121. *Complex Compounds of Tertiary Phosphines with Rhenium*(IV) *and Rhenium*(V).

By J. CHATT, J. D. GARFORTH, N. P. JOHNSON, and G. A. ROWE.

Some complexes of diethylphenylphosphine and triphenylphosphine, of the type $[ReX_4(PR_3)_2]$ (X = Cl or Br), have been prepared by (*a*) oxidation of complexes of the type $[ReX_3(PR_3)_3]$ by X_2, (*b*) pyrolysis of the salts $[PHR_3]_2[ReX_6]$, or (*c*) reduction of $[ReOX_3(PR_3)_2]$ in HX. The " violet complex " obtained by the interaction of per-rhenates, diethylphenylphosphine, and hydrochloric acid in boiling ethanol is shown to be a solid solution of some 15% of *trans*-$[ReCl_4(PEt_2Ph)_2]$ in *trans*-$[ReOCl_3(PEt_2Ph)_2]$. Ligand displacement provides a convenient preparation of the otherwise difficult to obtain trialkyl- and tertiary alkaryl-phosphine and -arsine complexes of the type $[ReOCl_3(MR_3)_2]$ (M = P or As) from the readily available *trans*-$[ReOCl_3(PPh_3)_2]$.

Recently, in describing a number of complexes of tertiary phosphines with rhenium(v), rhenium(III), and rhenium(II), we mentioned a mysterious violet complex to which we were unable to assign a formula, but we tentatively suggested it might be $[Re(OH)Cl_3(PEt_2Ph)_2]$.[1] It was obtained together with *cis*- and *trans*-$[ReOCl_3(PEt_2Ph)_2]$ by the interaction of per-rhenates, diethylphenylphosphine, and hydrochloric acid in boiling ethanol. We now find that this complex is a solid solution of 10—22% of a new, intensely violet, complex, *trans*-$[ReCl_4(PEt_2Ph)_2]$, in green *trans*-$[ReOCl_3(PEt_2Ph)_2]$. Here we describe this tetrachloro-complex and related complexes of rhenium(IV), all of which are strongly coloured [(I), (II), and (III); Table 1], and also an improved method of obtaining some complexes of the types *cis*- and *trans*-$[ReOCl_3L_2]$ by ligand displacement from the readily available *trans*-$[ReOCl_3(PPh_3)_2]$.

Rhenium(IV) *Complexes.*—The " violet complex " (ref. 1) is not a convenient source of *trans*-$[ReCl_4(PEt_2Ph)_2]$, but this is readily obtained by the oxidation of $[ReCl_3(PEt_2Ph)_3]$ with chlorine in carbon tetrachloride, or, surprisingly, by treating the same trichloro-complex with hydrazine dihydrochloride in boiling ethanol. It is also obtained by the pyrolysis of $[PHEt_2Ph]_2[ReCl_6]$ (prepared from $K_2[ReCl_6]$ and diethylphenylphosphonium hydrochloride in hydrochloric acid), analogous to the preparation of $[ReCl_4py_2]$ from $[pyH]_2[ReCl_6]$.[2] We were unsuccessful in attempts to obtain *trans*-$[ReCl_4(PEt_2Ph)_2]$ directly from $K_2[ReCl_6]$ and diethylphenylphosphine, the potassium salt proving completely unreactive. Previously, it was noted that *cis*-$[ReOCl_3(PEt_2Ph)_2]$ in boiling butan-2-ol gives the violet complex, but attempts to reduce the oxotrichloro-complex by other reagents were unsuccessful.

The corresponding bromide, $[ReBr_4(PEt_2Ph)_2]$, is obtained by pyrolysis of $[PHEt_2Ph]_2[ReBr_6]$, prepared either by the action of diethylphenylphosphonium bromide in hydrobromic acid on $K_2[ReBr_6]$ or from *cis*-$[ReOBr_3(PEt_2Ph)_2]$ and concentrated hydrobromic acid in ethanol.

Of the triphenylphosphine analogues, $[ReX_4(PPh_3)_2]$, those with X = Br or I, obtained from the corresponding rhenium tetrahalides, have been reported,[3] and those with X = Cl or Br have been mentioned but not characterised.[4] We now report $[ReCl_4(PPh_3)_2]$, obtained in poor yield by the reduction of *trans*-$[ReOCl_3(PPh_3)_2]$ in benzene solution by a boiling solution of titanous chloride in hydrochloric acid. By treating $[ReCl_4(PPh_3)_2]$ with an excess of diethylphenylphosphine in boiling benzene it is converted into *trans*-$[ReCl_4(PEt_2Ph)_2]$.

[1] Chatt and Rowe, *J.*, 1962, 4019.
[2] Tronev and Babeshkina, *Zhur. neorg. Khim.*, 1958, **3**, 2458; *Russ. J. Inorg. Chem.*, 1962, **7**, 108.
[3] Colton and Wilkinson, *Chem. and Ind.*, 1959, 1316.
[4] Malatesta, Freni, and Valenti, *Angew. Chem.*, 1961, **73**, 273; Malatesta, " Advances in the Chemistry of Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 245.

trans-$[ReCl_4(PEt_2Ph)_2]$ was investigated in detail for comparison with the " violet complex." [1] It is monomeric in benzene solution, a non-conductor in nitrobenzene, and the solid is paramagnetic ($\mu_{eff.} = 3{\cdot}64$ B.M. at 20°) in accord with expectation for rhenium(IV). Although its measured dipole moment was not zero (0·87 D), because the atom polarisation is uncertain and the estimated value may be slightly in error, and because diethylphenylphosphine is not symmetrical and will introduce a small dipole moment, it nevertheless indicates a *trans*-configuration. This was corroborated by preliminary *X*-ray studies which show it to be monomeric in the solid state and to have the same configuration as *trans*-$[ReOCl_3(PEt_2Ph)_2]$.[5] Although the two substances are not isomorphous, the tetrachloro-forms a solid solution in the oxotrichloro-complex lattice,[6] and this solid solution constitutes the " violet complex." [1]

The chemical reactions of the two components of the violet complex are somewhat similar. Thus, each reacts with diethylphenylphosphine in boiling ethanol to form $[ReCl_3(PEt_2Ph)_3]$, the tetrachloro- much more slowly than the oxotrichloro-complex, and with aniline in benzene to form *trans*-$[ReCl_3(NPh)(PEt_2Ph)_2]$.[1]

The separation of the violet complex into its components was only partly achieved. Recrystallisation produced no detectable separation, and on most chromatographic column fillings the complex was recovered unchanged or was completely destroyed. However, " Woelm acid alumina, grade I " produced, from a benzene solution, a transient green band and a lower violet band. This latter band, eluted with benzene and ethyl acetate–benzene, was shown to be *trans*-$[ReCl_4(PEt_2Ph)_2]$. The green *trans*-$[ReOCl_3(PEt_2Ph)_2]$ was destroyed on the column. Using *trans*-$[ReCl_4(PEt_2Ph)_2]$ in admixture with pure *trans*-$[ReOCl_3(PEt_2Ph)_2]$, the recovery of the tetrachloro-complex was quantitative, and for any one preparation of the violet complex the recovery was constant though it varied from preparation to preparation over a range of 10—22%. This indicates the range of admixture of *trans*-$[ReCl_4(PEt_2Ph)_2]$ in *trans*-$[ReOCl_3(PEt_2Ph)_2]$ which constitutes the violet complex. The violet complex and *trans*-$[ReOCl_3(PEt_2Ph)_2]$ have almost identical infrared (i.r.) spectra (Nujol mull). The i.r., visible, and proton nuclear magnetic resonance (n.m.r.) spectra of the violet complex were shown to be compounded from the spectra of its constituents (see Experimental section and Tables 2 and 3).

The salts $[PHEt_2Ph]_2[ReCl_6]$ and its hexabromo-analogue are weak electrolytes in nitrobenzene at 20°. The hexachlororhenate has much less, and the hexabromorhenate somewhat less, than the molar conductivity expected for a uni-bivalent electrolyte. It seems very probable that association of the ions occurs through the *P*-hydrogen and *Re*-halogen atoms, P–H · · · Cl–Re and P–H · · · Br–Re, since such hydrogen bonding should be greater in the chloride. In agreement with this suggestion, $[AsPh_4]_2[ReCl_6]$ has the molar conductivity expected of a uni-bivalent electrolyte in nitrobenzene, and a different colour from $[PHEt_2Ph]_2[ReCl_6]$ [(VIII) and (VI); Table 1].

TABLE 1.

Compound		Colour	M. p. (decomp.)
trans-$[ReCl_4(PEt_2Ph)_2]$	(I)	Deep violet	161—168°
$[ReBr_4(PEt_2Ph)_2]$	(II)	Dark purple	182—187
$[ReCl_4(PPh_3)_2]$	(III)	Red violet	226—229
cis-$[ReOBr_3(PEt_2Ph)_2]$	(IV)	Green	171—175
$[ReOBr_2(OMe)(PEt_2Ph)_2]$	(V)	Pale brown-violet	132—136
$[PHEt_2Ph]_2[ReCl_6]$	(VI)	Pale green	175—183
$[PHEt_2Ph]_2[ReBr_6]$	(VII)	Yellow	174—177
$[AsPh_4]_2[ReCl_6]$	(VIII)	Cream	295—300
cis-$[ReOCl_3(PPr^n_3)_2]$	(IX)	Blue	110—115
cis-$[ReOCl_3(AsMe_2Ph)_2]$	(X)	Blue	170—175

Oxotrichlororhenium(v) *Complexes by Ligand Replacement.*—We have noted that, whereas *trans*-$[ReOCl_3(PPh_3)_2]$, which is very slightly soluble, can be prepared in good

[5] J. M. Rowe, personal communication.
[6] Ehrlich, personal communication.

yield from sodium per-rhenate, the tertiary phosphine, and hydrochloric acid in boiling ethanol in less than half an hour,[1] the aliphatic tertiary phosphines react very slowly, *e.g.*, triethylphosphine requires 40 hours, and the yields are poor. Nevertheless, the trialkyl- and tertiary alkaryl-phosphines and -arsines readily displace thetriphenyl phosphine from *trans*-$[ReOCl_3(PPh_3)_2]$ in benzene at 20°, thus providing a very convenient preparation of the aliphatic analogues. The scope of this displacement reaction has not been investigated, but it probably has wide application. The products do not necessarily have a *trans*-configuration, as shown by the following list of compounds prepared by this method: *trans*-$[ReOCl_3(PEt_2Ph)_2]$; *cis*- and *trans*-$[ReOCl_3(PEt_3)_2]$; *cis*- and *trans*-$[ReOCl_3(PPr^n_3)_2]$; and *cis*-$[ReOCl_3(AsMe_2Ph)_2]$. New rhenium(V) complexes are also listed in Table 1, which provides the key to the numbering in the Experimental section.

Experimental

M. p.s were determined on a Kofler hot-stage and are corrected. All reactions were carried out under nitrogen.

trans-*Tetrachlorobis(diethylphenylphosphine)rhenium*(IV) (I).—(*a*) A solution of chlorine in carbon tetrachloride (0·20N; 7·5 c.c.) was added at room temperature to a solution of trichlorotris(diethylphenylphosphine)rhenium(III) [1] (0·4 g.) in carbon tetrachloride (20 c.c.). The resultant violet crystalline precipitate (0·30 g.) was recrystallised from benzene–light petroleum (b. p. 30—40°) to yield plates of *compound* (I) [Found: C, 36·6; H, 4·7; Cl, 21·6%; *M* (ebullioscopy, 1·73% solution in benzene), 638 (*X*-ray) 674 ± 12. $C_{20}H_{30}Cl_4P_2Re$ requires C, 36·4; H, 4·6; Cl, 21·5%; *M*, 660]. Crystal data: monoclinic; $a = 9·32 \pm 0·03$, $b = 14·00 \pm 0·04$, $c = 9·72 \pm 0·03$ Å; $\beta = 106·1 \pm 0·2°$; $U = 1218$ Å^3, $D_m = 1·837$ g. cm.$^{-3}$ (by flotation); $Z = 4$; space-group, *C*2, *Cm*, or *C*2/*m*. The complex is a non-conductor in nitrobenzene and is paramagnetic in the solid state ($\mu_{eff.} = 3·64$ B.M. at 20°).

(*b*) Bis(diethylphenylphosphonium) hexachlororhenate(IV) (VI, see below) (0·05 g.) was heated in a stream of nitrogen for 5½ hr. at the temperature of boiling xylene, causing hydrogen chloride to be evolved. The residue was extracted with benzene (10 c.c.), leaving some (VI) (0·03 g.), and the extract was evaporated to dryness. The resultant violet solid (0·016 g.) was recrystallised from benzene–light petroleum (b. p. 30—40°) to give (I).

(*c*) An ethanol solution (50 c.c.) of trichlorotris(diethylphenylphosphine)rhenium(III) [1] (1·0 g.) and hydrazine dihydrochloride (0·5 g.) was refluxed for 1 hr. and then cooled. The violet crystalline precipitate was washed with water and then ice-cold ethanol to yield plates of (I) (0·7 g.) (Found: C, 36·4; H, 4·4; P, 9·5; Re, 27·9. Calc. for $C_{20}H_{30}Cl_4P_2Re$: C, 36·4; H, 4·6; P, 9·4; Re, 28·2%).

(*d*) A benzene solution (100 c.c.) of tetrachlorobistriphenylphosphinerhenium(IV) (III) (0·17 g.) and diethylphenylphosphine (1·3 g., large excess) was refluxed for 4 hr. and then cooled. The free phosphines (excess diethylphenylphosphine, and triphenylphosphine) were extracted four times with concentrated hydrochloric acid (50 c.c.) and the benzene solution then washed thrice with water (100 c.c.), and dried (Na_2SO_4). Evaporation at 11 mm. and crystallisation of the residue (0·13 g.) from benzene–light petroleum (b. p. 40—60°) gave (I). Its i.r. spectrum was identical with those of the products from (*a*), (*b*), and (*c*).

Tetrabromobis(diethylphenylphosphine)rhenium(IV) (II).—Bis(diethylphenylphosphonium) hexabromorhenate(IV) (VII, see below) (0·05 g.) was heated for 18 hr. as for (I) [(*b*), above], and the product was extracted with benzene (2 c.c.). The extract was passed through a chromatographic column of Woelm alumina (grade I, acid; 1 cm. × 12·5 cm.) and the resultant purple band eluted with dry benzene; evaporation gave a crystalline residue (0·027 g.). This, recrystallised from benzene–light petroleum (b. p. 30—40°), yielded prisms of *compound* (II) (Found: C, 29·0; H, 3·8. $C_{20}H_{30}Br_4P_2Re$ requires C, 28·7; H, 3·6%).

Tetrachlorobistriphenylphosphinerhenium(IV) (III).—A benzene solution (500 c.c.) of *trans*-oxotrichlorobistriphenylphosphinerhenium(V) [1] (2 g., 1 mol.) was boiled, with stirring, for 1 hr. with titanous chloride solution (15% w/v, 5·0 c.c., 2·6 mol.) in concentrated hydrochloric acid (50 c.c.) and water (50 c.c.). The benzene layer was then separated, washed thrice with water (200 c.c.), and dried (Na_2SO_4). Light petroleum (b. p. 100—120°; 50 c.c.) was then added and the solution evaporated at 11 mm. pressure to *ca.* 70 c.c. and kept overnight in the refrigerator. The reddish-violet precipitate (0·2 g.) was recrystallised from benzene–light

bromopicrin (XI) derived from the picric acid (XII). Barium carbonate obtained from the carboxyl group of the lactone has 97·5% of the specific activity of the barium carbonate derived from quantitative Van Slyke–Folch [13] oxidation of the lactone itself. When account is taken of the relative contribution of C-6 to the lactone-carboxyl group, the inactivity of C-5 and C-7, and the numbers of carbon atoms involved, C-6 is found to possess 32·5% of the activity of the lactone.

By oxidative degradation of stipitatic acid, Bentley [6] obtained aconitic acid.[14] This was oxidized to malonic and oxalic acid, thus showing by difference that C-2 + C-6 possessed 56% of the activity when derived from [1-^{14}C]acetate-biosynthesized stipitatic acid. Consequently, C-2 in this acid must bear 20—25% of the activity (this range is given because decarboxylation [6,9] of [1-^{14}C]acetate-derived stipitatic acid suggests that C-8 has 3% of the activity of the metabolite). It is thus confirmed that C-2 of stipitatonic acid is derived from the carboxyl of acetate and that in the alkali-isomerizations of stipitatic (Ia; R = H) and decarboxylated stipitatic acid (V), C-1 *alone* is extruded to become a carboxyl group in 5-hydroxyisophthalic (IV) and *m*-hydroxybenzoic acid (VI), respectively. The effects of the hydroxyl and carboxyl groups (as anions) on the course of these rearrangements are considered in the Addendum of this paper.

In order to assay C-2 + C-4, the lævulic acid (X) was converted into iodoform and this was eventually counted as barium carbonate after Van Slyke–Folch oxidation.[13] The specific activity of the iodoform-derived barium carbonate was 95·4% of that of the lactone-derived barium carbonate. At this stage it is established that C-2, C-4, C-5, and C-7 make equal contributions to the iodoform-carbon atom. As C-5 and C-7 are unlabelled, and in view of the number of carbon atoms involved, C-2 and C-4 have an average activity of 31·8% of that of the lactone. Bentley [6] found C-4 to possess 41% of the activity of the [1-^{14}C]acetate-derived stipitatic acid. This figure is essentially compatible with that determined above and demands that C-2 contributes ~25% of the activity of the skeletal carbons of stipitatic acid. On the other hand, Richards and Ferretti [7,8] found that C-2 + C-6 had 76 ± 12% and C-4 24 ± 14% of the activity of [1-^{14}C]acetate-derived puberulonic acid while C-8 and C-9 were unlabelled.

The values obtained above for C-2, C-4, and C-6 may, of course, be interpreted in terms of equality of labelling of these three positions. This is in accord with the equality of labelling of the corresponding positions in [1-^{14}C]acetate-derived 6-methylsalicylic acid (XIII) studied under a variety of conditions by Birch *et al.*[15] Birch and his co-workers [16] have also shown that the three labelled positions of [1-^{14}C]acetate-derived penicillic acid (XIV) are equally labelled; thus the three corresponding positions in the nucleus of orsellinic acid (XV) must be equally labelled, Mosbach [17] having established that orsellinic acid is the precursor of penicillic acid in *P. barnense* cultures. Further, Mosbach [18] has demonstrated the participation of malonate (malonyl-coenzyme A) and acetate (acetyl-coenzyme A) in the biosynthesis of orsellinic acid as in fatty acid biosynthesis. More recently, Birkinshaw and Gowlland [19] have shown that in [1-^{14}C]-acetate-derived orsellinic acid from *P. madriti* the labelling is equally distributed among four of the eight carbon atoms, consistently with its production by the head-to-tail linkage of four acetyl-coenzyme A units. Their results with [1-^{14}C]butyrate show breakdown to C_2 units before incorporation, as required for participation [18] of malonyl-coenzyme A. Bentley [20] has demonstrated a similar role of malonate in stipitatonic acid biosynthesis.

[13] Van Slyke and Folch, *J. Biol. Chem.*, 1940, **136**, 509; Calvin, Heidelberger, Reid, Tolbert, and Yankwich, "Isotopic Carbon," J. Wiley and Sons, Inc., New York, 1949, p. 93.
[14] Corbett, Johnson, and Todd, *J.*, 1950, 147.
[15] Birch, Cassera, and Rickards, *Chem. and Ind.*, 1961, 792.
[16] Birch, Blance, and Smith, *J.*, 1958, 4582.
[17] Mosbach, *Acta Chem. Scand.*, 1960, **14**, 457.
[18] Mosbach, *Naturwiss.*, 1961, **15**, 525.
[19] Birkinshaw and Gowlland, *Biochem. J.*, 1962, **84**, 342.
[20] Bentley, *Fed. Proc.*, 1961, **20**, 80.

TABLE 3.

N.m.r. spectra of the violet complex and its constituents.

Compound	Positions of bands: τ values	Multiplicity	Assignments	Positions of bands: τ values	Multiplicity	Assignments
trans-[$ReOCl_3(PEt_2Ph)_2$]	8·80	Multiplet	4 × CH_3	2·58	Multiplet	Phenyl-*H*'s
	7·34	,,	4 × CH_2	2·38	,,	,,
trans-[$ReCl_4(PEt_2Ph)_2$]	8·83	Very weak		0·42	Broad singlet	
	6·43	,,		−3·19	Triplet	
	3·96	,,		−4·70	Broad singlet	
Violet complex.....	8·82	Multiplet	4 × CH_3	0·50	,,	
	7·37	,,	4 × CH_2	−3·04	Triplet	
	2·61	,,	Phenyl-*H*'s	−4·50	Broad singlet	
	2·33	,,	,,			

light petroleum (b. p. 40—60°) to the chloroform extract caused precipitation of green crystals (0·91 g.) which were recrystallised from *o*-dichlorobenzene–light petroleum (b. p. 40—60°), to give needles of *compound* (IV) (Found: C, 30·7; H, 3·85. $C_{20}H_{30}Br_3OP_2Re$ requires C, 31·0; H, 3·9%). The i.r. spectrum showed a characteristic strong doublet at 997, 977 cm.$^{-1}$, indicative of ν(Re=O).[1] The complex was a non-conductor in nitrobenzene and was diamagnetic in the solid state. Recrystallisation of (IV) from boiling methanol gave *oxomethoxydibromobis(diethylphenylphosphine)rhenium*(V) (V) as needles (Found: C, 34·8; H, 4·6. $C_{21}H_{33}Br_2O_2P_2Re$ requires C, 34·8; H, 4·6%). It had a strong band in its i.r. spectrum at 942 cm.$^{-1}$, indicative of an oxoalkoxy-complex, and no absorption at *ca.* 910 cm.$^{-1}$, indicating that the alkoxy-group was methoxy.[1]

Bis(diethylphenylphosphonium) Hexachlororhenate (IV) (VI).—To a mixture of dipotassium hexachlororhenate(IV) (0·2 g.),[8] concentrated hydrochloric acid (3 c.c.), and water (2 c.c.), was added ethanol (25 c.c.) followed by diethylphenylphosphine (1·0 g.), and the resultant suspension was refluxed for 7 hr., and then filtered hot. The pale green residue (0·29 g.) was washed with ethanol and recrystallised from dimethylformamide–diethyl ether to give needles of the *salt* (VI) (Found: C, 32·5; H, 4·4; P, 8·2. $C_{20}H_{32}Cl_6P_2Re$ requires C, 32·75; H, 4·4; P, 8·45%). The i.r. spectrum showed a band at 2433 cm.$^{-1}$, assignable to ν(P–H), and a 0·01% w/v nitrobenzene solution at 19° had a molar conductivity of 18·5 mhos.

Bis(diethylphenylphosphonium) Hexabromorhenate(IV) (VII).—(*a*) A similar procedure to that described above for (VI), but with dipotassium hexabromorhenate(IV) [8] (0·2 g.), gave the yellow microcrystalline *salt* (VII) (0·09 g.) (Found: C, 24·2; H, 3·2; P, 6·1. $C_{20}H_{32}Br_6P_2Re$ requires C, 24·1; H, 3·0; P, 6·2%). The i.r. spectrum showed absorption at 2412 cm.$^{-1}$, assignable to ν(P–H), and a 0·015% w/v nitrobenzene solution at 19° had a molar conductivity of 32·3 mhos.

(*b*) A suspension of *cis*-oxotribromobis(diethylphenylphosphine)rhenium(V) (IV) (0·125 g.) in ethanol (25 c.c.) and concentrated hydrobromic acid (5 c.c.) was refluxed until a clear golden-brown solution was obtained (5 min.), and was then evaporated to dryness at 11 mm. The residual gum was rapidly crystallised from methanol to give yellow crystals of (VII) (0·04 g.) (Found: C, 24·0; H, 3·25%).

(*c*) The yellow chloroform-insoluble material obtained during the preparation of *cis*-oxotribromobis(diethylphosphine)rhenium(V) (IV) was recrystallised from dimethylformamide–diethyl ether and gave crystals of (VII) (Found: C, 24·2; H, 3·2%).

Bistetraphenylarsonium Hexachlororhenate(IV) (VIII).—A suspension of the salt (VI) (0·2 g.) in concentrated hydrochloric acid (20 c.c.) was slowly heated to boiling and then water (20 c.c.) was added dropwise. The resultant solution was cooled and filtered, and an aqueous solution (2 c.c.) of tetraphenylarsonium chloride (0·25 g.) added with vigorous agitation. The resultant suspension was heated to boiling, filtered hot, and the residue of the *salt* (VIII) (0·25 g.) washed with water and dried over phosphorus pentoxide *in vacuo* (Found: C, 49·5; H, 3·7. $C_{48}H_{40}As_2Cl_6Re$ requires C, 49·5; H, 3·5%). The molar conductivity of a 0·126% w/v nitrobenzene solution at 19° was 47·3 mhos.

Oxotrichlororhenium(V) *Complexes by Ligand Displacement.—Oxotrichlorobis(diethylphenylphosphine)rhenium*(V).[1] A suspension of *trans*-oxotrichlorobistriphenylphosphinerhenium(V) [1]

[8] Hurd and Reinders, *Inorg. Synth.*, 1939, **1**, 178; Brauer and Allardt, *Z. anorg. Chem.*, 1962, **316**, 134.

(1·6 g.) in benzene (400 c.c.) containing diethylphenylphosphine (1·34 g.) was allowed to stand at room temperature for 16 hr. and the resultant green solution was evaporated at 11 mm. The residue was extracted with cold methanol, to remove yellow trichlorotris(diethylphenylphosphine)rhenium(III), and the remaining green product (0·9 g.) was recrystallised from benzene–light petroleum (b. p. 40—60°), to yield prisms of *trans*-oxotrichlorobis(diethylphenylphosphine)rhenium(V),[1] m. p. 166—169° (decomp.) (Found: C, 37·9; H, 4·9; O, 3·1; Cl, 16·3. Calc. for $C_{30}H_{30}Cl_3OP_2Re$: C, 37·5; H, 4·7; O, 2·5; Cl, 16·6%).

cis- *and* trans-*Oxotrichlorobistriethylphosphinerhenium*(V).[1] (*a*) A suspension of *trans*-oxotrichlorobistriphenylphosphinerhenium(V) (2 g.) in benzene (300 c.c.) containing triethylphosphine (1·13 g.) was kept for 16 hr. at room temperature and the resultant green solution was washed six times with concentrated hydrochloric acid (50 c.c.), to remove the excess of triethylphosphine and the displaced triphenylphosphine, and then washed four times with water (200 c.c.). The dried solution (Na_2SO_4) was evaporated at 11 mm. and the residue extracted with ether. The extract was concentrated to give chunky prisms (0·19 g.) of the *trans*-isomer, m. p. 164—174° (decomp.) (Found: C, 26·4; H, 5·6; O, 2·9. Calc. for $C_{12}H_{30}Cl_3OP_2Re$: C, 26·45; H, 5·55; O, 2·95%). Crystallisation from acetone of the ether-insoluble residue (0·38 g.) gave needles (0·22 g.) of the *cis*-isomer, m. p. 126—129° (decomp.) (Found: C, 27·0; H, 5·6; O, 3·05%).

(*b*) Procedure (*a*) above, but with omission of the hydrochloric acid extraction, gave only the *cis*-isomer (0·58 g.) which crystallised as needles (0·35 g.) from acetone (Found: C, 26·3; H, 5·55%).

cis- *and* trans-*Oxotrichlorobistri-n-propylphosphinerhenium*(V). Use of procedure (*a*) (above), but using tri-n-propylphosphine (2·34 g.), gave, after evaporation of the benzene, a greenish-blue mixture of isomers (2·35 g.). Extraction with light petroleum (b. p. 40—60°) and subsequent concentration gave green prisms (0·61 g.) of *trans*-oxotrichlorobistri-n-propylphosphinerhenium(V),[1] m. p. 130—134° (decomp.).

TABLE 4.

Dipole moments.

Compound	10^3w	$\Delta\varepsilon/w$	$10^2\Delta n/w$	$-\Delta v/w$	Compound	10^3w	$\Delta\varepsilon/w$	$10^2\Delta n/w$	$-\Delta v/w$
(I)	3·538	0·566	—	—	(IV)	2·667	17·78	—	—
	2·870	0·570	—	—		2·858	17·67	—	(0·61)
	18·52	—	8·66	—	(IX)	1·221	19·502	—	—
	19·48	—	9·85	—		1·393	19·508	—	(0·56)
	4·716	—	—	0·513	(X)	2·407	16·810	—	—
	3·972	—	—	0·579		2·670	16·625	—	(0·56)

Compound	$_TP$	$_EP$	$_OP$	μ (±0·1D)	Compound	$_TP$	$_EP$	$_OP$	μ (±0·1D)
(I)	182·9	145·7	15·3	0·87	(IX)	2421·6 *	(144·6)	2255·3 *	10·5 *
(IV)	2710 *	(160)	2527 *	11·1 *	(X)	2248·2 *	(134·8)	2093·2 *	10·1 *

* Calculated by using the estimated values of densities and refractivities shown in parentheses.[9]

The residue remaining from the light-petroleum extraction, recrystallised from acetone, gave blue needles (0·54 g.) of cis-*oxotrichlorobistri-n-propylphosphinerhenium*(V) (IX) (Found: C, 34·6; H, 6·6; O, 2·8. $C_{18}H_{42}Cl_3OP_2Re$ requires C, 34·4; H, 6·7; O, 3·5%).

cis-*Oxotrichlorobis(dimethylphenylarsine)rhenium*(V) (X).—Use of procedure (*a*) above, but using dimethylphenylarsine (1·6 g.), gave a blue product (0·15 g.) on concentration of the carbon-treated ether extract. This was added to the residue (1·0 g.) remaining from the ether extraction, and the whole was recrystallised from acetone to give needles of *compound* (X) (0·85 g.) (Found: C, 29·05; H, 3·4; O, 3·4. $C_{16}H_{22}As_2Cl_3ORe$ requires C, 28·6; H, 3·3; O, 2·4%). The i.r. spectrum showed a very strong doublet at 984 and 989 cm.$^{-1}$ indicative of Re=O.[1]

Dipole Moments.—The method of determination and the significance of the symbols in Table 4 are given in ref. 9.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, HEAVY ORGANIC CHEMICALS DIVISION,
AKERS RESEARCH LABORATORIES, THE FRYTHE,
WELWYN, HERTS.

[*Received, March 21st,* 1963.]

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