

204. *Amine, Phosphine, Arsine, and Stibine Complexes of Rhenium-(III), -(IV), and -(V).*

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Two products, both originally formulated as trichlorobis(triphenylphosphine)rhenium(III), have been shown to contain oxygen and to be oxotrichlorobis(triphenylphosphine)rhenium(V) and trichlorobis(triphenylphosphine oxide)rhenium(III). The complexes $(\text{ReOX}_3\text{L}_2)$ ($\text{X} = \text{Cl}$ or Br ; $\text{L} = \text{AsPh}_3$ or SbPh_3) have been prepared by using similar reaction conditions as for $[\text{ReOCl}_3(\text{PPh}_3)_2]$. Products thought to be dihalides $[\text{ReX}_2(\text{PPh}_3)_2]$ are shown to be ethoxo-compounds of $[\text{ReOX}_2(\text{OEt})(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}$, Br , or I). The interaction of the latter or $\text{ReOX}_3(\text{PPh}_3)_2$ with pyridine gives salts of the ion $[\text{ReO}_2\text{py}_4]^+$; these and similar ethylenediamine complexes are considered to have a *trans* O=Re=O grouping.

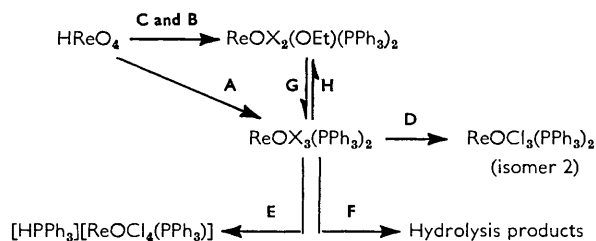
It has been shown¹ that the purple-red² and yellow³ products, both of which were originally described as trichlorobis(triphenylphosphine)rhenium(III), contain oxygen and are, respectively, trichlorobis(triphenylphosphine oxide)rhenium(III) and oxotrichlorobis(triphenylphosphine)rhenium(V); no complexes of the latter type had been reported

¹ Lock and Wilkinson, *Chem. and Ind.*, 1962, 40.

² Colton, Levitus, and Wilkinson, *J.*, 1960, 4121.

³ Freni and Valenti, *J. Inorg. Nuclear Chem.*, 1961, 16, 240.

previously and oxotrichlororhenium(v) has not been prepared. A number of other rhenium complexes, claimed to contain Re(II) or Re(III), were prepared by similar methods to, or directly from, $[\text{ReOCl}_3(\text{PPh}_3)_2]$. It was probable that these were also incorrectly formulated and all have been re-examined. Similar conclusions concerning the nature of Freni and Valenti's products were reached independently⁴ and a more extended account dealing mainly with the more soluble diethylphenylphosphine complexes appeared recently.⁵ Details are given here of our work on the substituted oxohalide complexes and on some amine complexes, containing the ions $[\text{ReO}_2\text{py}_4]^+$ and $[\text{ReO}_2\text{en}_2]^+$, derived from them. Reaction schemes for the preparation of the compounds are given in the Figure, and the compounds investigated are listed in Tables 1 and 2.



- A. Ethanol, triphenylphosphine, and hydrohalic acid (X = Cl).
 B. Ethanol, triphenylphosphine, and hydrohalic acid (X = Br or I).
 C. Ethanol, triphenylphosphine, and hydrazine hydrochloride (X = Cl).
 D. Boiling acetone.
 E. Benzene solution and hydrogen chloride.
 F. Dichloromethane solution and water (X = Cl, Br, or I).
 G. Dichloromethane solution and hydrohalic acid (X = Cl, Br, or I).
 H. Ethanol (X = Cl, Br, or I).

TABLE 1.

Infrared spectra of rhenium complexes (Nujol mulls in cm^{-1}).

Complex	Isomer	$\nu(\text{Re}=\text{O})$	Other bands
$[\text{ReOCl}_3(\text{PPh}_3)_2]$	1	969vs	
	2	981vs	
	3	986vs	
$[\text{ReOBr}_3(\text{PPh}_3)_2]$		981vs	
$[\text{ReOI}_3(\text{PPh}_3)_2]$		982vs	
$[\text{ReOCl}_3(\text{AsPh}_3)_2]$		967vs	
$[\text{ReOBr}_3(\text{AsPh}_3)_2]$		980vs, 974sh	
$[\text{ReOCl}_3(\text{SbPh}_3)_2]$		976vs	
$[\text{ReOBr}_3(\text{SbPh}_3)_2]$		969, 973vs	
$[\text{ReOCl}_2(\text{OMe})(\text{PPh}_3)_2]$	{	948vs	
	{	939vs *	
$[\text{ReOBr}_2(\text{OMe})(\text{PPh}_3)_2]$	{	944vs, 933sh	
	{	938vs *	
$[\text{ReOI}_2(\text{OMe})(\text{PPh}_3)_2]$	{	944sh, 931vs	
	{	931vs *	
$[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$	1	949s	909vs δOCH_2
	2	953s	910vs "
$[\text{ReOBr}_2(\text{OEt})(\text{PPh}_3)_2]$		960s	911vs "
$[\text{ReOI}_2(\text{OEt})(\text{PPh}_3)_2]$		947s	903vs "
$[\text{HPPH}_3][\text{ReOCl}_4(\text{PPh}_3)]$		979vs	2405m, $\nu(\text{P}-\text{H})$
$[\text{ReCl}_3(\text{Ph}_3\text{PO})_2]$			1137vs $\nu(\text{P}=\text{O})$
$[\text{ReCl}_3(\text{Ph}_3\text{PO})]_n$			1143vs "
$[\text{ReCl}_3(\text{Ph}_3\text{AsO})]_n$			850sb $\nu(\text{As}=\text{O})$

* Measured in dichloromethane solution.

Oxotrichlorobis(triphenylphosphine)rhenium(v) and Related Compounds.—In view of the unreliability of standard methods of direct oxygen analysis for phosphorus-containing

⁴ Chatt and Rowe, *Chem. and Ind.*, 1962, 92.⁵ Chatt and Rowe, *J.*, 1962, 4019.

TABLE 2.

Infrared stretching frequencies for octahedral dioxo- and related compounds between 800 and 990 cm^{-1} .

Compound	$\nu_{\text{M=O}}$	$\delta\text{-OH}$	Others	Reference
$[\text{Re}(\text{py})_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$	814vs			a
$[\text{Re}(\text{py})_4\text{O}_2]\text{Br}\cdot 2\text{H}_2\text{O}$	819vs			a
$[\text{Re}(\text{py})_4\text{O}_2]\text{I}\cdot \text{H}_2\text{O}$	824vs			a
$[\text{Re}(\text{py})_4\text{O}_2]_2\text{PtCl}_6\cdot 4\text{H}_2\text{O}$	816vs			a
$[\text{Re}(\text{py})_4\text{O}_2]\text{BPh}_4$	812vs			a
$[\text{Re}(\text{en})_2\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$	814vs		879vw, 894w	a
$[\text{Re}(\text{en})_2\text{O}_2]\text{I}$	819vs		874w, 882w	a
$[\text{Re}(\text{en})_2\text{O}\cdot\text{OH}](\text{ClO}_4)_2$	981m	929w	873vw, 884w	a
$[\text{Re}(\text{en})_2(\text{OH})_2](\text{ClO}_4)_2\text{Cl}$		927m	894vw, 887w	a
$[\text{Re}(\text{en})_2(\text{OH})_2]_2[\text{PtCl}_6]_3$			880w, 890w	a
$\text{MoO}_2(\text{acac})_2$	906vs		935vs	a
$\text{K}_3[\text{ReO}_2(\text{CN})_4]$	780vs, br			a
$\text{Cs}_2[\text{RuO}_2\text{Cl}_4]$	814, 824			b
$\text{K}_2[\text{OsO}_2(\text{OH})_4]$	790vs			c
$\text{K}_2[\text{OsO}_4(\text{OH})_2]$	815			d
$\text{K}_2[\text{OsO}_2\text{Cl}_4]$	837			d
$\text{Cs}_2[\text{OsO}_2(\text{CN})_4]$	830vs			c
$\text{K}_2[\text{OsO}_2(\text{C}_2\text{O}_4)_2]$	824			d
$[\text{OsO}_2(\text{NH}_3)_4]\text{Cl}_2$	808			d
$\text{K}_2[\text{OsO}_2(\text{OH})_4(\text{NO}_2)_2]$	883s *			c
$\text{K}_2[\text{OsO}_2(\text{OCH}_3)_4]$	820br			d
$\text{K}_2[\text{OsO}_2(\text{NO}_3)(\text{NO}_2)_3]$	871s *			c

* These compounds contain other strong bands in the 800—900 cm^{-1} region. It is possible that these bands were incorrectly assigned.

a, This work. b, Woodhead and Fletcher, United Kingdom Atomic Energy Authority Report AERE-R 4123, Harwell, Dec. 1962. c, Griffith, J., 1962, 3248. d, Griffith, J., 1964, 245.

compounds,⁶ the initial evidence for the re-formulation of Freni and Valenti's " $\text{ReCl}_3(\text{PPh}_3)_2$ " was the presence in the infrared spectrum of a strong band at 969 cm^{-1} , which did not occur in authentic $(\text{ReCl}_3, \text{PPh}_3)_2$. This band was in the region where M=O stretching frequencies are normally found.⁷

It was not possible to prepare Freni and Valenti's compound by the direct interaction of hexachlorodirhenium(III) with triphenylphosphine in acetone solution. However, old samples of hexachlorodirhenium(III), which had been exposed for some weeks, on extraction with acetone immediately gave a green solution. This was separated from the residual hexachlorodirhenium(III), which dissolved much more slowly giving a red solution. The green solution probably contained the unknown oxotrichlororhenium(v), and on treatment with triphenylphosphine gave oxotrichlorobis(triphenylphosphine)rhenium(v). The oxohalide could not be isolated. Boiling solutions of hexachlorodirhenium(III) in acetone or diethyl ether when treated with dry oxygen were unchanged after 4 days.

Using the original procedure³ of the interaction of triphenylphosphine, per-rhenic acid, and halogen acid in ethanol, we could only isolate the yellow oxotrichloride $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (isomer I) (reaction A); the tribromo- and the tri-iodo-complexes were so readily ethanolised that the reaction gave the ethoxides (reaction B), or methoxides if methanol was used as the solvent. It was shown also that if the quantity of hydrochloric acid used in the preparation of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ was reduced below that recommended,³ the compound when ethanolised gave first a green isomer of $[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$ and when heated further a purple isomer. A study of the pure oxotrihalide complexes showed that it was necessary to boil the trichloro-compound in ethanol for about 2 hours for complete reaction, whereas complete conversion of the tri-iodo-complex was obtained by merely washing it with warm ethanol. For all three halides, however, only one halogen atom

⁶ Oliver, in "Comprehensive Analytical Chemistry," ed. Wilson and Wilson, Elsevier, New York, 1960, Vol. IB, p. 577.

⁷ Barraclough, Lewis, and Nyholm, J., 1959, 3552.

could be replaced on boiling with ethanol, so that evidently one halogen atom of the trihalide is far more labile than the other two; it was assumed that this is the halogen atom *trans* to the oxygen atom bound to the rhenium.

The infrared spectra of the alkoxo-compounds show the strong $\nu(\text{Re}=\text{O})$ band seen in the oxotrihalide complexes, but at a slight lower frequency. The ethoxo-compounds have an additional band at about 910 cm^{-1} which is not present in either the trihalide or the methoxo-compounds and has been assigned to the $\delta(\text{OCH}_2)$ vibration.⁵

It was suggested³ that the interaction of the "dihalides" (*i.e.*, the ethoxo-complexes) with the corresponding halogens in benzene solution gave the "trihalides" (*i.e.*, the oxotrihalogeno-complexes). However, on treatment with halogens in benzene solution the dihalogenoethoxo-complexes gave only tars, and on recrystallisation from hydroxylic solvents the products showed strong bands in the infrared spectra characteristic of triphenylphosphine oxide.⁸ Although the solid dihalogenoethoxo-compounds do not react with aqueous halogen acids, when dissolved in dichloromethane they do so smoothly, and completely when shaken with the 1 : 1 aqueous halogen acid. Green (chloride and bromide) or red (iodide) dichloromethane solutions were obtained, which on evaporation or addition of petroleum yielded the crystalline oxotrihalogeno-complexes. The dichloromethane solutions differed in colour from the solid, and it is possible that this was caused by the presence of protonated products in the presence of excess of acid. A solution of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (yellow) in benzene gave a precipitate of the green salt $[\text{HPPH}_3][\text{ReOCl}_4(\text{PPh}_3)]$ when treated with dry hydrogen chloride. When the dichloromethane solutions were washed with water, hydrolysis occurred to give red (Cl and Br) or purple (I) solutions. Brown solids were isolated from the chloride and bromide solutions by precipitation with petroleum and purple crystals from the iodide solution on evaporation, but analyses were unsatisfactory. The infrared spectra of these compounds indicated the presence of hydroxyl groups.

Oxotrichlorobis(triphenylphosphine)rhenium(v) and the bromine analogue were more readily prepared by using cold glacial acetic acid as the solvent. In this solvent the following compounds $[\text{ReOX}_3\text{L}_2]$ ($\text{X} = \text{Cl}$ or Br ; $\text{L} = \text{PPh}_3$, AsPh_3 , or SbPh_3) were obtained; BiPh_3 did not react.

Two further isomers of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ have been prepared. A green insoluble isomer was precipitated when a solution of the yellow isomer in acetone or dichloromethane was heated under reflux for some hours. The third possible isomer was prepared as insoluble yellow plates when solutions of perrhenic acid in dilute hydrochloric acid, hydrazine hydrochloride in water, and triphenylphosphine in ethanol, were mixed and heated under reflux. The product was identified by its carbon, hydrogen, nitrogen, and oxygen analyses and the characteristic $\nu(\text{Re}=\text{O})$ band of its infrared spectrum. It should be noted that this compound was prepared under the same conditions as Chatt *et al.*⁹ used in the preparation of $[\text{ReCl}_2\text{N}(\text{PPh}_3)_2]$ except that perrhenic acid was substituted for sodium perrhenate.

Freni and Valenti reported³ that the "dihalides" were paramagnetic in solution with a magnetic moment corresponding to one unpaired electron. All complexes of rhenium(v) examined by us were diamagnetic as the solid and in solution. Octahedral complexes of a d^2 ion should be paramagnetic with two unpaired spins. The X-ray structure of oxotrichlorobis(diethylphenylphosphine)rhenium(v) has shown that the M-O bond is almost a triple bond.¹⁰ This will be made up of a σ bond between the p_z orbital of the oxygen and one of the sp^3d^2 hybrid orbitals on the metal, and two π -bonds between the oxygen p_x and p_y orbitals and the d_{xz} , d_{yz} orbitals on the metal. This will introduce a distortion into the t_{2g} levels, increasing the energy of the d_{xz} , d_{yz} orbitals and consequently

⁸ Horner and Tyree, *Inorg. Chem.*, 1962, 1, 122.

⁹ Chatt, Garforth, and Rowe, *Chem. and Ind.*, 1963, 332.

¹⁰ Ehrlich and Owston, "Proc. 7th Internat. Conf. Co-ordination Chemistry," Stockholm and Uppsala, Sweden, 1962, p. 223.

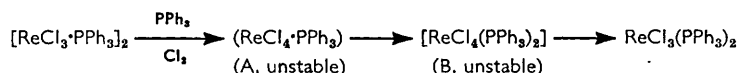
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lowering the energy of the d_{xy} orbital, giving a diamagnetic species. Lott and Symons¹¹ have explained the diamagnetism observed in octahedral osmyl complexes in this way.

A summary of the infrared data of these compounds is given in Table I.

Trichlorobis(triphenylphosphine oxide)rhenium(III) and Related Compounds.—The infrared spectrum of the compound formulated by Colton *et al.*² as $[\text{ReCl}_3(\text{PPh}_3)_2]$ showed it to be a complex of triphenylphosphine oxide. A band, characteristic of co-ordinated triphenylphosphine oxide, was observed at about 1130 cm^{-1} . A further very strong band was observed at 720 cm^{-1} in addition to the two bands at 685 and 740 cm^{-1} which also occur in triphenylphosphine complexes. The compound was shown not to be a mixed phosphine–phosphine oxide complex, as the band at 1090 cm^{-1} , characteristic of triphenylphosphine, was missing. No bands were observed in the regions 3100 and 780 – 1000 cm^{-1} showing that $=\text{O}$, $-\text{OH}$, and OH_2 groups were absent. On the basis of the spectrum and the analyses, the compound was re-formulated as trichlorobis(triphenylphosphine oxide)rhenium(III). Subsequently, trichloro(triphenylphosphine oxide)rhenium(III) (in good yield) and trichlorobis(triphenylphosphine oxide)rhenium(III) (in poor yield) were made by the interaction of triphenylphosphine oxide and hexachlorodirhenium(III) in acetone. The infrared spectra of these compounds were identical with that of Colton's compound.

Colton² suggested a reaction scheme:



Both the intermediates have now been prepared (A, this work; B, see ref. 12) and have been shown to be stable compounds. A more probable mechanism is the chlorination of the phosphine and subsequent hydrolysis to the phosphine oxide, a reaction that is well known.¹³ The hydrolysis probably occurs by reaction with water. Colton stated that the reaction was complete in 30 minutes. We found that in acetone, dried with molecular sieve, complete reaction took up to 14 hours in air. However, the addition of a few drops of water shortened the reaction time to a few minutes. It was not possible to decide why this reaction gave good yields of the bis(phosphine oxide) complex, when direct reaction of triphenylphosphine oxide with hexachlorodirhenium(III) gave very poor yields of the bis(phosphine oxide) complex, but work on this is continuing.

Triphenylarsine oxide with hexachlorodirhenium(III) under the conditions used for triphenylphosphine oxide gave only the monosubstituted trichloro(triphenylarsine oxide)rhenium(III) as a red polymer. The infrared spectrum showed a strong broad band at 850 cm^{-1} , characteristic of co-ordinated arsine oxide.⁸ Similar compounds were also obtained with triphenylarsine and triphenylphosphine as ligands. The complex with the latter ligand, $[\text{ReCl}_3 \cdot \text{PPh}_3]_2$, has been claimed to be monomeric² and a rather unusual d^3s tetrahedral co-ordination had to be invoked to explain the diamagnetism of the compound. We have prepared the compound by a number of different methods and have shown that in benzene it is a dimer, presumably having halogen bridges. In acetone, however, the compound is monomeric, and we postulate that this is because of the formation of an adduct, $[\text{ReCl}_3(\text{PPh}_3)(\text{acetone})]$; this will be five co-ordinate and can be diamagnetic if it has the trigonal bipyramidal structure.

The reaction of triphenylphosphine and pentachlororhenium(v) in dichloromethane or dry acetone gave a green, weakly paramagnetic substance ($\mu_{\text{eff}} = 1.2\text{ B.M.}$ at 298°K corrected for ligands), which was tetrachloro(triphenylphosphine)rhenium(IV). The substance was apparently polymeric, being insoluble in all common solvents.

¹¹ Lott and Symons, *J.*, 1960, 973.

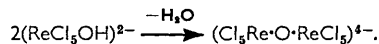
¹² Malatesta, "Advances in the Chemistry of Co-ordination Compounds," Proc. 6th Internat. Conf. Co-ordination Chemistry, ed. by S. Kirschner, Macmillan, New York, 1961, p. 475.

¹³ Kosolapoff, "Organophosphorus Compounds," Wiley, New York, 1950, p. 100.

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Dioxo-complexes of Rhenium.—Since hydrazine was found to exert a large catalytic effect on the ethanolsis of oxotrichlorobis(triphenylphosphine)rhenium(v), it seemed possible that pyridine might also catalyse the reaction without causing the subsequent decomposition observed in the hydrazine reaction. However, the reaction of pyridine with the complex followed a different course and an orange product was obtained, which could be precipitated from pyridine solution by addition of diethyl ether. The product, which was a 1 : 1 salt (from its conductivity in water), was shown from the analytical results to be $[\text{Re py}_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ or $[\text{Re py}_4(\text{OH})_4]\text{Cl}$. The material could not be dehydrated *in vacuo* at 105° and showed no $\text{Re}=\text{O}$ stretch in the usually accepted diagnostic region of $900\text{--}1100\text{ cm}^{-1}$.⁷ A compound $[\text{Re py}_4\text{O}_2]\text{Cl}$ had been reported by Russian workers,¹⁴ but since that compound was formulated only on the basis of rhenium, nitrogen, and chlorine analyses it seemed possible that it might be identical with our compound and that both might be the eight-co-ordinate hydroxo-species. Griffith *et al.*¹⁵ had already suggested that $[\text{MoO}_2(\text{CN})_4]^{4-}$ should be re-formulated as $[\text{Mo}(\text{OH})_4(\text{CN})_4]^{4-}$. Nuclear magnetic resonance examination of an acetone solution of the salt, which showed it was diamagnetic, was otherwise inconclusive. A peak of relative intensity corresponding to about 4 protons was found in the region in which either H_2O or OH could occur. Analogous bromide, iodide, hexachloroplatinate(IV), and tetraphenylborate salts of the pyridine-containing cation and a similar hydrated ethylenediamine complex salt as the chloride were prepared, the latter by substituting ethylenediamine for pyridine in the initial reaction with $[\text{ReOCl}_3(\text{PPh}_3)_2]$. The bromide, hexachloroplatinate, and ethylenediamine complex all had two molecules of water per cation grouping, but the iodide was a monohydrate and the tetraphenylborate was anhydrous. None of these salts gave infrared absorptions in the $\text{Re}=\text{O}$ diagnostic region ($900\text{--}1100\text{ cm}^{-1}$).⁷

There was a possibility that, in the case of the tetraphenylborate, a polymeric cation grouping existed, in which water had been eliminated but in which no $\text{Re}=\text{O}$ groupings had been formed, as is known for rhenium compounds,¹⁶ *e.g.*,



In the bridged oxo-species, the $\text{Re}-\text{O}$ stretching frequency is at 867 cm^{-1} .¹⁷ That such polymerisation had not occurred was proved by molecular-weight determinations. The molecular weight found (450) was in agreement with that for a 1 : 1 monomeric salt (425). A dimeric 1 : 2 salt would have required a molecular weight of 570 and even higher values would occur with greater polymerisation.

A more detailed examination of the infrared spectra of all these salts showed that there was a strong peak at 820 cm^{-1} which was not present in other compounds containing co-ordinated pyridine.¹⁸ This peak was assigned to the $\text{Re}=\text{O}$ stretch. Values of metal-oxygen stretching frequencies below the normal $\text{M}=\text{O}$ region⁷ have previously been observed in tetrahedral complexes.^{19,20}

The following argument and explanation is given in support of this assignment. The possibility of lowering of the $\nu(\text{Re}=\text{O})$ frequency, because of interaction with the water in the hydrates such as $[\text{Re py}_4\text{O}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$, can be discarded for the tetraphenylborate is anhydrous and yet absorbs at 812 cm^{-1} . It is postulated that the very low stretching frequency is a direct consequence of the linear $\text{O}\cdot\text{Re}\cdot\text{O}$ system. The infrared spectral data for a number of dioxo-complexes are presented in Table 2.

In a distorted octahedral rhenium system, $[\text{ReOCl}_3(\text{PPh}_3)_2]$, with a single oxygen atom,

¹⁴ Lebendinskii and Ivanov-Emin, *Zhur. neorg. Khim.*, 1959, **4**, 1762.

¹⁵ Griffith, Lewis, and Wilkinson, *J.*, 1959, 872.

¹⁶ Jezowska-Trzebiatowska, *Bull. Acad. polon. Sci. classe III*, 1954, **2**, 249.

¹⁷ Jezowska-Trzebiatowska, private communication.

¹⁸ Gill, Nuttall, Scaife, and Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

¹⁹ Lewis and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **6**, 12.

²⁰ Woodhead, Fletcher, and Deane, *J.*, 1961, 5041.

practically a triple bond existed between the metal and the oxygen,¹⁰ as noted previously. In a linear O·Re·O system both oxygen atoms will be competing for the d_{xz} and d_{yz} orbitals in order to form multiple bonds. We suggest that one oxygen will form a π -bond between its p_x orbital and the d_{xz} orbital on the metal, and the other a π -bond between its p_y orbital and the d_{yz} orbital on the metal. Instead of having an almost triple Re–O bond as in the phosphine complexes where the Re–O stretching frequency was 950–990 cm^{-1} , we have in these complexes at the most a double bond between the rhenium and the oxygen and the stretching frequency is lowered. Another effect which will also lower the stretching frequency depends on the other ligands present. Like the nitrido-cyanide of rhenium, discussed elsewhere,²¹ the orbitals normally used for back bonding to the ligands are now used in bonding to the oxygen. There is therefore no method of removing charge from the central metal atom other than weakening the metal–ligand σ bonds and the metal–oxygen bonds. For a very strong π -bond ligand such as cyanide, we would therefore expect considerable weakening of the Re–O bond, and this was observed, the Re=O stretching frequency dropping from $\sim 820 \text{ cm}^{-1}$ in the amine complexes of rhenium to 780 cm^{-1} in the dioxocyanorhenate(v) ion.

There is considerable evidence in support of the structure suggested for these ions. Only one band which can be assigned to an Re=O stretch is seen in the infrared spectrum, as would be expected for an ion of the suggested structure. If the oxygen atoms were in a *cis*-position there should be two infrared-active Re=O stretches. Griffith^{22,23} has shown that octahedral osmyl complexes of the type $(\text{OsO}_2\text{L}_4)^n$ also have Os=O stretching frequencies between 800 and 850 cm^{-1} and in this case the structure of two of these compounds, $\text{K}_2[\text{OsO}_2\text{Cl}_4]$ and $\text{K}_2[\text{OsO}_2(\text{OH})_4]$, have been shown by X-ray methods to be of this type.^{24,25} Furthermore, examination of the infrared spectrum of $[\text{Re en}_2\text{O}_2]^+$ salts in the region 850–900 cm^{-1} suggests that the ethylenediamine groups are *trans* rather than *cis* (based on Baldwin's criteria²⁶), which is in accord with the structure suggested.

If this explanation is accepted, it is possible to make certain other predictions which can be checked experimentally. In $[\text{ReOX}_3(\text{PPh}_3)_2]$ complexes it is not possible to protonate the oxygen atom because the electrons are delocalised in the triple bond. In these dioxo-complexes, however, each oxygen should have two lone pairs of electrons localised on the oxygen atom, and the oxygen should be easily protonated. Once one oxygen is protonated the *trans*-dioxo-system is destroyed and we shall revert to the system observed in the phosphine complexes of rhenium(v). The Re=O stretching frequency should increase to about 950 cm^{-1} and the second oxygen should be much more difficult to protonate. This also was observed experimentally (cf. Table 2). Further evidence has been provided by protonation studies on $[\text{ReO}_2 \text{en}_2]^+$ in which the first association constant has been measured but the second one is extremely small.²⁷

It is evident that the infrared diagnostic region for M=O stretching frequencies must now be extended downwards to at least 780 cm^{-1} .

One infrared assignment in Table 2 which is of interest is the Mo=O stretching frequency of dioxobis(propene-2,4-dionato)molybdenum(vi). If this compound is of the same structure as the other dioxo-complexes, the propene-2,4-dione groups will lie in the equatorial plane. The spectrum of the compound was compared with that of propene-2,4-dionatocopper(II), which is planar, and they were identical apart from the strong band at 906 cm^{-1} in the molybdenum complex. Nakamoto *et al.*²⁸ have examined the infrared

²¹ Lock and Wilkinson, *J.*, 1964, in the press.

²² Griffith, *J.*, 1962, 3248.

²³ Griffith, *J.*, 1964, 245.

²⁴ Kruze, *Acta Cryst.*, 1961, **14**, 1035.

²⁵ Porai-Koshits, Atovmyan, and Andrianov, *Zhur. Strukt. Khim.*, 1961, **2**, 743.

²⁶ Baldwin, *J.*, 1960, 4369.

²⁷ Murmann and Foerster, *J. Phys. Chem.*, 1963, **67**, 1383.

²⁸ Nakamoto, McCarthy, Ruby, and Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 1066; Nakamoto, McCarthy, and Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 1273; Nakamoto, Morimoto, and Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 4533.

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spectra of many propane-2,4-dione complexes of several different structural types. In all these compounds a band was observed at approximately 930 cm^{-1} , the upper and lower limits of this band being 944 and 921 cm^{-1} . No other bands were observed below this in the spectrum until much lower frequencies ($\sim 800\text{ cm}^{-1}$). The spectrum of $\text{MoO}_2\text{ acac}_2$ shows two very sharp strong bands in this region at 906 and 935 cm^{-1} . From the above observation it seems certain that the band at 935 cm^{-1} should be assigned to a propane-2,4-dione mode and that the 906 cm^{-1} band should be assigned to the $\text{Mo}=\text{O}$ stretch. This differs from previous work²⁹ where the 935 cm^{-1} band was assigned to the $\text{Mo}=\text{O}$ stretch.

EXPERIMENTAL

Analyses were performed by the Microanalytical Laboratories of Imperial College. Molecular weights were determined by the ebullioscopic method in benzene unless otherwise stated. Infrared spectra were performed on Nujol mulls and recorded on a Perkin-Elmer model 21 infrared spectrometer with sodium chloride optics. Magnetic moments were measured in the solid state by the Gouy method and in solution by the method of Evans on a Varian Associates model 3400B nuclear magnetic resonance spectrometer at 56.45 Mc/sec .

Oxodichloroethoxobis(triphenylphosphine)rhenium(IV) (Isomer 1).—Perrhenic acid (1.0 g.), hydrazine hydrochloride (1 g.), triphenylphosphine (3 g.), and ethanol (20 ml.) were boiled for about 1 min. The purple crystals were filtered off, recrystallised (dichloromethane-ethanol), and dried ($25^\circ/0.1\text{ mm.}$), giving the compound (2.6 g., 78%) (Found: C, 54.0; H, 4.3; Cl, 8.5%). The reaction time must be as short as possible as further reaction caused decomposition of the required product.

A more satisfactory preparation started with a suspension of oxotrichlorobis(triphenylphosphine)rhenium(V) (2.0 g.) in ethanol, which was boiled for about 2 hr. The purple crystals were collected, washed thoroughly with ethanol and dried ($40^\circ/0.1\text{ mm.}$), giving the compound, (1.8 g., 89%) m. p. 190° (decomp.) (Found: C, 54.2; H, 4.2; Cl, 8.2; OEt, 5.4%; M , 789. $\text{C}_{38}\text{H}_{35}\text{Cl}_2\text{O}_2\text{P}_2\text{Re}$ requires C, 54.2; H, 4.2; Cl, 8.4; OEt, 5.4%; M , 843). The compound was diamagnetic both as the solid and in solution.

Oxodichloroethoxobis(triphenylphosphine)rhenium(V) (Isomer 2).—Rhenium metal (5.0 g.) was dissolved in excess of hydrogen peroxide (30%), the solution was evaporated to dryness, the solid dissolved in concentrated hydrochloric acid (10 ml.), and the solution diluted with ethanol (50 ml.). A saturated solution of triphenylphosphine (25 g.) in hot ethanol was added to the solution of perrhenic acid heated under reflux, which was heated for a further 3 min. The green crystals were filtered from the hot solution, to give the compound (15.0 g., 65%). A portion was reprecipitated for analysis from cold benzene by addition of light petroleum (b. p. $30\text{--}40^\circ$) (Found: C, 54.2; H, 4.4%).

Conversion of Isomer 2 into Isomer 1.—Oxodichloroethoxobis(triphenylphosphine)rhenium(V) (isomer 2) (0.5 g.), dissolved in a mixture of benzene (25 ml.) and ethanol (5 ml.), was heated under reflux in a nitrogen atmosphere for 3 hr. The solution was cooled and filtered, to give purple plates of the compound (0.37 g., 74%) (Found: C, 53.5; H, 4.2%). The infrared spectrum of this compound was identical with that of $\text{ReOCl}_2\text{OEt}(\text{Ph}_3\text{P})_2$ (isomer 1).

Oxodibromoethoxobis(triphenylphosphine)rhenium(V).—Perrhenic acid (1.0 g.), concentrated hydrobromic acid (1 ml.), triphenylphosphine (5 g.), and ethanol (20 ml.) were boiled for about 5 min. The purple crystals were collected, recrystallised (dichloromethane-ethanol), and dried ($40^\circ/0.1\text{ mm.}$) giving the compound (3.1 g., 84%) m. p. 150° (decomp.) (Found: C, 49.2; H, 4.5; Br, 16.2; OEt, 4.9%; M , 912. $\text{C}_{38}\text{H}_{35}\text{Br}_2\text{P}_2\text{Re}$ requires C, 49.0; H, 3.8; Br, 17.2; OEt, 4.9%; M , 932). The solid was diamagnetic both as the solid and in dichloromethane solution.

Oxodiiodoethoxobis(triphenylphosphine)rhenium(V).—Perrhenic acid (1.0 g.), 45% hydriodic acid (2 ml.), triphenylphosphine (5 g.), and ethanol (20 ml.) were boiled for about 5 min. The green crystals were filtered off, recrystallised (dichloromethane-ethanol), and dried ($25^\circ/0.1\text{ mm.}$) giving the compound (3.1 g., 76%) m. p. 155° (decomp.) (Found: C, 44.3; H, 3.4; I, 24.3; OEt, 4.0%; M , 1034. $\text{C}_{38}\text{H}_{35}\text{I}_2\text{O}_2\text{P}_2\text{Re}$ requires C, 44.5; H, 3.4; I, 24.7; OEt, 4.4%; M , 1026). The compound was diamagnetic as the solid and in dichloromethane solution.

Oxotrichlorobis(triphenylphosphine)rhenium(V) (Isomer 1).—Method A. A boiling solution

²⁹ Larson and Moore, *Inorg. Chem.*, 1962, 1, 856.

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of triphenylphosphine (5 g.) in ethanol (10 ml.) was added to a boiling solution of perrhenic acid (1 g.) and concentrated hydrochloric acid (1 ml.) in ethanol (10 ml.), and the mixture boiled for 3—5 min. The *yellow crystals* were recrystallised (benzene), giving the *compound* (2.6 g., 78%) (Found: C, 51.0; H, 3.8. $C_{36}H_{30}Cl_3OP_2Re$ requires C, 51.9; H, 3.5; Cl, 12.8; O, 1.9%). The compound prepared by this method was sometimes contaminated with small amounts of oxodichloroethoxobis(triphenylphosphine)rhenium(v).

Method B. An alternative method was to shake a solution of either isomer of oxodichlorobis(triphenylphosphine)rhenium(v) in dichloromethane with 6*M*-hydrochloric acid (10 ml.) for 10 min. The green dichloromethane layer, which was carefully separated, started to deposit yellow crystals immediately; a large excess of light petroleum (b. p. 40—60°) was added to ensure complete precipitation. The *compound* was filtered off and dissolved in boiling benzene, and the hot solution was filtered and treated with excess of light petroleum (b. p. 40—60°). The solid was dried (40°/0.1 mm.), giving the *compound* (0.8 g., 79%), m. p. 200° (decomp.) (Found: C, 51.8; H, 3.8; Cl, 12.6%). The solid compound was diamagnetic.

Method C. Rhenium metal (3.0 g.) was dissolved in excess of hydrogen peroxide (30%), and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in concentrated hydrochloric acid (7 ml.), and the solution added to a stirred suspension of triphenylphosphine (25 g.) in glacial acetic acid (250 ml.). After being stirred for $\frac{1}{2}$ hr., the product was filtered off and washed with glacial acetic acid and diethyl ether to give yellow *microcrystals* (11.4 g., 85%) (Found: C, 52.3; H, 3.7; O, 1.9%).

Oxotrichlorobis(triphenylphosphine)rhenium(v) (Isomer 2).—Oxotrichlorobis(triphenylphosphine)rhenium(v) (isomer 1) was suspended in acetone (50 ml.) and heated under reflux in nitrogen overnight. The green *crystals*, which had precipitated, were filtered off, washed thoroughly with acetone and diethyl ether, and dried (25°/0.1 mm.) (Found: C, 51.8; H, 3.9%). The compound was diamagnetic as the solid and not very soluble in organic solvents. The infrared spectrum showed no peaks characteristic of the OH, OH₂, P—H, and P=O groupings.

The same compound could be obtained by substituting oxodichloroethoxobis(triphenylphosphine)rhenium(v) in the above reaction, but the yield was much lower (~50%). The supernatant solution, which was red-brown after reaction, yielded a brown tar on evaporation, which was reprecipitated from dichloromethane solution by light petroleum, but could not be obtained pure. The infrared spectrum showed no Re=O band, but the compound contained Ph₃P, Ph₃P=O, OEt, and OH groupings.

Oxotrichlorobis(triphenylphosphine)rhenium(v) (Isomer 3). Rhenium metal (2.0 g.) was dissolved in excess of hydrogen peroxide (30%) and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in hydrochloric acid (2*N*; 7.5 ml.) and added to a solution of triphenylphosphine (15 g.) and hydrazine dihydrochloride (3 g.) in a mixture of ethanol (200 ml.) and water (15 ml.). The solution was distilled under nitrogen, and benzene was added to maintain the volume constant, until after 20 min. all the water had been removed by azeotropic distillation. The solution was heated under reflux for a further 30 min., cooled, and filtered. The solid was washed with hot ethanol (200 ml.) and then with water; the dry product was further purified by extracting with boiling benzene (2 × 200 ml.) to give yellow plates (4.5 g., 20%) (Found: C, 51.8; H, 4.0; N, absent; O, 1.85%).

Oxotribromobis(triphenylphosphine)rhenium(v).—*Method A.* Oxodibromoethoxobis(triphenylphosphine)rhenium(v) (2.0 g.) was dissolved in dichloromethane (100 ml.), and the solution was shaken with concentrated hydrobromic acid (5 ml.). The green dichloromethane layer was separated and treated with excess of light petroleum (b. p. 40—60°). The yellow solid was recrystallised from boiling benzene, and dried (25°/0.1 mm.), giving the *compound* (0.7 g., 67%) (Found: C, 44.9; H, 3.7; Br, 25.0. $C_{36}H_{30}Br_3OP_2Re$ requires C, 44.7; H, 3.2; Br, 24.8%).

Method B. Rhenium metal (1.5 g.) was dissolved in excess of hydrogen peroxide (30%), and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in concentrated hydrobromic acid (4.5 ml.) and added to a suspension of triphenylphosphine (12 g.) in glacial acetic acid (120 ml.). After the suspension had been stirred for $\frac{1}{2}$ hr., the product was filtered off and washed with glacial acetic acid and diethyl ether to give yellow *microcrystals* (6.7 g., 86%) (Found: C, 44.7; H, 3.3%).

Oxotri-iodobis(triphenylphosphine)rhenium(v).—By a similar manner (method A) to that of the preceding compound, but using 45% hydriodic acid instead of hydrobromic acid, the *compound* (0.9 g., 83%) was prepared (Found: C, 38.5; H, 3.1; I, 34.8%; *M*, 1100. $C_{36}H_{30}I_3OP_2Re$ requires C, 39.1; H, 2.7; I, 34.4%; *M*, 1107).

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Oxodichloromethoxobis(triphenylphosphine)rhenium(v).—A suspension of oxotrichlorobis(triphenylphosphine)rhenium(v) (isomer 1) (0.5 g.) in benzene (20 ml.) and methanol (20 ml.) was heated under reflux in a nitrogen atmosphere for 1½ hr. The solution was filtered hot and the required product precipitated with light petroleum (b. p. 30–40°), forming grey *plates* (0.32 g., 64%) (Found: C, 53.6; H, 4.0. $C_{37}H_{33}Cl_2O_2P_2Re$ requires C, 53.6; H, 4.0%).

Oxodibromomethoxobis(triphenylphosphine)rhenium(v).—A suspension of oxotribromobis(triphenylphosphine)rhenium(v) (0.5 g.) in benzene (20 ml.) and methanol (20 ml.) was heated under reflux in a nitrogen atmosphere for 2½ hr. The solution was filtered hot and the required product precipitated with light petroleum (b. p. 30–40°), forming grey *needles* (0.38 g., 79%) (Found: C, 48.2; H, 3.9. $C_{37}H_{33}Br_2O_2P_2Re$ requires C, 48.4; H, 3.6%).

Oxodi-iodomethoxobis(triphenylphosphine)rhenium(v).—Rhenium metal (0.25 g.) was dissolved in excess of hydrogen peroxide (30%), and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in cold methanol (10 ml.) and added to a solution of triphenylphosphine (3 g.) and concentrated hydriodic acid (1.5 ml.) in methanol (50 ml.) heated under reflux for ½ hr. The product was filtered from the hot solution, dissolved in benzene, and reprecipitated with light petroleum, forming yellow-grey *plates* (0.68 g., 50%) (Found: C, 44.5; H, 3.3. $C_{37}H_{33}I_2O_2P_2Re$ requires C, 43.9; H, 3.3%).

Hydrolysis of Oxotrichlorobis(triphenylphosphine)rhenium(v).—Oxodichloroethoxobis(triphenylphosphine)rhenium(v) (1.0 g.) was dissolved in dichloromethane (100 ml.) and shaken for 2 min. with 6*M*-hydrochloric acid (100 ml.). The aqueous layer was discarded. The dichloromethane layer was shaken vigorously for 3 min. each with three separate 20-ml. portions of water. The dichloromethane layer became maroon-brown. It was poured into light petroleum (b. p. 40–60°) (400 ml.), a brown solid being precipitated. The solid was redissolved in the minimum amount of dichloromethane and reprecipitated by slow addition of light petroleum (b. p. 40–60°) (300 ml.) with vigorous stirring. The brown crystals of oxohydroxodichlorobis(triphenylphosphine)rhenium(v) which separated were washed thoroughly with diethyl ether and dried (25°/0.1 mm.), giving the *compound* (0.7 g., ca. 70%) (Found: C, 53.8; H, 5.0; Cl, 9.7%; *M*, 789. $C_{36}H_{31}Cl_2O_2P_2Re$ requires C, 53.1; H, 3.4; Cl, 8.7%; *M*, 814). The analysis corresponded to about 75% conversion to the required product.

Hydrolysis of Oxotribromobis(triphenylphosphine)rhenium(v).—Oxodibromoethoxobis(triphenylphosphine)rhenium(v) was treated in a similar manner to the chloro-compound above; a similar coloured solution was obtained and a darker brown precipitate, which gave the *compound* (0.6 g., 60%) (Found: C, 44.7; H, 4.7; Br, 21.3%; *M*, 927. $C_{36}H_{31}Br_2O_2P_2Re$ requires C, 47.9; H, 3.5; Br, 17.7%; *M*, 904). The analysis corresponded to about 50% conversion.

Hydrolysis of Oxotri-iodobis(triphenylphosphine)rhenium(v).—Oxodi-iodoethoxobis(triphenylphosphine)rhenium(v) was treated in a similar manner to the chloro-compound above. A bright purple solution was obtained with a small amount of black precipitate. The filtered dichloromethane solution was poured into light petroleum (b. p. 40–60°) (500 ml.), but no precipitate was obtained. Purple *crystals* slowly separated which were washed with light petroleum and dried (25°/0.1 mm.), giving the *compound* (0.3 g., ca. 30%) (Found: C, 47.6; H, 3.5; I, 17.1%; *M*, 900. $C_{36}H_{31}IO_3P_2Re$ requires C, 48.7; H, 3.6; I, 14.3%; *M*, 888. $C_{36}H_{30}IO_2P_2Re$ requires C, 49.7; H, 3.5; I, 14.6%; *M*, 870). It was not possible to decide which of these formulations were correct. Expressed as hydrolysis of $ReOI_3(Ph_3P)_2$ the results correspond to about 85% conversion. Further attempts at purification gave complete decomposition.

Oxotrichlorobis(triphenylarsine)rhenium(v).—Rhenium metal (1.0 g.) was dissolved carefully in 30% hydrogen peroxide (50 ml.) and the solution evaporated to dryness. The resulting perrhenic acid was dissolved in concentrated hydrochloric acid (1.0 ml.) and added to a suspension of triphenylarsine (3 g.) in glacial acetic acid (50 ml.). The suspension was stirred for 1 hr., then the solid filtered off, washed with glacial acetic acid and diethyl ether, and dried (25°/0.1 mm.), to give the required product as green-yellow *microcrystals* (3.2 g., 64%) (Found: C, 46.6; H, 3.3; Cl, 11.6. $C_{36}H_{30}As_2Cl_3ORe$ requires C, 47.0; H, 3.3; Cl, 11.2%). The moist compound is readily oxidised in air, but is stable when dry. It is moderately soluble in benzene and chloroform.

Oxotribromobis(triphenylarsine)rhenium(v).—Rhenium metal (0.25 g.) was dissolved in excess of hydrogen peroxide (30%), and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in concentrated hydrobromic acid (1.0 ml.) and added to a suspension of triphenylarsine (3 g.) in glacial acetic acid (50 ml.). The suspension was stirred for 1 hr.

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The solid was filtered from the solution, washed with glacial acetic acid and diethyl ether, and dried (25°/0.1 mm.) to give the required product as yellow *microcrystals* (0.77 g., 54%) (Found: C, 40.95; H, 3.0. $C_{36}H_{30}As_2Br_3ORe$ requires C, 41.0; H, 2.85%). The compound is soluble in chloroform and dichloromethane and, like the chloro-compound, is readily oxidised when moist.

Oxotrichlorobis(triphenylstibine)rhenium(v).—Rhenium metal (0.25 g.) was dissolved in excess of hydrogen peroxide (30%), and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in concentrated hydrochloric acid (0.6 ml.) and added to a suspension of triphenylstibine (6 g.) in glacial acetic acid (75 ml.). The suspension was stirred for 1½ hr. The solid was filtered from the solution, washed with glacial acetic acid and diethyl ether, and dried *in vacuo* to give the required product as green *platelets* (0.69 g., 51%) (Found: C, 42.45; H, 2.95. $C_{36}H_{30}Cl_3OReSb_2$ requires C, 42.6; H, 3.0%). The properties are the same as the previous two complexes.

Oxotribromobis(triphenylstibine)rhenium(v).—Rhenium metal (0.25 g.) was dissolved in excess of hydrogen peroxide (30%) and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in concentrated hydrobromic acid (1 ml.) and added to a stirred suspension of triphenylstibine (6 g.) in glacial acetic acid (75 ml.). After being stirred for ½ hr., the product was filtered from the solution and washed with glacial acetic acid and diethyl ether to give green *microcrystals* (0.45 g., 29%) (Found: C, 37.7; H, 2.6. $C_{36}H_{30}Br_3OReSb_2$ requires C, 37.7; H, 2.6%). The properties are the same as those of the previous compound.

Triphenylphosphonium Oxotetrachloro(triphenylphosphine)rhenate(v).—Oxotrichlorobis(triphenylphosphine)rhenium(v) (isomer 1) (1.0 g.) was dissolved in boiling benzene (50 ml.). A slow stream of hydrogen chloride was passed through the solution as it was cooling and green *crystals* separated; they were filtered off, washed thoroughly with warm benzene and diethyl ether, and dried (25°/0.1 mm.) to give the *compound* (0.9 g., 89%) (Found: C, 49.2; H, 3.1; Cl, 16.0. $C_{36}H_{31}Cl_4OP_2Re$ requires C, 49.7; H, 3.6; Cl, 16.3%). The compound was diamagnetic.

Hexachlorobis(triphenylphosphine)dirhenium(III).—This purple-red compound was believed to be monomeric.¹ Molecular-weight determinations in benzene (ebullioscopically) for samples prepared by three different methods have shown it to be dimeric. The methods of preparation were (a) reaction of hexachlorodirhenium(III) with triphenylphosphine in acetone solution, (b) fusion of the product from (a) with excess of triphenylphosphine, (c) fusion of hexachlorodirhenium(III) with triphenylphosphine [Found: C, (a) 39.7, (b) 39.5, (c) 39.6; H, (a) 3.1, (b) 3.1, (c) 2.9; Cl, (a) 19.4%; M, (a) 1120, (b) 1070, (c) 1070. Calc. for $C_{36}H_{30}Cl_6P_2Re_2$: C, 39.0; H, 2.7; Cl, 19.2%; M, 1109].

Tetrachloro(triphenylphosphine)rhenium(IV).—Solutions of rhenium pentachloride (1.0 g.) and triphenylphosphine (3 g.) in dichloromethane (or acetone) (100 ml.) were mixed. The green *complex* which separated was filtered off, washed with ethanol and diethyl ether, and dried (40°/0.1 mm.), giving the *compound* (0.6 g., 37%) (Found: C, 37.9; H, 2.2; Cl, 24.1; P, 5.3. $C_{18}H_{15}Cl_4PRe$ requires C, 36.6; H, 2.2; Cl, 24.0; P, 5.3%). The compound was insoluble in the common organic solvents and was probably polymeric. No bands were observed in the infrared spectrum in the characteristic O—H, M=O, P=O, and P—H stretching regions. The magnetic moment was *ca.* 1.2 B.M. at 296°K in the solid, corrected for diamagnetism of the ligands.

Trichlorobis(triphenylphosphine oxide)rhenium(III).—Hexachlorobis(triphenylphosphine)dirhenium(III) (1 g.) and triphenylphosphine (0.5 g.) were suspended in acetone (100 ml.) and 2 drops of water added. Chlorine was bubbled through the solution until it became hot, and a bright, clear, red solution was obtained. Passage of chlorine was continued for a further 15 min. The solution was reduced in volume (to 10 ml.) under vacuum and then poured into diethyl ether (200 ml.), which was stirred vigorously. The solid was collected, redissolved in acetone (10 ml.), and reprecipitated with diethyl ether (200 ml.). The solid *complex* was collected and dried (25°/0.1 mm.) to give the required *compound* (1.1 g., 72%) (Found: C, 51.9; H, 4.1; Cl, 13.1%; M, 810. $C_{36}H_{30}Cl_3O_2P_2Re$ requires C, 50.9; H, 3.6; Cl, 12.5%; M, 849). The compound was diamagnetic, readily soluble in acetone, ethanol, and chlorobenzene, sparingly soluble in dichloromethane and benzene, and insoluble in diethyl ether and light petroleum.

Trichloro(triphenylphosphine oxide)rhenium(III).—A solution of hexachlorodirhenium(III) (1.0 g.) in acetone (50 ml.) was added to a boiling solution of triphenylphosphine oxide (2 g.) in acetone (50 ml.). The solution was boiled gently for a few minutes and the red-purple crystals of the compound filtered off; it was washed with a little acetone and diethyl ether and dried

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(25°/0.1 mm.), giving the compound (1.5 g., 90%) (Found: C, 36.0; H, 2.5; Cl 19.7. $C_{18}H_{15}Cl_3OPRe$ requires C, 37.9; H, 2.6; Cl, 18.6%). The material was not appreciably soluble in the common organic solvents.

The supernatant solution from the above reaction, on evaporation to a small volume and removal of trichloro(triphenylphosphine oxide)rhenium(III) which separated, yielded a small quantity of trichlorobis(triphenylphosphine oxide)rhenium(III) when poured into excess of ether (Found: C, 49.6; H, 3.5%).

Trichloro(triphenylarsine)rhenium(III).—This was obtained in an exactly similar manner to the above compound, substituting triphenylarsine for triphenylphosphine oxide in the reaction, to give the compound (0.9 g., 44%) (Found: C, 34.8; H, 2.2. $C_{18}H_{15}AsCl_3Re$ requires C, 36.1; H, 2.5%).

Trichloro(triphenylarsine oxide)rhenium(III).—This was prepared as the above two compounds, but using triphenylarsine oxide as the ligand, to give the compound (1.2 g., 57%) (Found: C, 36.0; H, 2.4. $C_{18}H_{15}AsCl_3ORE$ requires C, 35.2; H, 2.5%).

Dioxotetrapyridinerhenium(v) Chloride Dihydrate.—Oxotrichlorobis(triphenylphosphine)rhenium(v) (1.0 g.) and pyridine (2 ml.) in ethanol (20 ml.) was boiled under reflux for about 2 hr. The orange solution was treated with an excess of diethyl ether (200 ml.) and stirred vigorously. The precipitated yellow-orange complex was filtered off, recrystallised from ethanol, and dried (100°/0.1 mm.) for 48 hr. before analysis, giving the dihydrate (0.55 g., 75%) (Found: C, 39.6; H, 3.9; N, 9.1; O, 10.8; Cl, 5.9. $C_{20}H_{24}ClN_4O_4Re$ requires C, 39.6; H, 4.0; N, 9.2; O, 10.6; Cl, 5.9%).

This compound was also obtained as one of the products formed by the addition of pyridine to an acetone solution of pentachlororhenium(v). Neither solvent was rigorously dried. The green solid (not yet characterised) which separated was filtered off and the orange supernatant liquid was evaporated under reduced pressure (25°/0.1 mm.). Orange crystals separated which were recrystallised (ethanol) (Found: C, 39.7; H, 4.1; N, 9.6; O, 10.2; Cl, 5.9%).

This compound is soluble in water, pyridine, and ethanol, but is sparingly soluble in chloroform and acetone, and insoluble in benzene, nitrobenzene, and chlorobenzene. It decomposes in hot water but is stable indefinitely in ethanol containing a trace of pyridine. The conductivity in water [Λ ($1 \times 10^{-3}M$) = 61.0 mho] is that expected for a uni-univalent electrolyte. The compound was diamagnetic both as solid and in solution.

Dioxotetrapyridinerhenium(v) Bromide Dihydrate.—In a similar preparation to that used for the chloride but starting with oxodibromoethoxobis(triphenylphosphine)rhenium(v), the orange bromide dihydrate (0.5 g., 72%) was prepared (Found: C, 37.0; H, 3.9; O, 9.9; Br, 12.6. $C_{20}H_{24}BrN_4O_4Re$ requires C, 36.9; H, 3.7; O, 9.8; Br, 12.2%). The compound was readily soluble in water, methanol, and ethanol, sparingly soluble in acetone, but insoluble in other common organic solvents.

Dioxotetrapyridinerhenium(v) Iodide Monohydrate.—*Method A*. In a similar manner to that used for the chloride and bromide, but starting with oxodi-iodoethoxobis(triphenylphosphine)rhenium(v) (1.0 g.), the orange-red iodide monohydrate (0.4 g., 60%) was prepared (Found: C, 36.0; H, 3.5; O, 6.9; I, 19.0. $C_{20}H_{22}IN_4O_3Re$ requires C, 35.4; H, 3.3; O, 7.1; I, 18.7%).

Method B. The compound was also precipitated from a solution of dioxotetrapyridinerhenium(v) chloride dihydrate (1.0 g.) in water (25 ml.) by the addition of a saturated solution of potassium iodide. The precipitate was filtered off, washed with saturated aqueous potassium iodide solution, ethanol, and ether, and dried (25°/0.1 mm.), to give the required compound (0.5 g., 45%) (Found: C, 36.0; H, 3.3; O, 6.9; I, 18.2%). The salt was moderately soluble in water and methanol, sparingly soluble in ethanol, and insoluble in other organic solvents.

Bis(dioxotetrapyridinerhenium(v) Hexachloroplatinate(IV) Tetrahydrate.—An aqueous solution (20 ml.) of the corresponding chloride (0.5 g.) was treated with a small excess of a saturated solution of hexachloroplatinic acid. The yellow crystals which separated were filtered off, washed with a little cold water, then with ethanol and diethyl ether, and dried (25°/0.1 mm.) for 48 hr., giving the required compound (0.5 g., ca. 90%) (Found: C, 31.1; H, 3.1; O, 8.4. $C_{40}H_{48}Cl_6N_8O_8PtRe_2$ requires C, 31.0; H, 3.1; O, 8.3%). Drying at 100° caused gradual decomposition. The compound was slightly soluble in water but insoluble in the common organic solvents.

Dioxotetrapyridinerhenium(v) Tetraphenylborate.—An aqueous solution of the corresponding chloride was treated with an aqueous solution of sodium tetraphenylborate. The pale yellow

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precipitate was filtered off, washed thoroughly with water, and dried (25°/0.1 mm.) for 48 hr. before analysis (Found: C, 60.5; H, 4.7; O, 3.8. $C_{44}H_{40}BN_4O_2Re$ requires C, 61.9; H, 4.7; O, 3.8%). The compound is insoluble in water but is readily soluble in acetone. Ebullioscopic measurements in anhydrous acetone gave a value corresponding to two monomeric ions (Found, 450; required, 426).

Hydroxiodotetrapyridinerhenium(v) Tris(tri-iodide).—Dioxotetrapyridinerhenium iodide monohydrate (1 g.) was boiled under reflux with 45% hydriodic acid (25 ml.) for some hours until shining black crystals separated. They were filtered off, washed thoroughly with water, and dried (40°/0.1 mm.) for 48 hr. (Found: C, 13.2; H, 1.4; N, 3.1; O, 2.6; I, 69.6. $C_{20}H_{21}I_{10}N_4ORe$ requires C, 13.6; H, 1.4; N, 3.1; O, 2.6; I, 71.2%). The infrared spectrum showed no pyridinium group, co-ordinated water, or double-bonded oxygen.

Dioxobis(ethylenediamine)rhenium(v) Chloride Dihydrate.—Oxodichloroethoxobis(triphenylphosphine)rhenium(v) (1.0 g.) was suspended in ethanol (25 ml.), and ethylenediamine hydrate (2 ml.) was added. The mixture was boiled under reflux for 1 hr. The solid was filtered off and dissolved in water (20 ml.), and the solution filtered into vigorously stirred ethanol (20 ml.). The pale yellow *crystals* were filtered off, washed thoroughly with ethanol and diethyl ether, and dried (40°/0.1 mm.) (Found: C, 12.0; H, 4.7; N, 13.3; O, 14.8; Cl, 8.8. $C_4H_{20}ClN_4O_4Re$ requires C, 11.7; H, 4.9; N, 13.7; O, 15.6; Cl, 8.7%). The compound was slowly hydrolysed by water giving an almost white substance. The infrared spectrum of this material showed a strong broad peak at 906 cm^{-1} , about the region normally associated with perrhenate, or other oxides of rhenium. A similar substance had been obtained by Russian workers³⁰ who formulated it as $en \cdot ReO_3$. We were not able to characterise the compound but the analyses fit this formulation quite closely. The chloride found may be an impurity as on this formulation it corresponds to a Cl:Re ratio of 0.33:1 (Found: C, 8.5; H, 2.7; N, 8.8; O, 17.6; Cl, 4.0. $C_2H_8N_2O_3Re$ requires C, 8.2; H, 2.7; N, 9.5; O, 16.3%).

Dioxobis(ethylenediamine)rhenium(v) Iodide.—The corresponding chloride (1.0 g.) was dissolved in water (10 ml.) and a saturated solution of potassium iodide (10 ml.) added. The solid was filtered off, washed thoroughly with ethanol and diethyl ether, and dried (25°/0.1 mm.), giving the *compound* (0.6 g., 50%) (Found: C, 9.7; H, 3.5; N, 12.2; I, 27.5. $C_4H_{16}IN_4O_2Re$ requires C, 10.3; H, 3.5; N, 12.0; I, 27.3%).

Bisdihydroxobis(ethylenediamine)rhenium(v) Tris(hexachloroplatinate(IV)).—This was prepared by Murmann's method³¹ (Found: C, 5.0; H, 2.0; O, 3.5. Calc. for $C_8H_{36}Cl_{18}N_8O_4Pt_3Re_2$: C, 5.0; H, 1.9; O, 3.4%).

Oxohydroxobis(ethylenediamine)rhenium(v) Diperchlorate.—This was prepared by Murmann's method³¹ (Found: C, 9.5; H, 3.0; N, 10.7; O, 28.0; ClO_4 , 36.9. Calc. for $C_4H_{17}Cl_2N_4O_{10}Re$: C, 8.9; H, 3.2; N, 10.4; O, 29.7; ClO_4 , 37.0%).

Dihydroxobis(ethylenediamine)rhenium(v) Diperchlorate Chloride.—The purple crystals of the previous compound (1.0 g.) were suspended in concentrated hydrochloric acid (10 ml.), and 60% perchloric acid (2 ml.) was added, with continuous stirring. The purple crystals slowly dissolved and at the same time bright blue needle-like crystals were precipitated. When reaction was complete, the *compound* was filtered off, washed thoroughly with anhydrous ether, and dried (25°/0.1 mm.), giving the *chloride* (1 g., ~100%) [Found: C, 9.0; H, 2.8; N, 10.2; Cl (ionic), 6.3; O, 26.4; ClO_4 , 34.3. $C_4H_{18}Cl_3N_4O_{10}Re$ requires C, 8.4; H, 3.2; N, 9.8; Cl (ionic), 6.2; O, 27.8; ClO_4 , 34.5%).

Dioxobis(propene-2,4-dionato)molybdenum(VI).—The compound was prepared by the method in *Inorganic Syntheses*³² (Found: C, 36.5; H, 4.2. Calc. for $C_{10}H_{14}MoO_6$: C, 36.8; H, 4.3%).

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³⁰ Lebendinskii, Ivanov-Emin, *Zhur. obshchei Khim.*, 1943, **13**, 253.

³¹ Murmann, *Inorg. Synth.*, 1963, **9**, in the press.

³² Fernelius, Terada, and Bryant, *Inorg. Synth.*, 1960, **6**, 147.