, deposited green crystals on cooling. These, when recrystallised from ethanol, gave a mixture of green and blue crystals from which the green were extracted with diethyl ether. The residue (0.03 g.) consisted

of small needles of complex (XX; R = Et) (Found: C, 26.8; H, 5.5.  $C_{12}H_{30}Cl_3OP_2Re$  requires C, 26.5; H, 5.6%).

*trans-Oxotrchlorobistriethylphosphinerhenium(v)* (XXI; R = Et). This compound was isolated from the ethereal extract from the previous preparation and recrystallised from diethyl ether as prisms (0.23 g.) (Found: C, 26.7; H, 5.5%).

*trans-Oxotrchlorobistripropylphosphinerhenium(v)* (XXI; R = Pr<sup>n</sup>). A mixture of potassium per-rhenate (3 g.), concentrated hydrochloric acid (10 c.c.), tri-*n*-propylphosphine (5 g.), and ethanol (50 c.c.) was refluxed under nitrogen for 16 hr., stirred with charcoal and Hyflo-supercel, then filtered. The filtrate, concentrated to one-quarter and cooled, gave a green crystalline precipitate (0.85 g.), which from ethanol afforded plates of *complex* (XXI; R = Pr<sup>n</sup>) (Found: C, 34.7; H, 6.75.  $C_{18}H_{42}Cl_3OP_2Re$  requires C, 34.4; H, 6.7%).

*Oxotrchlorobistri(chloromethyl)phosphinerhenium(v)* (XXII). Sodium per-rhenate (1 g.), tri(chloromethyl)phosphine (1.96 g.), and concentrated hydrochloric acid (10 c.c.) in ethanol (50 c.c.) were refluxed for 1 hr., during which the colourless solution became yellow and then green. The gum obtained by evaporating the solution at 11 mm. was treated with cold methanol, and the resulting solid recrystallised from chloroform–light petroleum (b. p. 40–60°) to give crystals of *complex* (XXII) (0.14 g.) (Found: C, 10.6; H, 2.0.  $C_6H_{12}Cl_3OP_2Re$  requires C, 10.8; H, 1.8%).

*Oxotrchloro(ethylenebis(diphenylphosphine)rhenium(v)* (XXVI). Ethylenebis(diphenylphosphine) (9 g.) in hot propan-1-ol (250 c.c.) was added during 3 hr. to a refluxing mixture of sodium per-rhenate (3.5 g.) and concentrated hydrochloric acid (10 c.c.), then allowed to cool. A bluish-green precipitate was formed; it was washed successively with ethanol, water, and ethanol, then dried. The product (4.9 g.), recrystallised successively from dimethylformamide–diethyl ether, dimethylformamide–chloroform, and dimethylformamide–diethyl ether, afforded prisms of *complex* (XXVI) (Found: C, 44.4; H, 3.5.  $C_{26}H_{24}Cl_3OP_2Re$  requires C, 44.2; H, 3.4%). It was insufficiently soluble for determination of its molecular weight, dipole moment, or conductivity.

*Oxotrchloro(ethylenebis(diethylphosphine)rhenium(v)* (XXX). Potassium per-rhenate (2.3 g.) ethylenebis(diethylphosphine) (8.7 g.), and concentrated hydrochloric acid (10 c.c.) in ethanol (100 c.c.) were stirred and boiled under reflux for 1½ hr., filtered, and allowed to cool, so yielding a blue precipitate which was filtered off. The filtrate, kept at 0° overnight, deposited more of the blue product. The combined residues, recrystallised from acetone–propan-1-ol (2:1), gave plates (3.5 g.) of *complex* (XXX) (Found: C, 23.3; H, 4.7.  $C_{10}H_{24}Cl_3OP_2Re$  requires C, 23.3; H, 4.7%). This was too poorly soluble in organic solvents for determination of its molecular weight, dipole moment, or conductivity.

*Oxotrchlorobis(diethylphenylarsine)rhenium(v)* (XXXI). Potassium per-rhenate (0.5 g.), concentrated hydrochloric acid (2.5 c.c.), and diethylphenylarsine (1.6 g.) in ethanol (50 c.c.) were refluxed for 1 hr., filtered, and allowed to cool. A greenish-blue crystalline *product* (XXXI) (0.4 g.) separated and recrystallised as needles from benzene–light petroleum (b. p. 40–60°) (Found: C, 33.0; H, 4.2.  $C_{20}H_{30}As_2Cl_3ORe$  requires C, 33.0; H, 4.15%). Repeated crystallisation from benzene–light petroleum (b. p. 40–60°) gave products of differing shades of blue but the same analyses. It appeared that two isomers were present, the one greenish-blue, the other very much greener, but only partial separation was effected. In benzene the greenish-blue compound had an initial dipole moment of at least 9 D which dropped to ca. 8 D in several minutes.

*Oxoalkoxy-complexes.*—*Oxomethoxydichlorobis(diethylphenylphosphine)rhenium(v)* (V; R = Me). *trans*-[ $ReOCl_2(Et_2PhP)_2$ ] (0.2 g.) in methanol (25 c.c.) was boiled for 10 min., cooled, and kept in the refrigerator overnight; crystals (0.18 g.) of *complex* (V; R = Me) were deposited (Found: C, 39.6; H, 5.3; O, 6.1; OMe, 5.2.  $C_{21}H_{33}Cl_2O_2P_2Re$  requires C, 39.6; H, 5.2; O, 5.0; OMe, 4.9%).

*Oxoethoxydichlorobis(diethylphenylphosphine)rhenium(v)* (V; R = Et). (a) *cis*-Oxotrchlorobis(diethylphenylphosphine)rhenium (v) (0.3 g.) in ethanol (20 c.c.) was refluxed for 6 hr., then concentrated to half its volume, and allowed to cool, so depositing needles (0.22 g.) of *compound* (V; R = Et) (Found: C, 40.4; H, 5.3; O, 5.7; OEt, 7.3.  $C_{22}H_{35}Cl_2O_2P_2Re$  requires C, 40.6; H, 5.4; O, 4.9; OEt, 6.9%).

(b) The violet complex (III) (0.5 g.) in ethanol (20 c.c.) was refluxed for 7½ hr., then allowed to cool; needles of substance (V; R = Et) (0.39 g.) separated (Found: C, 40.6; H, 5.3; O, 5.7; OEt, 7.4%).

(c) *trans*-Oxotrichlorobis(diethylphenylphosphine)rhenium(v) (0.2 g.) in ethanol (50 c.c.) was refluxed for 1 hr., evaporated to one-quarter, and allowed to cool. A dull-violet crystalline precipitate was obtained and recrystallised from ethanol to give dull-violet needles (0.14 g.), m. p. 122–127° (decomp.) (Found: C, 40.3; H, 5.4%). The infrared spectra and X-ray powder photographs of the three products were identical, but the slightly different colour, m. p., and dipole moment of the product of (c) suggests the existence of isomers.

*Oxobenzoyloxydichlorobisdiethylphenylphosphinerhenium*(v) (V; R = CH<sub>2</sub>Ph). *cis*-Oxotrichlorobis(diethylphenylphosphine)rhenium(v) (0.5 g.) in benzyl alcohol (15 c.c.) was kept at 100° ± 5° for 7 hr., then cooled. Addition of diethyl ether (30 c.c.) caused large crystals (0.2 g.) of *complex* (V; R = CH<sub>2</sub>Ph) to be deposited slowly (Found: C, 45.3; H, 5.2; O, 6.0. C<sub>27</sub>H<sub>37</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Re requires C, 45.5; H, 5.2; O, 4.5%). The complex was too poorly soluble for determination of the dipole moment and was too unstable for determination of the molecular weight by ebullioscopic methods.

*Oxomethoxydichlorobistriphenylphosphinerhenium*(v) (XII; R = Me). Oxotrichlorobistriphenylphosphinerhenium(v) (5.5 g.) in benzene (150 c.c.) and methanol (200 c.c.) suspension was refluxed for 1 hr. The resultant pale pink solution deposited grey plates (4 g.) on cooling, which, recrystallised from benzene-ethanol, afforded graphite-like crystals of *compound* (XII; R = Me) [Found: C, 53.8; H, 4.1; O, 5.5; OMe, 4.1%; *M* (X-ray), 824 ± 8. C<sub>37</sub>H<sub>33</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Re requires C, 53.6; H, 4.0; O, 3.9; OMe, 3.75%; *M*, 828.7]. Crystal data: triclinic; *a* sin  $\gamma$  = 8.62 ± 0.02, *b* = 11.63 ± 0.03, *c* sin  $\alpha$  = 16.78 ± 0.04 Å,  $\beta^*$  = 87° 11', *U* = 1684 Å<sup>3</sup>; *D<sub>m</sub>* = 1.626 g. cm.<sup>-3</sup> (by flotation); *Z* = 2; space group, *P*1̄ or *P*1̄ (*C*<sub>1</sub><sup>1</sup> or *C*<sub>1</sub><sup>1</sup> Nos. 2 or 1). The solid was diamagnetic at 20°.

*Oxoethoxydichlorobistriphenylphosphinerhenium*(v) (XII; R = Et). (a) Analogous procedure to that employed for the preparation of compound (XII; R = Me) gave a similar yield of *product* (XII; R = Et) as plates (Found: C, 54.1; H, 4.4; O, 4.7; OEt, 6.1. C<sub>38</sub>H<sub>35</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Re requires C, 54.2; H, 4.2; O, 3.9; OEt, 5.35%). The solid was diamagnetic at 20°.

(b) The reaction employed for the preparation of *trans*-oxotrichlorobistriphenylphosphinerhenium(v) (XI; above), performed under anhydrous conditions with dry hydrogen chloride, yielded compound (XII; R = Et) instead of (XI).

*Oxobenzoyloxydichlorobistriphenylphosphinerhenium*(v) (XII; R = CH<sub>2</sub>Ph). Oxotrichlorobistriphenylphosphinerhenium(v) (5.5 g.) in benzyl alcohol (55 c.c.) was refluxed for 2 min., then allowed to cool. The grey crystalline precipitate (3.5 g.), recrystallised from benzyl alcohol-ether, gave plates of *complex* (XII; R = CH<sub>2</sub>Ph) (Found: C, 57.2; H, 4.2; O, 4.5. C<sub>42</sub>H<sub>37</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Re requires C, 57.1; H, 4.1; O, 3.5%). The solid was diamagnetic at 20° and was too insoluble for determination of the dipole moment.

*Oxoethoxydibromobistriphenylphosphinerhenium*(v) (XVIII; X = Br). (a) Rhenium heptoxide (0.5 g.) and concentrated hydrobromic acid (1 c.c.) in ethanol (10 c.c.) were refluxed for 5 min., then triphenylphosphine (2.5 g.) was added and boiling continued for several minutes. On cooling, brown crystals separated and were washed with ethanol, water, and ethanol, affording needles of *complex* (XVIII; X = Br) (1.76 g.) [Found: C, 49.2; H, 3.9; O, 4.0; OEt, 5.0; Br, 17.7%; *M* (ebullioscopic in 0.897% benzene solution), 927. C<sub>38</sub>H<sub>35</sub>Br<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Re requires C, 49.0; H, 3.8; O, 3.4; OEt, 4.8; Br, 17.2%; *M*, 931.7]. The complex was diamagnetic in the solid state and in chloroform solution at 20°.

When the above reactants were mixed and kept at room temperature for 2 hr. a similar yield of the bromo-compound was obtained.

(b) Rhenium heptoxide (1 g.) in ethanol (5 c.c.) was added to a saturated ethanolic solution (10 c.c.) of dry hydrogen bromide, and the pale green solution boiled for 5 min. A hot solution of triphenylphosphine (5 g.) in ethanol (15 c.c.) was then added, and the mixture heated to the b. p. and allowed to cool. The product (XVIII; X = Br) separated, and was purified as in (a) above (3.8 g.) (Found: C, 49.1; H, 3.9%); its identity with (XVIII; X = Br) was also shown by its infrared spectrum.

*Oxoethoxydi-iodobistriphenylphosphinerhenium*(v) (XVIII; X = I). (a) This *compound* was prepared analogously to (XVIII; X = Br) by procedure (a) as green plates [Found: C, 44.7; H, 3.45; O, 3.6; OEt, 4.75%; *M* (ebullioscopic in 2.45% benzene solution), 1019. C<sub>38</sub>H<sub>35</sub>I<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Re requires C, 44.5; H, 3.4; O, 3.1; OEt, 4.4%; *M*, 1025.7]. It was diamagnetic in the solid state and in chloroform solution at 20°.

(b) Triphenylphosphine (6 g.) in acetone (40 c.c.) was added to a solution of potassium hexaiodorhenate, K<sub>2</sub>ReI<sub>6</sub> (4 g.), in acetone (35 c.c.), and the purplish-brown mixture kept at

room temperature for 6 hr. A very dark crystalline precipitate (4.1 g.) was formed. This, after recrystallising twice from benzene-ethanol, yielded fine needles of compound (XVIII; X = I) (Found: C, 44.6; H, 3.5%). The infrared spectrum of this complex and of that described under (a) above were identical.

*Oxo-propoxydi-iodobistriphenylphosphinerhenium(v)* (XVI). Ammonium per-rhenate (1 g.) in water (5 c.c.) and concentrated hydriodic acid (5 c.c.) were boiled for 10 min. (iodine evolved), then added to a refluxing solution of triphenylphosphine (5 g.) in propan-1-ol (200 c.c.). The olive-green solution which was formed on boiling for 10 min. deposited green crystals; these were filtered from the hot solution and washed with propan-1-ol, then diethyl ether, to give crystals (1.2 g.) of compound (XVI) (Found: C, 44.5; H, 3.7.  $C_{39}H_{37}I_2O_2P_2Re$  requires C, 45.05; H, 3.6%).

*Oxo-(2-methoxyethoxy)di-iodobistriphenylphosphinerhenium(v)* (XV). The oxo-propoxy-complex (XVI) (1 g.), recrystallised twice from hot 2-methoxyethanol, gave needles (0.68 g.) of compound (XV) (Found: C, 44.3; H, 3.7; I, 24.5.  $C_{39}H_{37}I_2O_3P_2Re$  requires C, 44.4; H, 3.5; I, 24.0%). The same complex was obtained by boiling the oxoethoxy-complex (XVIII; X = I) in 2-methoxyethanol for 3 min., then allowing the solution to cool.

*Oxomethoxydichlorobistri(chloromethyl)phosphinerhenium(v)* (XXIII). The corresponding oxotrichloro-complex (XXII), on recrystallisation from boiling methanol, afforded needles of compound (XXIII) almost quantitatively (Found: C, 13.0; H, 2.4.  $C_7H_{15}Cl_3O_2P_2Re$  requires C, 12.7; H, 2.2%).

*Oxoethoxydichlorobis(ethyl)phosphine)rhenium(v)* (XXIV). A mixture of sodium per-rhenate (1 g.), concentrated hydrochloric acid (10 c.c.), ethyldiphenylphosphine (2.4 g.), and ethanol (50 c.c.) was refluxed for 2 hr., evaporated to one-third, and allowed to cool. The mauve precipitate (0.64 g.), washed with ether and recrystallised twice from chloroform-light petroleum (b. p. 40–60°), gave crystals of compound (XXIV) (Found: C, 47.8; H, 4.9; OEt, 6.4.  $C_{30}H_{35}Cl_2O_2P_2Re$  requires C, 48.3; H, 4.7; OEt, 6.0%).

*Oxo-(2-methoxyethoxy)dichlorobis(dipropyl)phenylphosphinerhenium(v)* (XXV). Potassium per-rhenate (2.7 g.), phenyldi-n-propylphosphine (12.0 g.), and concentrated hydrochloric acid (5 c.c.) in 2-methoxyethanol (130 c.c.) were refluxed for 2½ hr., then allowed to cool. Overnight a light purple precipitate separated. This, when washed with ethanol then diethyl ether and recrystallised from benzene-light petroleum (b. p. 40–60°), afforded plates (0.5 g.) of compound (XXV) (Found: C, 43.8; H, 6.1.  $C_{27}H_{45}Cl_2O_3P_2Re$  requires C, 44.0; H, 6.2%).

*Phenylimido-complex.*—*Trichlorophenylimidobis(diethylphenylphosphine)rhenium(v)* (VI). (a) A benzene solution (50 c.c.) of *cis*-oxotrichlorobis(diethylphenylphosphine)rhenium(v) (0.3 g.) and aniline (5 c.c.) was refluxed for 1 hr. and the resultant green solution evaporated almost to dryness at 11 mm. Addition of an excess of diethyl ether precipitated aniline hydrochloride which was filtered off. The ether was evaporated from the filtrate; adding aqueous acetic acid (1 : 1) to the oily residue gave a green solid product (VI) which recrystallised from benzene-light petroleum (b. p. 40–60°) as needles (0.1 g.) (Found: C, 43.6; H, 4.95; N, 2.05.  $C_{26}H_{35}Cl_3NP_2Re$  requires C, 43.6; H, 4.9; N, 2.0%).

(b) The same product (VI) was obtained by the above procedure starting from *trans*-oxotrichlorobis(diethylphenylphosphine)rhenium(v) (0.3 g.) and refluxing for 1½ hr., or from the violet complex (III) (0.3 g.) and refluxing for 18 hr., in yields of 0.19 g. and 0.16 g., respectively. The identity of the products was shown by infrared spectra and analyses. No absorption characteristic of Re:O or -NH- was observed.

*Rhenium(III) Complexes.*—*Trichlorodiethylphenylphosphinerhenium(III)* (IX). Diethylphenylphosphine (0.123 g.) in ethanol (2.5 c.c.) was added to a filtered ethanolic solution, (25 c.c.) of rhenium trichloride (0.217 g., 1 mol.). A red-brown solid was precipitated immediately and, as filtration was difficult, the suspension was evaporated to dryness at 11 mm. The residue, recrystallised from dimethylformamide, gave small rhombs (0.24 g.) of compound (IX) (Found: C, 26.3; H, 3.5.  $C_{10}H_{15}Cl_3PRe$  requires C, 26.2; H, 3.3%). This was too insoluble for determination of the molecular weight, conductivity, or dipole moment. Its infrared spectrum showed no absorption bands which could be assigned to Re:O or P:O.

No reaction was observed during prolonged boiling of an ethanolic suspension of the complex with an excess of diethylphenylphosphine.

*Trichlorotris(diethylphenylphosphine)rhenium(III)* (IV). (a) A mixture of *trans*-oxotrichlorobis(diethylphenylphosphine)rhenium(v) (0.3 g.), diethylphenylphosphine (1.54 g.), and ethanol (30 c.c.) was refluxed for 5 min. and then allowed to cool. The yellow crystalline product (IV)

that was precipitated recrystallised from ethyl alcohol as needles (0.18 g.) (Found: C, 45.5; H, 5.8.  $C_{30}H_{45}Cl_3P_3Re$  requires C, 45.5; H, 5.7%). It had no  $Re:O$  band in its infrared spectrum and was a non-conductor in nitrobenzene.

(b) Similarly *cis*-oxotrichlorobis(diethylphenylphosphine)rhenium(v) (0.3 g.) was converted into product (IV) (0.17 g.) by 20 minutes' refluxing. In benzene as solvent in place of ethanol the conversion required 20 hr.

(c) The violet complex (III) (0.3 g.) under conditions as in (a) above required 5 hr. for conversion into the product (IV) (0.16 g.).

(d) To a solution of rhenium heptoxide (1 g.) in dry ethanol (100 c.c.) were added successively a dry saturated ethanolic solution (5 c.c.) of hydrogen chloride and a dry ethanolic solution (100 c.c.) of diethylphenylphosphine (5.5 g.). The whole was refluxed for 1 hr., and the yellow-brown solution evaporated to one third, and allowed to cool. An orange crystalline precipitate was obtained which, recrystallised from ethyl alcohol, yielded needles (0.46 g.) of compound (IV).

*Trichlorotriphenylphosphinerhenium*(III) (XVII). Prepared as described,<sup>2</sup> but recrystallised from a large volume of ethanol, this formed plates (0.1 g.) (Found: C, 38.4; H, 2.9. Calc. for  $C_{18}H_{15}Cl_3PRe$ : C, 38.95; H, 2.7%).

*Trichloro*(diethylphenylphosphine)(ethylenebisdiethylphenylphosphine)rhenium(III) (VIII). A solution of *cis*-oxotrichlorobis(diethylphenylphosphine)rhenium(v) (0.3 g.) and ethylenebis(diphenylphosphine) (0.2 g.) in propan-1-ol (25 c.c.) was refluxed for 0.5 hr. and filtered hot. The yellow precipitate (0.1 g.), recrystallised successively from butan-1-ol and chloroform-methanol, afforded needles of complex (VIII) (Found: C, 50.3; H, 4.6.  $C_{36}H_{39}Cl_3P_3Re$  requires C, 50.4; H, 4.6%).

*Dichlorobis*(ethylenebisdiethylphenylphosphine)rhenium(III) chloride (XXVIII). Ethylenebisdiethylphenylphosphine (3.36 g.) and concentrated hydrochloric acid (2.5 c.c.) in propan-1-ol (50 c.c.) were added to potassium per-rhenate (0.4 g.), and the mixture was refluxed for 1½ hr., concentrated to one-third of its volume, and allowed to cool. The yellow solution, decanted from a heavy white precipitate (mainly ethylenebisdiethylphenylphosphine) and evaporated to dryness at 11 mm., yielded an orange gum. This became solid on trituration with diethyl ether, light petroleum (b. p. 40–60°), and diethyl ether again. The solid was then treated with cold ethanol (35 c.c.) and the suspension filtered from undissolved ethylenebisdiethylphenylphosphine. Addition of an excess of diethyl ether to the filtrate precipitated plates of the pure chloride (XXVIII) (0.66 g.) (Found: C, 57.75; H, 4.6.  $C_{52}H_{48}Cl_3P_4Re$  requires C, 57.3; H, 4.4%). It had no  $Re:O$  bond in its infrared spectrum, and its 0.320% w/v nitrobenzene solution at 19° had a molar conductivity of 18.8 mhos.

*Rhenium*(II) Complexes.—*Dichlorobistriphenylphosphinerhenium*(II) (XIII). Hydrazine dihydrochloride (1 g.) in water (5 c.c.) and triphenylphosphine (5 g.) in ethanol (200 c.c.) were added in that order to a solution of sodium per-rhenate (1 g.) in 0.5N-hydrochloric acid (10 c.c.). The whole was heated to the b. p., then benzene (250 c.c.) was added dropwise and the mixture simultaneously distilled to remove the benzene-ethanol-water azeotrope. When almost all of the azeotrope had been removed a brick-red precipitate was formed rapidly. This product (XIII) (1.8 g.) crystallised from benzene-ethanol as plates (Found: C, 55.3; H, 3.9; Cl, 8.7.  $C_{36}H_{30}Cl_2P_2Re$  requires C, 55.3; H, 3.9; Cl, 9.1%). The solid was diamagnetic at 20° and was too insoluble for determination of the molecular weight or accurate dipole moment.

*Di-iodobistriphenylphosphinerhenium*(II) (XIV). Sodium iodide (1.5 g.) in acetone (125 c.c.) was added to a solution of dichlorobistriphenylphosphinerhenium(II) (0.45 g.) in benzene (250 c.c.). The resultant clear mixture was boiled under reflux for 1 hr., then filtered whilst hot and diluted with light petroleum (20 c.c.; b. p. 100–120°). The solution was then evaporated to a small volume and set aside. Dull plates (0.27 g.) of compound (XIV) were deposited [Found: C, 44.5; H, 3.2%; *M*, (ebullioscopic in 1.759% benzene solution) 1068, (in 2.564% chloroform solution) 971.  $C_{36}H_{30}I_2P_2Re$  requires C, 44.4; H, 3.1%; *M*, 964.6]. The infrared spectrum of this compound was very similar to that of the chloro-analogue (XIII); both were devoid of the characteristic absorption ascribed to  $Re:O$ . The solid complex was diamagnetic.

*Dichlorobis*(ethylenebisdiethylphenylphosphine)rhenium(II) (XXIX). *Dichlorobis*(ethylenebisdiethylphenylphosphine)rhenium(III) chloride (0.5 g.) in ethanol (20 c.c.) was treated with an aqueous solution (5 c.c.) of sodium borohydride (0.16 g.) at room temperature. There was an immediate effervescence and precipitation of a yellow solid complex (XXIX) (0.24 g.) which recrystallised

from benzene-methyl alcohol as plates (Found: C, 59.1; H, 4.7. C<sub>52</sub>H<sub>48</sub>Cl<sub>2</sub>P<sub>4</sub>Re requires C, 59.3; H, 4.6%). This was too insoluble in benzene for determination of the dipole moment and molecular weight and was a non-conductor in nitrobenzene.

*Dipole Moments.*—The method of determination and significance of the symbols in Table 2 are given in ref. 18.

TABLE 2.  
Dipole moments.

Compound	10 <sup>3</sup> ω	Δε/ω	10 <sup>2</sup> Δn/ω	−Δv/ω	Compound	10 <sup>3</sup> ω	Δε/ω	10 <sup>2</sup> Δn/ω	−Δv/ω
I	1.787	20.32	—	—	XII; R = Me	1.985	1.383	—	—
	3.744	20.30	—	—		3.254	1.309	—	(0.49)
	5.314	—	—	0.583	XII; R = Et	2.742	1.451	—	—
	5.701	—	—	0.561		3.539	1.369	—	(0.49)
II	2.760	0.963	—	—	XVIII; X = Br	2.697	1.229	—	—
	6.062	0.955	—	—		3.311	1.226	—	—
	23.33	—	9.67	—		20.86	—	12.43	—
	27.57	—	9.71	—		34.75	—	12.92	—
	3.549	—	—	0.535		6.001	—	—	0.580
	3.620	—	—	0.525		7.247	—	—	0.562
III	1.313	1.985	—	—	XVIII; X = I	3.567	1.194	—	—
	1.615	2.002	—	—		3.934	1.196	—	—
	3.074	—	—	0.586		19.24	—	12.42	—
	4.411	—	—	0.567		23.10	—	12.91	—
X	2.318	15.89	—	—		4.281	—	—	0.619
	3.451	15.83	—	(0.660)		7.621	—	—	0.629
XI	1.960	1.249	—	—	VI	2.350	5.915	—	—
	4.384	1.278	—	(0.56)		3.096	5.894	—	(0.49)
XIX; X = SCN	2.255	3.481	—	—	IV	4.972	6.006	—	—
	2.822	3.505	—	—		5.195	6.008	—	—
	3.813	—	—	0.459		30.64	—	11.35	—
	3.968	—	—	0.446		45.58	—	11.19	—
XX; R = Et	1.945	21.54	—	—		6.052	—	—	0.496
	2.240	21.53	—	(0.56)		7.617	—	—	0.499
XXI; R = Et	2.083	1.051	—	—	XIII	1.416	0.935 †	—	—
	4.712	1.003	—	(0.56)		2.297	0.849	—	(0.50)
XXI; R = Pr <sup>n</sup>	1.906	0.793	—	—	XIV	2.978	0.591	—	—
	2.611	0.782	—	(0.56)		3.628	0.590	—	—
XXXI	2.451	15.95	—	—		10.530	—	12.04	—
	2.554	15.87	—	—		21.520	—	11.69	—
	14.32	—	5.86	—		9.516	—	—	0.623
	5.056	—	—	0.583					

Compound	$\tau^P$	$\epsilon^P$	$\sigma^P$	$\mu$ (±0.2D)	Compound	$\tau^P$	$\epsilon^P$	$\sigma^P$	$\mu$ (±0.2D)
I	2562	(151)	2388 *	10.8 *	XII; R = Me	372 *	(209)	132 *	2.55 *
II	233.5	151.3	59.5	1.7	XII; R = Et	389 *	(214)	143 *	2.65 *
III	349.6	(151)	175.6 *	2.95 *	XVIII; X = Br	375.1	224.6	116.8	2.4
X	2868 *	(175)	2666 *	11.4 *	XVIII; X = I	390.6	231.4	124.5	2.45
XI	344 *	(211)	101 *	2.25 *	VI	937 *	(176)	734 *	6.0
XIX; X = SCN	779.4	(232)	513 *	5.0 *	IV	1048.3	201.4	816.7	6.3
XX; R = Et	2306 *	(122)	2166 *	10.3 *	XIII	282 *	(201)	51 *	1.6 *
XXI; R = Et	201 *	(122)	61 *	1.7 *					±0.3
XII; R = Pr <sup>n</sup>	203 *	(145)	37 *	1.35 *	XIV	257.6	213.5	12.1	0.75
XXXI	2307	144.8	2141	10.25					±0.5

\* Calc. by using estimated values of densities and refractivities. † Poor agreement owing to low solubility.

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<sup>18</sup> Chatt and Shaw, *J.*, 1959, 705.