CHEMISTRY OF RHENIUM COMPLEXES.

A Thesis submitted

by

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To my parents.

Felix qui potuit rerum cognoscere causas.

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Abbreviations.

Me	methyl
Et	ethyl
Ph	phenyl
acac	pentane2-4dionato (acetylacetonato) anion
ac	acetato anion
Pr^n	normal propyl
py	pyridine
en	ethylenediamine
en-H	ethylenediamine which has lost a proton i.e. $H_2NCH_2CH_2NH^-$.
dipy	2.2' dipyridyl
o-phen	1-10 phenanthroline

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ABSTRACT.

The range of reactivity of oxophosphinerhenium(V) compounds has been extended to include nitrogen doners, carbon monoxide and β-diketones. In the latter case a wide variety of different compounds were obtained in differing formal oxidation states of the rhenium, including tetrachlorotetrakis(pentane2-4dionato) dirhenium(IV) which is considered to have bridging pentane2-4dione groups. At high temperatures pentane2-4dione has been shown to form acetate complexes.

The infra-red spectra of a number of trans-dioxo compounds have been re-examined and new assignments are given for the metal oxygen asymmetric stretching mode. A complete assignment of the bands in trans-dioxotetrammineosmium(VI) dichloride has been performed, although this proved impossible for the isoelectronic rhenium(V) analogue. The reaction of trans-dioxobis(ethylenediamine)rhenium(V) chloride with hydrochloric acid has been investigated in detail and several new compounds have been isolated. The compound formulated originally as trioxoethylenediaminerhenium(VI) has been reformulated as di-μ-hydroxotetroxobis(ethylenediamine)dirhenium(V).

The preparation of a wide variety of oxopentachlororhenate(V) compounds is described together with their spectroscopic and magnetic properties. During the course of this study, two dimethylsulphoxide complexes were obtained, which from infra-red evidence appear to bond differently to the rhenium; one being via the oxygen and the other via the sulphur.

Rhenium pentachloride has been shown to hydrolyse in two

different ways. In the presence of triphenylphosphine, either oxotrichlorobis(triphenylphosphine)rhenium(V) or bis(triphenylphosphonium) oxopentachlororhenate(V) is obtained.

The reaction of perrhenic acid with concentrated hydrochloric acid leads to the formation of the trans-trioxotrichlororhenate(VII) ion, although the corresponding fluorine compound could not be obtained.

INTRODUCTION.

The post-war period has seen a vast increase in the study of transition metals and the complexes which they form. In spite of the limited quantities available, a great deal of work has been performed with rhenium and its compounds and a number of novel features have been discovered, which have subsequently been extended to include other transition metals. Rhenium chemistry is complicated in that the element possesses nine formal oxidation states ranging from Re(VII) to Re(-1), and complexes are known for all these states; also there are number of compounds with unusual stoichiometries e.g. ReF_7^-, $Re(CN)_8^{2-}$, ReH_9^{2-}. So few physical parameters have been ascertained with any certainty for third row transition metal complexes that theoretical studies, except in the simplest of cases, are very unreliable. Thus, it is in an endeavour to extend the scope, and clarify some of the earlier misconceptions that the present work was initiated.

A number of review articles and books have appeared (1, 2, 3, 4, 5) but all deal essentially with the "simple" chemistry of the element, there being little or no mention of the complexes. However, very recently two similar books have appeared (6, 7) which endeavour to rectify this omission by including a lot of data which has appeared in the literature in the last four or five years, most of which concerns complexes. From this point of view, the book by Peacock (7) contains

much more recent data - the book by Colton (6) can be said to be complete only to the end of 1964.

Until relatively recently Re(V) was considered to be a somewhat rare oxidation state, either in the complexed or uncomplexed state. Although ReX_5 (X= F, Cl, Br) are known, only recently has the simple oxide Re_2O_5 been satisfactorily authenticated (8) using X-ray methods. A feature of the chemistry of Re(V) is the ease with which oxygen and nitrogen form multiple bonds to the metal atom. Surprisingly though, none of the oxotrihalides is known with any degree of certainty, although the technetium analogues are known. However the complex anions $(ReOCl_5)^{2-}$ (X= Cl, Br, I) have been claimed (see Chapter 4) and recently $(TcOCl_5)^{2-}$ has been prepared (9).

Recently tertiary phosphines have been used to stabilise the $(ReO)^{3+}$ unit and a wide range of air stable complexes have been prepared. At first, however these were considered to be Re(III) derivatives (10), but subsequent work (11, 12) showed that the compounds should be reformulated as derivatives of $(ReO)^{3+}$. Tertiary phosphines have also been used to stabilise a number of nitrido complexes of general formula $ReNX_2L_2$ and $ReNX_2L_3$ (X= halogen, L= phosphine) and arylimido complexes such as $Re(NR)X_3L_2$ (R= aryl) (13).

The idealised metal-oxygen (nitrogen) bond order in $(ReO)^{3+}$ and $(ReN)^{2+}$ is 3 and a molecular orbital scheme for this type of system is given in Fig. 1. Introduction of another oxygen atom <u>trans</u> to the first would be expected to give a π-bonded system not unlike that of carbon dioxide with

a subsequent drop in the metal-oxygen bond order to 2 (the orbital energy scheme remaining qualitatively the same). Such compounds are known for rhenium - a number of trans-$(ReO_2)^+$ compounds have been synthesised (see Chapter 3), and are now well characterised. In compounds containing $(ReO)^{3+}$ where all the p-orbitals of the oxygen are utilised in bonding, protonation is either impossible or at best difficult, but in trans-$(ReO_2)^+$ complexes protonation occurs readily.

Very recently there have been a number of X-ray single crystal studies on $(ReOX_4S)^-$ (X= Br, S= H_2O (14), MeCN (15)), in which it is concluded that the bromine atoms are coplanar and there is a short Re=O distance of ca.1.72Å. The oxo group has a strong trans effect as shown by the fact that $(ReOX_4)^-$ bind solvent molecules such as H_2O and MeCN extremely weakly and lose them readily, confirmed by the large Re-solvent distances (14, 15).

In fact almost all Re(V) complexes contain either $(ReO)^{3+}$ or $(ReO_2)^+$. This is by no means a unique feature as there are a number of compounds containing $(MO)^{3+}$ (M= Nb, Ta, Mo, W, Os), although with none of these metals has the research been as extensive as in the case of rhenium.

CHAPTER I.

OXO-PHOSPHINE RHENIUM(V) COMPLEXES

a) Isomerism.

A large number of oxorhenium(V) compounds containing tertiary phosphines of the type $ReO(OR)X_2L_2$ and $ReOX_3L_2$ (R=Me, Et, CH_2Ph. X=Cl, Br, I. L=PPh_3, $PPhEt_2$) is known (12, 16). The air-stable solids oxoethoxodichlorobis(triphenylphosphine)rhenium(V), $ReO(OEt)Cl_2(PPh_3)_2$ and oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3(PPh_3)_2$, which are interconvertable, can both be prepared in excellent yield from the reduction of perrhenic acid (made by dissolving rhenium metal in 100 vol. hydrogen peroxide and evaporating to dryness) in hydrochloric acid with triphenylphosphine, in ethanol and glacial acetic acid respectively. (17)

As prepared above, $ReOCl_3(PPh_3)_2$ is obtained as a bright yellow/green microcrystalline powder and is considered to have the tertiary phosphines in the trans configuration, as the dipole moment is 2.25D. (12). This follows from the observation that compounds containing cis-phosphines tend to have very large dipole moments, e.g.

cis-$ReOCl_3(PPhEt_2)_2$ blue isomer μ=10.8D.

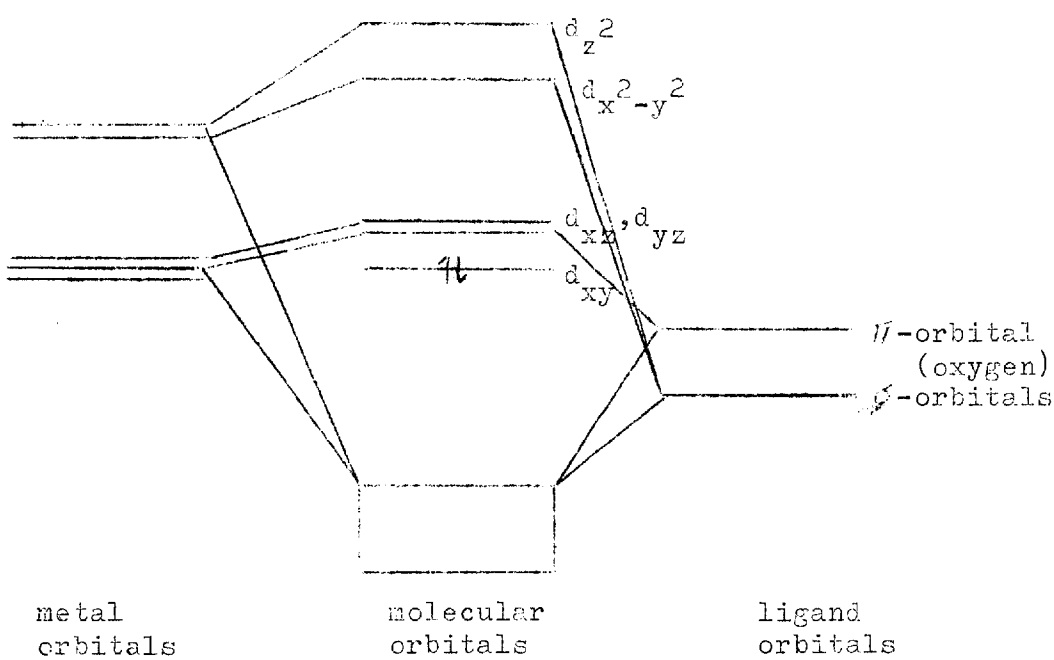
trans-$ReOCl_3(PPhEt_2)_2$ green isomer μ=1.7D. (12)

A full single-crystal X-ray determination on the green isomer of $ReOCl_3(PPhEt_2)_2$ has been performed (18) confirming the trans position of the two phosphines. The metal-oxygen distance is 1.60Å. However, although this figure has been

queried (19), a very short metal-oxygen distance is indicated. This is consistent with the observed diamagnetism of all these compounds.

A crude molecular orbital scheme can be constructed to explain these experimental observations. The filled p_y and p_x orbitals of the oxygen atom donate to the empty d_{yz} and d_{xz} orbitals of the rhenium atom respectively, forming two π-bonds. A σ-bond is formed between the p_z oxygen orbital and the d_z^2 rhenium orbital. (The $d_{x^2-y^2}$ orbital forms σ-bonds in the xy plane with the other ligands, leaving the d_{xy} orbital as a non-bonding orbital), see Fig. 1. Strictly speaking the d_z^2 and $d_{x^2-y^2}$ orbitals should be considered as

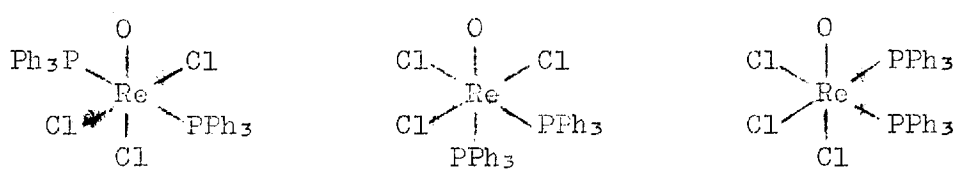
FIGURE I. Orbital splitting for large axial asymmetry caused by a strong π-donor in a six co-ordinate complex.



constituents of a hybrid orbital, however the important point is that the d_{xz} and d_{yz} molecular anti-bonding orbitals are destabilised relative to the d_{xy} orbital, resulting in a singlet ground state and the consequent diamagnetism of the (d^2) system. Thus to this degree of approximation there is a triple bond between the rhenium and the oxygen atoms, which is postulated as being the explanation for the short rhenium-oxygen distance. A very high rhenium oxygen stretching vibration (950-1010 cm^{-1}) is also indicative of multiple bonding in these compounds.

The three possible isomers of $ReOCl_3(PPh_3)_2$ have been prepared (16), and have different colours and different infra-red spectra. Unfortunately infra-red spectroscopy alone cannot be used as a diagnostic test of the absolute stereochemistry of the two cis-isomers. Naively, one might expect that as triphenylphosphine is a good π-acceptor, the metal oxygen stretching frequency should be greater in isomer (b), (see Fig. 2) than in (a) or (c), but the values obtained do not unambiguously assign isomers (b) and (c).

FIGURE 2. Isomers of $ReOCl_3(PPh_3)_2$



(a) (b) (c)

Re=O 969cm^{-1} 981cm^{-1} or 986cm^{-1} 986cm^{-1} or 981cm^{-1}

Simplified group theoretical arguments (neglecting site symmetry factors) predict that all three isomers should have

three infra-red active Re-Cl stretching frequencies, thus making unique structural assignments impossible. Also the solubilities in benzene are not sufficiently great to obtain an accurate value of the dipole moment, and even if this were possible, it is difficult to predict whether the dipole moment of (b) would be greater than that of (c) or vice-versa. There is evidence for isomerisation in dichloromethane, benzene and acetone as indicated by the disappearance of the band at $969cm^{-1}$ and the growth of another at $981cm^{-1}$, but the rate is very slow compared to the oxoethoxo compounds, probably due to the lower solubility of the oxotrihalogeno compounds.

However $ReO(OEt)Cl_2(PPh_3)_2$ is readily soluble in benzene and dipole moments of a number of this type of complex have been measured (12). No configurational assignments have been made because for each empirical formula there are six geometrical isomers, and in no case have more than three been made.

The visible spectrum of a solution of the green isomer of $ReO(OEt)Cl_2(PPh_3)_2$ in dry benzene has been observed to be time-dependent at ordinary temperatures, indicating quite rapid isomerisation, presumably to an equilibrium mixture over a period of several hours. This was confirmed by the isomerism within three hours in refluxing benzene/ethanol of green $ReO(OEt)Cl_2(PPh_3)_2$ to the purple isomer . A further slow reaction occurs, as is shown by the conversion of a solution of green $ReO(OEt)Cl_2(PPh_3)_2$ in dry benzene into trans-$ReOCl_3(PPh_3)_2$ when it is shaken for four days at 20^0. The visible spectrum of a nujol mull of green $ReO(OEt)Cl_2(PPh_3)_2$ is time-independent,

indicating that such changes do not occur in the solid state.

Similar rapid spectroscopic changes at room temperature were found in the benzene solution spectra of purple $ReO(OEt)Cl_2(PPh_3)_2$, $ReO(OEt)Cl_2(PPhEt_2)_2$ (12), $ReO(OEt)Br_2(PPh_3)_2$, $ReO(OEt)I_2(PPh_3)_2$, $ReO(OMe)Cl_2(PPh_3)_2$ and $ReO(OMe)I_2(PPh_3)_2$. These changes were apparent immediately the compounds had dissolved, and hence dipole moment measurements of all these compounds (12) are probably meaningless.

The spectrum of a fresh benzene solution of green $ReO(OEt)Cl_2(PPh_3)_2$ showed a maximum at about 535mμ, ($\epsilon \sim 40$) and a minimum at about 490mμ at room temperature. As time progressed, the absorbance increased and the positions of the maximum and minimum moved. There is a charge transfer band at about 450mμ. The spectrum of the purple isomer appeared as a series of shoulders on the charge transfer band. As expected, the spectra were temperature dependent: if a hot solution was allowed to cool, as time progressed the absorbance decreased. This can be explained by assuming that an equilibrium is set up in solution and is temperature dependent but kinetically controlled, the high temperature equilibrium being composed of predominantly high absorbing (higher ϵ) compound. Thus on cooling, this equilibrium is quenched and the absorbance decreases as time progresses. There are similar spectroscopic changes when the solvent is tetrahydrofuran.

The effects of solution isomerism can be experimentally observed in the differences in the rate of reaction with acetylacetone (acacH). Both green $ReO(OEt)Cl_2(PPh_3)_2$ and

the grey/green isomer react with neat acacH to give tetrachlorotetrakis(pentane2-4dionato)dirhenium(IV), $(ReCl_2(acac)_2)_2$, but the grey/green isomer gave the product after refluxing for thirty hours. The product obtained from the green isomer after this time was contaminated with some of the triphenylphosphine containing intermediates, and pure $(ReCl_2(acac)_2)_2$ was only obtained after refluxing for fifty hours. (Analysis after refluxing for thirty hours corresponded approximately to a mixture of 33%$(ReCl_2(acac)_2)_2$ and 67%$(ReCl(acac)_2PPh_3)$.

The difference in reacton rates was also shown by the reaction with acacH in benzene. The green isomer yielded a mixture of $ReCl_2acac(PPh_3)_2$ and $ReOCl_2acacPPh_3$, whereas under identical conditions the purple isomer yielded only $ReCl_2acac(PPh_3)_2$. It has been suggested that the green $ReOCl_2acac(PPh_3)$ is an intermediate in the formation of orange $ReCl_2acac(PPh_3)_2$ (20), which suggests the following reaction scheme:

$$\underset{\text{green}}{ReO(OEt)Cl_2(PPh_3)_2} \longrightarrow \underset{\text{purple}}{ReO(OEt)Cl_2(PPh_3)_2} \longrightarrow \underset{\text{green}}{ReOCl_2acacPPh_3} \longrightarrow \underset{\text{orange}}{ReCl_2acac(PPh_3)_2}$$

The infra-red spectra of the three isomers of $ReO(OEt)Cl_2(PPh_3)_2$ are given in the experimental section.

b) Reactivity

The oxo-phosphine rhenium(V) compounds react with a wide variety of ligands but the types of reaction can be divided

into two main groups:-

i) reactions in which the Re(V) oxidation state is maintained

ii) reactions in which the formal oxidation state is decreased, either by classical reduction or by disproportionation.

Group (i)

1. All the σ-bonding ligands can be exchanged for their analogues.

Thus, reaction with trialkylphosphines produces the corresponding trialkylphosphine complex. This is a convenient way of preparing these compounds, since the reduction of perrhenic acid with trialkylphosphines gives low yields of the required complex (21). Reaction with pseudohalogens can sometimes be affected, e.g.

$ReOCl_3(PPh_3)_2 + 3AgSCN \rightarrow ReO(SCN)_3(PPh_3)_2 + AgCl$ (12).

2. The oxotrihalogeno complexes react with alcohols to give the corresponding oxoalkoxo compounds $ReO(OR)Cl_2(PPh_3)_2$ R=Me, Et, Pr^n, $PhCH_2$, $CH_2=CHCH_2$, $MeO(CH_2)_2$. The allyl compound was made in an attempt to obtain an allyl group acting as a σ-donor at one end of the molecule and chelating via the π-bond at the other. To effect this, the compound was treated with perchloric acid, but unfortunately oxidation occurred and triphenylphosphine oxide was obtained. Reaction of $ReO(OEt)Cl_2(PPh_3)_2$ with perchloric acid in benzene produced a stable turquoise solution in the benzene layer from which only unco-ordinated triphenylphosphine oxide could be obtained.

3. The reaction with pyridine affords a number of different products depending on the exact reaction conditions. It has been reported (16) that the reaction of trans-$ReOCl_3(PPh_3)_2$ with pyridine in ethanol leads to the formation of trans-dioxotetrapyridinerhenium(V) chloride dihydrate, trans-$(ReO_2py_4)Cl.2H_2O$, in high (75%) yield. However it was found that the yield was much lower than this, unless the trans-$ReOCl_3(PPh_3)_2$ was completely free from acetic acid. If this were not the case, addition of ether resulted in the formation of an ethanol soluble tar.

Trans-$ReOCl_3(PPh_3)_2$ and moist pyridine (in a 1:3 molar ratio) react to give the binuclear species μ-oxodioxotetrachlorotetrakispyridinedirhenium(V) $Re_2O_3Cl_4py_4$, which reacts with ethanol to give oxoethoxodichlorobis(pyridine)rhenium(V), $ReO(OEt)Cl_2(py)_2$ (22).

4. Some other nitrogen donors have been used: green $ReO(OEt)Cl_2(PPh_3)_2$ reacts immediately with 2.2' dipyridyl or 1.10-phenanthroline to give $ReO(OEt)Cl_2L$. Both these compounds are blue, like the bis(pyridine) analogue, but are very soluble in water.

5. Cationic trans-dioxo compounds can be prepared from the oxoethoxo compounds, e.g.

$$ReO(OEt)Cl_2(PPh_3)_2 + 5L + H_2O \longrightarrow (ReO_2L_4)Cl + EtOH + LHCl + 2PPh_3$$

$L = \frac{1}{2}en, NH_3, py.$

Again the pyridine reaction is somewhat complicated owing to the possibility of the formation of $Re_2O_3Cl_4py_4$.

Similarly, reaction with potassium cyanide leads to the

formation of the anionic trans-dioxotetracyanorhenate(V) ion, trans-$(ReO_2(CN)_4)^{3-}$.

6. Addition of one or two moles of HCl can take place readily forming $(ReOCl_4PPh_3)^-$ (16) and $(ReOCl_5)^{2-}$ respectively.

7. There are a number of reactions in which the oxygen atom is removed. For example reaction with aniline affords a phenylimido complex (13).

8. Both trans-$ReOCl_3(PPh_3)_2$ and $ReO(OEt)Cl_2(PPh_3)_2$ react with dimethylsulphoxide (Me_2SO), giving $ReOCl_3PPh_3Me_2SO$ (in the presence of HCl) and $ReO_2Cl(Me_2SO)_2$ (in the absence of HCl). Infra-red evidence indicates that in the former complex, the Me_2SO is bonded to the metal via the sulphur atom and in the latter via the oxygen.

Group (ii)

Care has to be taken with prolonged reactions with these compounds, otherwise disproportionation occurs in the usual way for Re(V):

$$3ReOCl_3(PPh_3)_2 \rightarrow 2ReCl_4(PPh_3)_2 + ReO_3Cl + 2PPh_3.$$

However the yield of tetrachlorobis(triphenylphosphine)rhenium(IV) $ReCl_4(PPh_3)_2$, was greater than that predicted by the above reaction and thus the assumption is that the triphenylphosphine reduces the Re(VII):

$$ReO_3Cl + 3PPh_3 + 2HCl \rightarrow ReOCl_3(PPh_3)_2 + PPh_3O + H_2O.$$

If the reaction is performed in boiling xylene in an atmosphere of hydrogen chloride and in the presence of excess triphenylphosphine, almost 100% yield of $ReCl_4(PPh_3)_2$ is obtained (23). In fact this is one of the best preparative methods for

$ReCl_4(PPh_3)_2$. Thus it would appear that reduction has been achieved via disproportionation.

1. Reaction with carboxylic acids leads to two series of compounds $Re_2Cl_3(RCO_2)_2(PPh_3)_2$ and $Re_2OCl_5(RCO_2)(PPh_3)_2$ (23). In the presence of the appropriate anhydride, the above two sets of compounds are obtained together with the known $Re_2Cl_2(RCO_2)_4$ (23).

2. Quite a number of complexes with acacH have been isolated (24), and, like the carboxylates, a number of different oxidation states are obtained.

3. Genuine reduction occurs with carbon monoxide yielding the compound chlorotricarbonylbis(triphenylphosphine)rhenium(I) $ReCl(CO)_3(PPh_3)_2$. Trans-$ReOCl_3(PPh_3)_2$, $ReO(OEt)Cl_2(PPh_3)_2$ and $ReCl_4(PPh_3)_2$ can be reduced in the presence of triphenylphosphine and powdered copper with carbon monoxide to give the known diamagnetic Re(I) compound $ReCl(CO)_3(PPh_3)_2$ (10, 25).

4. A number of hydrides with unusual stoichiometries have been obtained from the reduction of $ReO(OEt)Cl_2(PPh_3)_2$ with sodium borohydride (26) e.g. $ReH_5(PPh_3)_3$ and $ReH_3(PPh_3)_4$. These hydrides are white, air stable, crystalline solids which are diamagnetic and non-conductors in nitrobenzene. Infra-red and nuclear magnetic resonance (n.m.r.) spectra together with gas volumetric reactions confirm the empirical formulae postulated.

c) Reaction with acacH and related compounds.

Prior to this work, only one acac complex of rhenium was

known, tris(pentane2-4dionato)rhenium(III), $Re(acac)_3$ (27) which was prepared by refluxing rhenium dioxide in acacH for two days.

From the reaction of green $ReO(OEt)Cl_2(PPh_3)_2$ with acacH four different types of acac complexes have been obtained, namely, oxodichloro(pentane2-4dionato)triphenylphosphinerhenium(V), $ReOCl_2(acac)PPh_3$; dichloro(pentane2-4dionato)bis(triphenylphosphine)rhenium(III), $ReCl_2acac(PPh_3)_2$; chlorobis(pentane2-4dionato)triphenylphosphinerhenium(III), $ReCl(acac)_2(PPh_3)$ and tetrachlorotetrakis(pentane2-4dionato)dirhenium(IV), $Re_2Cl_4(acac)_4$. The first two were obtained in an acacH/benzene mixture, and the last two in neat acacH. However, at no stage could $Re(acac)_3$ be obtained as the seemingly logical end-product of this sequence.

The initial product of the generalised reaction is green $ReOX_2(acac)PPh_3$, which has a characteristic strong band in the infra-red in the region expected for the metal oxygen stretching mode (see Table 4), and all are diamagnetic. These green complexes are difficult to prepare pure, since they rapidly react further with excess acacH to give the compounds described below.

When benzene solutions of $ReO(OEt)X_2(PPh_3)_2$ (X= Cl, Br) are boiled with acacH, reduction of the above Re(V) complex occurs and the orange/red Re(III) complexes $ReX_2acac(PPh_3)_2$ are formed. These compounds are paramagnetic, although the magnetic moment is considerably less than the "spin only" value of 2.83 B.M., which is to be expected for a third row transition element having a large single electron spin orbit coupling

constant. Accurate and meaningful values of ζ_{nd} are difficult to obtain, there being no obvious correlation between the values obtained from spectroscopic or magnetic studies. Furthermore the different assumptions made in essentially the same theoretical treatment lead to quite different values of ζ_{nd} (28). However, recently a value of ζ_{5d} for Re^{4+} of ca.2500 cm^{-1} has been proposed. (29a)

TABLE 1. Magnetic data for $ReX_2acac(PPh_3)_2$ (X= Cl, Br).

Compound	Temp.(°K)	χ'_M (c.g.s.)	μ_{eff} (B.M.)
$ReCl_2acac(PPh_3)_2$	293.0	797 x 10^{-6}	1.37
	248.3	797 "	1.27
	233.0	797 "	1.22
	223.0	797 "	1.20
	197.3	728 "	1.07
	161.2	728 "	0.97
	142.7	694 "	0.89
	125.0	694 "	0.84
	87.0	555 "	0.63
$ReBr_2acac(PPh_3)_2$	295.3	1016 "	1.55
	220.0	1033 "	1.35
	194.0	1016 "	1.26
	180.8	1033 "	1.23
	167.8	999 "	1.16
	157.7	965 "	1.11
	143.3	1033 "	1.09
	131.3	982 "	1.09
	126.3	932 "	0.98

The susceptibility of the two compounds was observed over a temperature range and was found to be more or less independant of temperature (which is predicted by the Kotani theory for a perfectly regular octahedral d^4 system (135)).

Although these compounds can hardly be considered as being perfectly octahedral, the linearity of μ(B.M.) against $T^{\frac{1}{2}}(^{o}K^{\frac{1}{2}})$ over such a wide temperature range was surprising. The values of the "spin orbit coupling constant" obtained from these figures are 6600±600 cm^{-1} for the chloride and 5800±600 cm^{-1} for the bromide. Using the same crude Kotani theory, a value of 6400 cm^{-1} was obtained for Os^{4+} (28). Because of the departure of strict octahedral symmetry, it is doubtful whether these figures have any physical significance, and certainly should not be compared to the value given by Figgis and Lewis (29a). The room temperature magnetic moments of these compounds are compared to those of other Re(III) systems in Table 2.

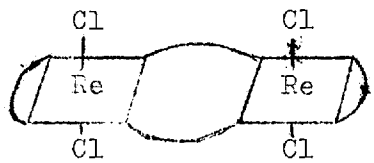
TABLE 2. Room temperature magnetic moments of some Re(III) compounds

Compound(a)	μ(B.M.)	Reference
$(ReD_2Cl_2)ClO_4$	2.1	30
$(ReD_2Br_2)ClO_4$	2.0	30
$(ReD_2I_2)ClO_4$	1.7	30
$ReI_3(P(OPh)_3)_3$	1.7	31
$ReI_3(P(OC_6H_4CH_3)_3)_3$	1.7	31
$Re(acac)_3$	2.3	27
$ReCl_2acac(PPh_3)_2$	1.4	
$ReBr_2acac(PPh_3)_2$	1.6	

(a) D= o-phenylenebis(dimethylarsine)

When a solution of $ReO(OEt)Cl_2(PPh_3)_2$ in neat acacH was refluxed, the reaction proceeded further than when in benzene. The initial product was $ReCl(acac)_2PPh_3$ and on prolonged reaction, the product obtained was $Re_2Cl_4(acac)_4$. The magnetic moment of this dimer was 2.9±0.2 B.M. per rhenium atom, in agreement with the expected value for Re(IV) of ca 3.1 B.M. (29b).

The only structure that in a simple way satisfies this result is where the octahedral Re(IV) configuration is preserved by the formation of pentane2-4dionato bridges i.e. the compound is considered to be di-μ-pentane2-4dionato-tetrachlorobis-(pentane2-4dionato)dirhenium(IV):



(=acac

There is no evidence at present to show whether the chlorine atoms are cis or trans to each other. An attempt was made to substitute the chlorines with carbon monoxide, but the compound did not react, even when at 200° and under 100 atms. pressure for a day. The compound is so stable that it can be recrystallised from dichloromethane, acetic acid and even trifluoroacetic acid. The melting point of the compound is greater than 300° and the molecular weight determined ebullioscopically in chlorobenzene still corresponds to that of the dimer.

All other possible structures involving either metal-metal bonds or bridging halides would involve heptaco-ordinate Re(IV), unless one of the pentane2-4dionato groups were bound through

only one oxygen or via the γ-C atom, possibilities which are excluded by the infra-red spectrum, which shows no band in the unco-ordinated keto region. Any such heptaco-ordinate structure that would give three unpaired spins per rhenium atom must involve utilisation in bonding of outer 6d orbitals, and this would appear to be energetically less favourable than the stereochemistry involved in the structure above. The complex gave no simple cleavage products when heated with an excess of pyridine in chloroform solution, which suggests the absence of chloride bridges.

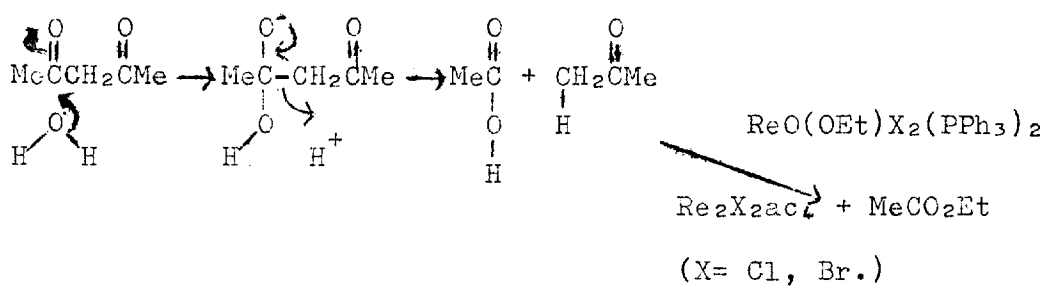
This is a new type of acac complex; in $(Ni(acac)_2)_3$ (32) and $(Co(acac)_2)_4$ (33) one oxygen is trico-ordinate, while in $(PtMe_3(acac))_2$ (34) and $K(Pt(acac)_2Cl)$ (35) there is a Pt-C bond to the γ-carbon atom of one of the acac groups. From infra-red studies, the acac in $PPh_3Au(acac)$ is considered to be monodentate being bonded to the Au atom via the γ-carbon atom (36). $Na_2(Pt(acac)_2Cl_2).5H_2O$ (37) is considered to have a unidentate acac group, although Wentworth et.al. (37), were unable to decide whether there were two γ-carbon bonded acac's or two oxygen bonded acac's or a mixture of both. Later n.m.r. work (38) suggests that two γ-carbon bonded acac's are present. It has been suggested that mercuric acetylacetonate should be written as $Hg(OCCH_3{=}CHCOCH_3)_2$ i.e. as the enolate (39). Thus it can be seen that since acac is such a versatile ligand, there seems to be no a priori reason why it should not act as a conventional bridging ligand. The Re-Re distance should be sufficiently great to eliminate any significant spin-spin interaction.

The compound could also be prepared from $ReCl_4(PPh_3)_2$ (23).

In an endeavour to obtain $Re(acac)_3$, some green $ReO(OEt)Cl_2(PPh_3)_2$ was put in a sealed tube with neat acacH and heated at 200° for 24 hours. However the desired product was not obtained - instead two compounds were isolated, blue trichloroacetatotriphenylphosphine oxiderhenium(IV) $ReCl_3acPPh_3O$ and red diamagnetic tetra-μ-acetatodichlorodirhenium(III), $Re_2Cl_2ac_4$ (prepared earlier by reaction of rhenium trichloride with acetic acid (40)).

The mechanism of this reaction is not clear, but presumably some form of hydrolysis of the acacH occurs, resulting in the cleavage of the molecule. Acetone and ethyl acetate (but not ethanol or acetic acid) could be seen on the Vapour Phase Chromatograph (V.P.C.) of the mother liquors. The vapour above the mixture in the sealed tube was examined in the infra-red, and bands were found at 2340 cm^{-1}, 3012 cm^{-1} and 1303 cm^{-1} which are assigned to the ν_3 mode of carbon dioxide (41a) and the ν_3 and ν_4 modes of methane (41b) respectively. No band corresponding to the carbon monoxide stretch (ca.2150 cm^{-1}) could be seen.

The following simplified mechanistic scheme is tentatively suggested:



In the preparation of anhydrous rhodium(II)acetate from rhodim(III)hydroxide (42), the role of the acetic acid was considered to be that of a reducing agent, since carbon dioxide was evolved during the course of the reaction. This observation alone, would not appear to conclusively prove the oxidising properties of the acetic acid.

Since no acetic acid was found in the mother liquors, it is tempting to suggest that radical disintegration had occurred resulting in the formation of carbon dioxide and methane:

$$MeCOOH \rightleftharpoons Me^{\bullet} + {}^{\bullet}COOH \rightleftharpoons MeH + CO_2$$

However, it was found that when acetic acid, or a mixture of acetic acide and acetone was substituted for the acacH in the sealed tube, the amount of methane and carbon dioxide formed was negligible, although both blue $ReCl_3acPPh_3O$, red $Re_2Cl_2ac_4$ and $MeCO_2Et$ were obtained as before. Furthermore, on heating acacH alone in the tube acetone was detected in the V.P.C. of the mother liquors and methane and carbon dioxide were detected in the infra-red spectrum of the gas in the tube. Thus it would appear that under these somewhat extreme conditions, acacH can also break down as follows:

$$MeCOCH_2COMe + 2H_2O \rightarrow 2CO_2 + 3MeH$$

However, the reaction is not as simple as is outlined above, since reaction of $ReCl_4(PPh_3)_2$ and acacH under the same experimental conditions afforded Me_2CO and $MeCO_2H$ in the V.P.C., MeH and CO_2 in the infra-red and blue $ReCl_3acPPh_3O$ only. At no stage was $Re_2Cl_2ac_4$ obtained - not even after heating in the sealed tube at 200° for a week.

The blue triphenylphosphine oxide containing compound is formed by aerial oxidation, since when the reaction is carried out with $ReCl_4(PPh_3)_2$ and acacH in a sealed tube in vacuo, the blue product is obtained only after about a minute's exposure to the atmosphere. This compound was never obtained in an analytically pure condition, and unfortunately reaction of $ReO(OEt)Br_2(PPh_3)_2$ with acacH produced only the red $Re_2Br_2ac_4$.

The blue compound was a non-conductor in nitrobenzene, diamagnetic both in the solid state and in solution, and monomeric in chloroform. The n.m.r. spectrum was examined in ethylene dicloride and showed a singlet at τ 8.1 (in addition to the phenyl protons), which is not inconsistent with a chelating acetato structure. The infra-red spectrum is given in the experimental section.

Reaction of the complex with pyridine gave a mixture of products, none of which contained triphenylphosphine oxide.

The reaction of green $ReO(OEt)Cl_2(PPh_3)_2$ with $MeCO_2H$ when refluxed for 20 hours, gave purple crystals of impure $Re_2Cl_3(ac)_2(PPh_3)_2$.

Nature of $M_2X_2ac_4$

A compound of similar stoichiometry to $Re_2X_2ac_4$ was reported by Russian workers (43), but was formulated as a rhenium(II) species $(ReCl2CH_3COOH)_2$ with a metal-metal bond to explain the observed diamagnetism. However the oxidation state of this and a whole series of other alledged Re(II) compounds (including $(pyH)HReCl_4$ - whose structure had been determined (44) and indicated the presence of $(Re_2Cl_8)^{4-}$) has been queried by

Cotton et.al. (45, 46). In fact these workers formulated the above pyridinium complex as $(pyH)_2(Re_2Cl_8)$- a result more in keeping with the known tendency of Re(III) to form metal-metal bonds and most of the Russian Re(II) species are shown to be Re(III) compounds. The crystal structure of $K_2(Re_2Cl_8).2H_2O$ has been determined (47) and an abnormally short metal-metal distance has been found; so short in fact, that the formation of a δ-bond between the two metal atoms has been proposed (48) i.e. a "quadruple" bond. This is considered to explain the eclipsed configuration of the anion, because were the anion staggered, there could be no overlap between the two d_{xy} orbitals and thus no δ-bond. Because of the ready inter-convertability of $(Re_2Cl_8)^{2-}$ and $Re_2Cl_2ac_4$, it is considered that there might well be a δ-bond present in $Re_2Cl_2ac_4$. Since then, Mo(II) acetate has been examined and found to have a very short metal-metal distance (49). The metal-metal distances in a number of binuclear structures with bridging acetates are summarised in Table 3.

TABLE 3. Metal-metal distances in binuclear bridged acetates and related compounds.

Compound	Metal-metal dist.(Å).	Bond order[a]	Reference
$Cu_2ac_4 2H_2O$	2.64	1	50
$Cu_2ac_4 2py$	2.63	1	51
$Cr_2ac_4 2H_2O$	2.64	1	52
$Rh_2ac_4 2H_2O$	2.45	2	53
"$(pyH)(HReCl_4)$"	2.22	4	44
"$(pyH)(HReBr_4)$"[b]	α -2.21	4	54
	β -2.27	4	54
$K_2(Re_2Cl_8)2H_2O$	2.24	4	47
$(NH_4)_3(Tc_2Cl_8)2H_2O$	2.13	4	55
$Mo_2(ac)_4$	2.11	4	49

a - The bond order is an empirical one based solely on the bond length (48).

b - "$(pyH)(HReBr_4)$" is said to exist in two different modifications - the α-form has a tetragonal unit cell: a= 1.908 ± 0.005 Å, b= 7.605 ± 0.003 Å; and the β-form has an orthorhombic unit cell: a= 7.76 ± 0.02 Å, b= 16.76 ± 0.04 Å, c= 16.83 ± 0.04 Å. (54).

Reaction of $ReO(CEt)Cl_2(PPh_3)_2$ with substituted β-diketones.

When a benzene solution of green $ReO(CEt)Cl_2(PPh_3)_2$ was heated with an excess of 1, 1, 1, trifluoropentane2-4dione, 1, 1, 1, 5, 5, 5 hexafluoropentane2-4dione or 4, 4, 4, trifluorol-2'thienylbutanel-3dione, (T.T.A.), compounds of the

type $ReCl_2acac(PPh_3)_2$ were obtained. All the compounds were monomeric and soluble in benzene. With phenyl substituted β-diketones rather different results were obtained. 1-phenyl-butanel-3dione reacted with $ReO(OEt)Cl_2(PPh_3)_2$ to give a compound of stoichiometry $ReCl_3(MeCOCHCOPh)PPh_3$, but the yield was never much greater than about 25%. 1-3diphenylpropanel-3dione yielded a compound of approximate composition $(ReCl_2(PhCOCHCOPh)(PPh_3)_2)_2$. In an endeavour to purify this complex, a benzene solution was allowed to pass down an alumina column and then the compound was reprecipitated with 30/40 petrol. Further polymerisation occured however; in one experiment a tetramer was obtained and in another a hexamer. This behaviour was not shown by the other complexes. For example $ReCl_2(CF_3CCCHCOCH_3)(PPh_3)_2$ on passing down an alumina column remained monomeric. Although the benzene solution of $ReCl_2(CF_3CCCHCOCH_3)(PPh_3)_2$ was absorbed on the column (in contrast to the PhCOCHCOPh derivative), elution of the column with chloroform removed the complex. Thus strictly speaking the two experiments are not analogous, but clearly there are differences between the two compounds, although the stoichiometries are the same. The reason for the random polymerisation of the PhCOCHCOPh derivative is difficult to understand.

A benzene solution of "$ReCl_2(PhCOCHCOPh)(PPh_3)_2$" exhibited dichromatism, being red when observed by transmitted light through a large thickness of solution, and green through a small thickness. Consider a medium which absorbes reasonably strongly in the blue, fairly weakly in the green and scarcely

at all in the red. A small thickness of the medium will be sufficient to absorb most of the blue region of the spectrum and when viewed by transmission with incident white light, the emergent red and green and blue light cause it to appear green. If a thick layer of the medium is viewed by transmission, all the blue and the green will be absorbed, causing the medium to appear red. Intermediate thicknesses will appear yellow. This phenomenon is called dichromatism. This is just the situation present in the benzene solution of "$ReCl_2(PhCOCHCOPh)(PPh_3)_2$" and measurement of the absorbtion coefficient at different wavelengths shows that:

$$\epsilon(450\ m\mu) : \epsilon(530\ m\mu) : \epsilon(730\ m\mu) = 36 : 9 : 1$$

All these compounds had the characteristic C=O stretch at 1520-1550 cm^{-1}, which is usual in oxygen co-ordinated β-diketones.

Salicylaldehyde (salH) can be considered to be a β-diketone when it co-ordinates via both oxygens. Reaction with trans-$ReOCl_3(PPh_3)_2$ yielded oxodichloro(salicylaldehydo)triphenylphosphine, $ReOCl_2(sal)PPh_3$. The complex is diamagnetic in acetone solution, as is expected for this type of complex, with a characteristically high rhenium oxygen stretching frequency. The compound was monomeric in acetone and dimeric in benzene, whereas the acac complexes were monomeric in benzene. Not surprisingly, reaction of trans-$ReOCl_3(PPh_3)_2$ with catechol, ($catH_2$) produced a compound of quite different stoichiometry from those obtained from the β-diketones above. A compound of stoichiometry $ReCl_3(cat)PPh_3$ is obtained. There is no

C-H stretch in the infra-red spectrum, indicating that the catechol is acting as a bidentate ligand. The complex is dimeric in acetone and benzene, thus unless heptaco-ordination is invoked, the complex would appear to contain catechol bridges. Another dimeric species was obtained from o-nitrophenol.

TABLE 4. β-diketonato complexes of rhenium.

Compound	Colour	m.p.	$\nu_{Re=O}$	μ_{eff}(B.M.)
$ReOCl_2(acac)PPh_3$	green	167-170	979	diamag
$ReOBr_2(acac)PPh_3$	green		976	diamag
$ReCl_2(acac)PPh_3$	green		975	
$ReOCl_2(sal)PPh_3$	dark green	134-137	978	diamag
$ReOCl_2(acac)PPhEt_2$	green		976	diamag
$ReCl_2acac(PPh_3)_2$	orange	182-185		1.4
$ReBr_2acac(PPh_3)_2$	orange	187-193		1.6
$ReI_2acac(PPh_3)_2$	red	176-177		
$ReCl_2acac(PPhEt_2)_2$	orange			
$ReCl_2(CF_3COCHCOMe)(PPh_3)_2$	purple-red	191-192		
$ReCl_2(CF_3COCHCOCF_3)(PPh_3)_2$	dark-blue	124-127		
$ReCl_2(T.T.A.)(PPh_3)_2$	lilac	188-192		
$ReCl_3(PhCOCHCOCH_3)PPh_3$	brown-red	132-134d		
$(ReCl_2(PhCOCHCOPh)(PPh_3)_2)_2$	dark green			
$ReCl(acac)_2PPh_3$	orange	198-199		
$Re_2Cl_4(acac)_4$	orange	297-299d		2.9

d) Reaction with aromatic tertiary amines.

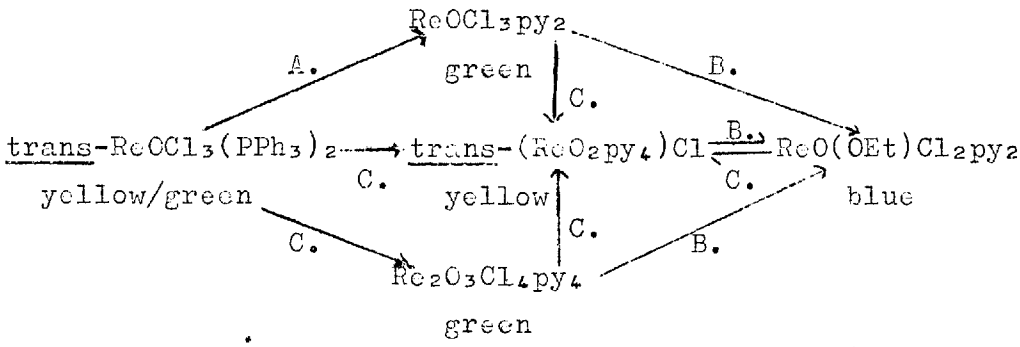
Trans-$ReOCl_3(PPh_3)_2$ reacts with pyridine to yield trans-$(ReO_2py_4)Cl.2H_2O$ (16) or $Re_2O_3Cl_4py_4$ (22), depending on the starting conditons. It has been shown (22) that the latter compound is an intermediate in the formation of the former. The structure of the binuclear species is considered to be that of two octahedra sharing a common oxygen atom (22). This compound can be cleaved with ethanol giving blue crystals of $ReO(OEt)Cl_2py_2$ (22). However oxotrichlorobis(pyridine)rhenium(V), $ReOCl_3py_2$ had not been prepared in any of the above reactions, although Chakravorti (56) claimed that the green compound formed on boiling trans-$(ReO_2py_4)Cl$ in 5M. HCl was $ReOCl_3py_2$, although no physical properties were given. In fact this compound is oxohydroxotetrapyridinerhenium(V)oxopentachlororhenate(V) $(ReO(OH)py_4)(ReOCl_5)$; see page 52.

$ReOCl_3py_2$ was prepared by suspending trans-$ReOCl_3(PPh_3)_2$ in dichloromethane and passing chlorine gas through until a red solution was obtained. Treatment of this solution with pyridine lead to the formation of $ReOCl_3py_2$. It could also be obtained from the reduction of silver perrhenate with thionyl chloride in the presence of pyridine. The green crystals of this compound were suspended in ethanol and refluxed for three hours affording the known blue $ReO(OEt)Cl_2py_2$. $ReO(OEt)Cl_2py_2$ was also obtained on boiling a solution of trans-$(ReO_2py_4)Cl$ in ethanol for five minutes. It was also obtained directly from trans-$ReOCl_3(PPh_3)_2$ by reaction with pyridine in ethanol.

It was found that unless the trans-$ReOCl_3(PPh_3)_2$ was

completely free from acetic acid, the yield of trans-$(ReO_2py_4)Cl$ was very small - an ethanol soluble tar was obtained on addition of ether (instead of yellow crystals of trans-$(ReO_2py_4)Cl$) and one could not therefore, recrystallise from this solvent, as suggested by the original authors (16). If the ethanolic solution was boiled, blue crystals of $ReO(OEt)Cl_2py_2$ separated out on cooling. The complete reaction scheme is given below in Fig. 3.

FIGURE 3. Reactions of $(ReO)^{3+}$ with pyridine.



A = Cl_2 + py

B = EtOH

C = py + H_2O

At no stage was $ReO(OH)Cl_2py_2$ obtained. According to Murmann (57), the compound is "extremely insoluble" and thus it is difficult to see why this compound was not isolated in the formation of $Re_2O_3Cl_4py_4$. The metal oxygen stretching frequency given by Murmann (57) of 980 cm^{-1} seems to be rather high in comparison to those compounds of similar stoichiometry - see Table 5. Repetition of Murmann's experimental procedure failed to yield a compound of this formulation.

Reaction of green $ReO(OEt)Cl_2(PPh_3)_2$ with o-phenanthroline (o-phen) and 2.2' dipyridyl(dipy.) resulted in the formation

of $ReO(OEt)Cl_2L$ (L = o-phen, dipy.). These compounds were blue, like the bis(pyridine) analogue, and had similar metal oxygen stretching frequencies (see Table 5).

TABLE 5. Metal-oxygen stretching frequencies in $ReO(OEt)X_2L_2$

Compound	Colour	$\nu_{Re=O}$	Reference
$ReO(OEt)Cl_2py_2$	blue	963	
$ReO(OEt)Cl_2(dipy)$	blue	952	
$ReO(OEt)Cl_2(o\text{-}phen)$	blue	958	
$ReO(OEt)Cl_2(PPh_3)_2$	green	949	
$ReO(OEt)Cl_2(PPh_3)_2$	purple	945	
$ReO(OEt)Cl_2(PPh_3)_2$	grey-green	945	
$ReO(OEt)Cl_2(PPhEt_2)_2$	violet	951	12
$ReO(OEt)Cl_2(PPhEt_2)_2$	purple	942	12
$ReO(OEt)Br_2(PPh_3)_2$	grey	941	
$ReO(OEt)I_2(PPh_3)_2$	grey	945	

Reaction of trans-$ReOCl_3(PPh_3)_2$ with dipy. did not give pure oxotrichloro(2.2' dipyridyl)rhenium(V), $ReOCl_3(dipy)$. The brown compound obtained was always contaminated; probably with $(ReO_2dipy_2)^+$. However, the pure compound could be obtained from reaction of oxotrichlorotriphenylphosphinedimethylsulphoxiderhenium(V), $ReOCl_3PPh_3Me_2SO$ (see page 55). The analogous reactions with o-phen. always gave a large number of by-products, which could not satisfactorily be separated.

e) Reaction with carbon monoxide.

Trans-$ReOCl_3(PPh_3)_2$, $ReO(OEt)Cl_2(PPh_3)_2$ (green isomer) and

$ReCl_4(PPh_3)_2$ could all be reduced in the presence of excess triphenylphosphine and copper powder with carbon monoxide at ca. 180 atms. to give the white complex $ReCl(CO)_3(PPh_3)_2$. The compound was diamagnetic in the solid state at 20°.

The formulation $(Re(CO)_4(PPh_3)_2)Cl$, proposed by Hieber and Schuster (58), was criticised (25) on the basis of its low conductivity in acetone (λ = 1.1 ohm^{-1} cm^2), and was reformulated by Abel (25) as $ReCl(CO)_3(PPh_3)_2$. The molar conductivity of the compound prepared above was 4.6 ohm^{-1} cm^2 which is still much lower than the conventionally accepted figure for a 1:1 electrolyte in acetone of ca. 100 ohm^{-1} cm^2. Unfortunately, at that time reliable oxygen analyses in the presence of phosphorus were impossible. However the compound prepared by Freni and Valenti (10) was analysed for carbonyl directly and found to fit the non-ionic formulation, which was supported by their finding a molar conductivity of less than 0.1 ohm^{-1} cm^2 in nitrobenzene. However, recently the reaction of $(Re(CO)_4(PPh_3)_2)Cl$ with alkoxide has been described (59).

$$(Re(CO)_4(PPh_3)_2)^+ + RO^- \underset{HX}{\overset{KOH}{\rightleftharpoons}} Re(CO)_3(PPh_3)_2COOR$$

R= Me, Et, C_5H_{11}, $PhCH_2$, X= Cl, Br.

It is difficult to see how this reaction is possible with a complex formulated as a tricarbonyl. Furthermore, although no method of preparation was given, the molar conductivity was stated to be 121 ohm^{-1} cm^2. Recently the technetium analogue $(Tc(CO)_4(PPh_3)_2)(AlCl_4)$ was prepared (60), with a molar conductivity of 126 ohm^{-1} cm^2. Thus it would

appear that both compounds are capable of existance although more work needs to be done to clarify the preparative procedures.

No pink chlorodicarbonylbis(triphenylphosphine)rhenium(I) $ReCl(CO)_2(PPh_3)_2$, was obtained during the course of the reaction, in contrast to the observations of Freni and Valenti (10). However the compound was obtained (together with a pale green isomer) by treating a suspension of green $ReO(OEt)Cl_2(PPh_3)_2$ in ethanol with carbon monoxide under pressure.

Both rhenium pentachloride ($ReCl_5$) and rhenium trichloride trimer $(ReCl_3)_3$ can be reduced with carbon monoxide under relatively mild conditions to yield rhenium pentacarbonyl-chloride $Re(CO)_5Cl$. This is a good way of using excess $ReCl_5$, since even in sealed ampoules its reactivity decreases with time. In addition $Re(CO)_5Cl$ is a useful preparative starting material.

f) Reaction with chlorine.

If chlorine gas was passed through a suspension of trans-$ReOCl_3(PPh_3)_2$ or green $ReO(OEt)Cl_2(PPh_3)_2$ in dicloromethane, chloroform or benzene, a red solution was obtained, which turned blue on hydrolysis. This suggested that a Re(VI) species was present, but no Re(VI) compound could be isolated by us. This red solution could also be obtained by allowing a mixture of solid chlorine and green $ReO(OEt)Cl_2(PPh_3)_2$ to warm up to room temperature in a sealed tube. When the tube was opened, and the chlorine allowed to evaporate, a blue tar remained.

Addition of pyridine to the dichloromethane solution resulted in the formation of the Re(V) complex $ReOCl_3py_2$.

On reacting the red dichloromethane solution with an ethanolic solution of tetraethylammonium chloride, $(Et_4N)Cl$, tetraethylammonium oxotetrachlorotriphenylphosphine oxiderhenate(V) $(Et_4N)(ReOCl_4PPh_3O)$, was obtained. This compound was a 1:1 electrolyte in nitrobenzene (Λ_M = 23 ohm^{-1} cm^2) and had a metal oxygen stretch at 979 cm^{-1}. Rhenium-chlorine stretching modes were found at 339 cm^{-1} and 300 cm^{-1} in the infra-red, suggesting that the anion has C_{4v} symmetry, i.e. with the oxygen atom trans to the triphenylphosphine oxide. (see page 55). The P=O stretch of the co-ordinated triphenylphosphine oxide was at 1151 cm^{-1}. (However substitution of $(Et_4N)Cl$ by tetraphenylarsonium chloride $(Ph_4As)Cl$, yielded only the well known Re(VII) species tetraphenylarsonium perrhenate $(Ph_4As)(ReO_4)$). The co-ordinated triphenylphosphine oxide could be removed by reacting further with β-diketones, still giving 1:1 electrolytes in nitrobenzene.

The solution could be reduced at 110° with carbon monoxide at 60 atms. pressure to give $Re(CO)_5Cl$.

Thus none of these reactions give much information concerning the nature of the species present in the dichloromethane solution.

In an endeavour to determine the strength of the oxidising agent required to affect this change, a suspension of trans-$ReOCl_3(PPh_3)_2$ in dichloromethane was treated with ozone. However only ligand oxidation occurred, giving oxotrichlorobis(triphenylphosphine oxide)rhenium(V) $ReOCl_3(PPh_3O)_2$.

CHAPTER 2.

RHENIUM(III) CLUSTERS.

The trimeric nature of a number of Re(III) tertiary phosphine adducts has been well authenticated by two different sets of workers (61, 62). However, the published data concerning the nature of the parent rhenium trichloride has been confusing and contradictory. Three sets of workers found two different results for the unit cell parameters:

	a(Å)	b(Å)	c(Å)	β(°)	Z
Cotton and Mague (63)	10.826±0.02	-	20.364±0.02	-	18
Lux (64)	10.14±0.03	-	20.19±0.09	-	18
Gellinek and Rüdorff (65)	14.6	10.15	8.88	113.7	12

However a single X-ray determination has subsequently been performed by Cotton (66), confirming his original findings of a space group of $R\bar{3}m$, with 18 $ReCl_3$ per hexagonal unit cell.

Rhenium trichloride and rhenium tribromide are not however isostructural; both Rüdorff (65) and Cotton (61) agree that rhenium tribromide has a monoclinic unit cell with the following dimensions:

a = 8.10 Å; b = 10.62 Å; c = 8.65 Å; β = 111°; Z = 6.

However it is interesting to note that (ReX_3PPhEt_2) (X = Cl, Br) are isostructural (67).

Similarly, from spectroscopic evidence, it was suggested that "$ReCl_3PPh_3$", as prepared by the method of Chatt *et.al.* (12)

had a trimeric structure. These crystals were described as purple black plates, in contrast to the red crystals, formulated as $ReCl_3PPh_3$ by Wilkinson et.al. (27). In fact the latter compound has been shown to be incorrectly formulated and should be nonachlorotris(triphenylphosphine)trirhenium(III) bis(acetone) $(ReCl_3PPh_3)_3.2(Me_2CO)$. This fits the original analytical results (27) better than does $ReCl_3PPh_3$; indeed, a mistake in the calculated carbon percentage (27), accentuates this difference. Also an oxygen analysis was not performed. The infra-red spectrum showed a medium strong band at 1740 cm^{-1} (C=O stretch) and a medium band at 1224 cm^{-1} (CH_3-C-O bend); both due to acetone (41c), in addition to the triphenylphosphine bands.

The compound was put on a thermogravimetric balance under a nitrogen atmosphere, and at temperatures greater than 140° there was a steady loss in weight, but not stepwise. On a vacuum thermogravimetric balance it appeared to sublime above 150°.

It was possible to prevent trimerisation of the type, $(ReCl_3L)_3$, by using the chelating diphosphine, 1,2bis(diphenylphosphine)ethane, $Ph_2PCH_2CH_2PPh_2$. Addition of an acetone solution of this compound to an acetone solution of rhenium trichloride resulted in the formation of a complex of stoichiometry $((ReCl_3)_2(Ph_2PCH_2CH_2PPh_2))_n$. Unfortunately the compound was insoluble in the usual organic solvents making a molecular weight determination impossible. There were no bands in the infra-red spectrum due to the solvent.

CHAPTER 3.

TRANS-DIOXO RHENIUM(V) COMPLEXES.

a) Infra-red spectra.

Quite a number of stable, diamagnetic dioxo rhenium(V) complexes, both cationic and anionic are known. The reduction of potassium perrhenate with hydrazine hydrate in the presence of potassium cyanide was said to produce $K_3(ReO(CN)_4)$ (68), but subsequent work (69) showed that the compound should be reformulated as one of the compounds prepared by Klemm et.al. (70), i.e. $K_3(ReO_2(CN)_4)$. Since then $K_3(ReO_2(CN)_4)$ has been subjected to an X-ray single crystal determination (71) and found to have the trans-dioxo configuration with a rhenium-oxygen bond length of 1.87 Å. Thus the compound is tri-potassium trans-dioxotetracyanorhenate(V). The unit cell is said to be triclinic (71):

a = 7.73 ± 0.02 Å	α = 107° 28' ± 10'
b = 7.35 ± 0.02 Å	β = 108° 20' ± 10'
c = 6.32 ± 0.02 Å	γ = 114° 20' ± 10'

This is in contrast to earlier claims of a monoclinic unit cell (69, 70), although in both cases no cell dimensions were given. A very sharp strong singlet C≡N stretch in the infra-red spectrum at 2119 cm^{-1} also suggests a trans configuration.

From infra-red evidence, dioxobis(ethylenediamine)rhenium(V) chloride $(ReO_2en_2)Cl$ is considered to be trans (16), and from the overall similarity and simplicity of the electronic spectra, it can reasonably be assumed that all these compounds are trans (72).

The reason for the diamagnetism is essentially the same as that in the oxo phosphine rhenium(V) complexes discussed previously, except that the p_x orbital of one oxygen atom donates to the vacant d_{xz} orbital on the rhenium and the p_y orbital of the other oxygen atom donates to the d_{yz} metal orbital. The result is, that a molecular orbital scheme like that in Fig. 1. is again produced giving a singlet ground state and hence diamagnetism. This explanation was put forward by Symons (73) to explain the diamagnetism of trans-$(OsO_2(CH)_4)^{2-}$ (74).

Thus each oxygen atom has a lone pair remaining, and so the metal oxygen bond order is decreased in the trans-dioxo compounds, 2, from that in the oxo compounds, 3. This is confirmed by the difference, in the infra-red spectra, of the rhenium oxygen stretching frequencies and in the different rhenium oxygen distances, from X-ray single crystal data.

A number of metal oxygen stretching frequencies tabulated below, differ from those previously given in the literature. Deuteration studies revealed that the rhenium oxygen stretch in trans-$(ReO_2en_2)Cl$ is at ca. 770 cm^{-1} and not at 814 cm^{-1}, as previously suggested (16). Unfortunately there appears to be a certain degree of hydrogen bonding in this type of complex, and thus the position of the rhenium oxygen stretch differs slightly on deuteration.

In view of the different interpretations of the spectrum of $(OsO_2(NH_3)_4)^{2+}$ (75, 76), and the somewhat unsatisfactory data on $(ReO_2(NH_3)_4)^+$, (see experimental section), it was decided to deuterate both samples in order to make a unique assignment possible.

TABLE 6. Metal oxygen asymmetric stretching fequencies in some trans-dioxo complexes.

Complex	ν M=O	Reference
$(ReO_2en_2)^+$	769	
	814	16
$(ReO_2py_4)^+$	814	16
$(ReO_2(NH_3)_4)^+$	855 m. 835 vs. b.	
$(OsO_2(NH_3)_4)^{2+}$	883	
	883	75
	808	76
$(ReO_2(o\text{-}C_6H_4(PEt_2)_2)_2)^+$	782	77
$(ReO_2(Me_2PCH_2CH_2PMe_2)_2)^+$	786	77
$(ReO_2(Ph_2PCH_2CH_2PPh_2)_2)^+$	784	77
	789	78
$(ReO_2(CN)_4)^{3-}$	775	

Unfortunately deuteration of $(ReO_2(NH_3)_4)Cl$ proved to be impractical due to hydrolysis. In fact slightly different starting conditions produced the monohydrate $(ReO_2(NH_3)_4)Cl.\ H_2O$. If acetone was used as the solvent, the hydrate was contaminated with ammonium chloride (the ν_4 band of NH_4^+ being apparent at ca.1420 cm^{-1}) (41b). This could be removed by boiling the impure compound in absolute ethanol. A suggested scheme for the formation of trans-$(ReO_2(NH_3)_4)^+$ from $ReO(OEt)Cl_2(PPh_3)_2$ is given overleaf.

$$ReO(OEt)Cl_2(PPh_3)_2 + H_2O + 5NH_3 \longrightarrow (ReO_2(NH_3)_4)Cl + NH_4Cl + 2PPh_3 + EtOH. \quad .....(1).$$
green yellow

$$(ReO_2(NH_3)_4)Cl + H_2O \longrightarrow (ReO_2(NH_3)_4)Cl.\ H_2O \quad .....(2).$$
yellow russet

$$3(ReO_2(NH_3)_4)Cl.\ H_2O + 7H_2O \longrightarrow 2ReO_2 + NH_4ReO_4 + 3NH_4Cl + 8NH_4OH \quad .....(3).$$
russet black

Thus in (1) the NH_4Cl is detectable in acetone, as it is less soluble in acetone than in ethanol, and thus boiling the crude material in ethanol has the effect of purifying the product by dissolving out the NH_4Cl. Equation (3) represents the usual disproportionation reaction of Re(V). Clearly the amount of water present is critical in determining which products are obtained.

Fortunately no such difficulties were encountered in the deuteration of $(OsO_2(NH_3)_4)^{2+}$, and the results are tabulated, together with assignments in Table 7.

The Russian workers (75) attempted to deuterate their sample by recrystallising from D_2O, but found that hydrolysis occurred. This was confirmed during the course of the present work; the only way to achieve satisfactory deuteration was to react potassium osmate with deuterated ammonium chloride ND_4Cl (see experimental). On the assumption that the NH_3 and ND_3 groups oscillate as a unit, i.e. that the coupling between the Os-N and the N-H(D) is small, the ratio $\nu_{Os-NH_3} : \nu_{Os-ND_3}$ should be $\left(\frac{20}{17}\right)^{0.5}$:1 i.e. 1.086:1.

The observed ratio is 1.09:1

Likewise the ratio $\nu_{N-H} : \nu_{N-D}$ should be $\left(\frac{30}{16}\right)^{0.5}$:1 i.e. 1.37:1 ideally.

The observed value is 1.36:1.

TABLE 7. Infra-red spectra of $(OsO_2(NH_3)_4)^{2+}$ and $(OsO_2(ND_3)_4)^{2+}$.

$(OsO_2(NH_3)_4)^{2+}$			$(OsO_2(ND_3)_4)^{2+}$	Assignment (41d)
Griffith (76)	Atovmyan (75)	present work	present work	
		3200 s.	2353 s.	N-H (N-D) stretch.
		3049 s.	2242 s.	
1605 w.		1610 w.		combination band.
	1649 m.			$NH_3(ND_3)$ degenerate
1558 s.	1593 s.	1563 s.	1152 s.	deformation.
			1065 m.	δ_4 mode ND_4Cl impurity
1350 s.	1371 s.	1351 s.	1042 s.	$NH_3(ND_3)$ symmetrical
1334 s.	1356 s.	1333 s.	1032 s.	deformation.
808 s.	883 s.	883 s.	864 s.	Os=O asym. stretch
867	817 s.	818 s.	684 m.	$NH_3(ND_3)$ rock
849			641 m.	
		483 m.	444 m.	Os=$NH_3(ND_3)$ stretch.

The band assigned as the NH_3 rocking mode is not particularly broad or intense compared to the osmium oxygen stretch, contradicting the generalisation of Svatos et. al. (79) that "the rocking vibration is very broad and intense". However the presence of a strong band at 864 cm^{-1} in the deuterated sample (the ND_3 rocking mode would be shifted down some hundreds of wavenumbers) favours the above assignments. In a partially deuterated sample the band at ca. 870 cm^{-1} has split into two components, indicating that this is not a pure asymmetric osmium oxygen stretch and that presumably there is some hydrogen

bonding occurring.

b) Electronic spectra.

The electronic spectra of a number of trans-dioxo rhenium(V) species have been examined and are contrasted (where data is available) with those of the mono- and di-protonated species. It has been known for some time (80) that $(ReO_2en_2)^+$ could be protonated readily and salts of oxohydroxobis(ethylenediamine)-rhenium(V), $(ReO(OH)en_2)^{2+}$ and bis(hydroxo)bis(ethylenediamine)-rhenium(V), $(Re(OH)_2en_2)^{3+}$ were isolated. These changes can be observed visually in hydrochloric acid. Addition of 2M. HCl to the yellow $(ReO_2en_2)^+$ gives the pink $(ReO(OH)en_2)^{2+}$ and addition of 10M. HCl gives blue $(Re(OH)_2en_2)^{3+}$. The acid association constants for both stages have been determined (81).

The monoprotonated $(ReO(OH)en_2)^{2+}$ is expected to be diamagnetic due to multiple bonding between the rhenium and the oxygen (Re=O stretch 980 cm^{-1})(an X-ray structure of $(ReO(OH)en_2)(ClO_4)_2$ is at present being carried out), (82), but in diprotonated $(Re(OH)_2en_2)^{3+}$, with less posibility of π-bonding, paramagnetism could result. However the compound is diamagnetic in solution at 25°.

Unfortunately only one strong band can be seen in each case, making a unique assignment impossible. The following is tentatively suggested as being the most likely interpretation-that the main band is the $(^1E_g \longleftarrow {}^1B_{2g})$ and the other is the $(^3E_g \longleftarrow {}^1B_{2g})$. One would expect the spin forbidden band to be at a lower energy due to stabilisation caused by the favourable

exchange energy.

TABLE 8. Electronic spectra of trans-dioxo rhenium(V) and related species.

Complex	Solvent	Band max. ($m\mu$)	ϵ max	$\Delta\nu_{\frac{1}{2}}$ (cm^{-1})[a]
$(ReO_2en_2)^+$	H_2O	550	3	
		435	23	3300
$(ReO(OH)en_2)^{2+}$	2M. HCl	650	6	
		484	22	3500
$(Re(OH)_2en_2)^{3+}$	10M. HCl	820	9	
		600	22	3400
$(ReO_2(NH_3)_4)^+$	nujol mull	590 sh.		
		446		
$(ReO_2(CN)_4)^{3-}$	H_2O	ca. 520 sh.	ca. 5	
		420	34	3500
$(ReO(OH)(CN)_4)^{2-}$	2M.HCl	660 sh.	ca.20	
		536	41	3800

a - $\Delta\nu_{\frac{1}{2}}$ is the width of the main band at half intensity, for use in obtaining the oscillator strength f.

$$f \sim 4.6 \quad 10^{-9} \epsilon_{max.} \Delta\nu_{\frac{1}{2}} .$$

Since we expect $(OH)^-$ to be a poorer π-donor than $(O)^{2-}$ i.e. that the E_g level would be progressively stabilised with increasing protonation of the system, we would expect the bands to move to succesively higher wavelengths as the protonation is increased. Inspection of Table 8. illustrates this for both the ethylenediamine and cyanide complexes. Furthermore we

would expect a greater difference between $(ReO(OH)en_2)^{2+}$ and $(Re(OH)_2en_2)^{3+}$, than between $(ReO(OH)en_2)^{2+}$ and $(ReO_2en_2)^{+}$, since there is little π-bonding in the bis(hydroxo) complex, as indicated by the Re-(OH) stretching frequency (see Table 15). Although the spectrum of $(ReO_2(NH_3)_4)^{+}$ was carried out on a nujol mull, it can be seen that the relative absorbtion energies follow that of the spectrochemical series, i.e. $CN^- > en > NH_3$. No data is given for $(ReO_2py_4)^{+}$ since it appears that the absorbtion spectrum is extremely sensitive to the solvent.(57).

The spectrum of $(Re(OH)_2en_2)^{3+}$ was observed over a period of 15 days, during which time the solution turned yellow and bands appeared at 1080, 785, 474, 410 mμ. These are characteristic of "$(ReOCl_5)$".

c) Reaction of trans-$(ReO_2py_4)^{+}$ with HCl.

The green insoluble product obtained by refluxing trans-$(ReO_2py_4)Cl$ in 5M.HCl has been variously described as $ReOCl_3py_2$ (56), $Re(OH)_2Cl_3py_2$ (83), $(ReO_2py_4)_2(ReOCl_5)$ (84) and $Re(OH)_2Cl_2py_2)Cl$ (57). No analytical data was presented to support the formulation $Re(OH)_2Cl_3py_2$. $ReOCl_3py_2$ has been prepared by other methods and differs from the compound produced in this reaction. Formulation as $(ReO_2py_4)_2(ReOCl_5)$ (84) seems unlikely since the same authers postulate monoprotonation and the formation of red trans-oxohydroxotetrapyridinerhenium(V) dichloride, $(ReO(OH)py_4)Cl_2$, merely by passing HCl gas over solid trans-$(ReO_2py_4)Cl$ at 20°. In fact the insoluble green compound is $(ReO(OH)py_4)(ReOCl_5)$. The cationic and anionic

Re=O stretches are at 968 cm^{-1} and 940 cm^{-1} respectively. The same compound was obtained in 10M. HCl and deuteration failed to shift the above bands, making Murmann's assignment of the compound as $(Re(OH)_2Cl_2py_2)Cl$ unlikely (57), since on this basis the bands must be assigned as O-H deformation modes. (A weak broad band at ca. 2350 cm^{-1} is assigned to the O-D stretch in the deuterated sample). Heating the compound in pyridine leads to the formation of the starting material, $(ReO_2py_4)Cl$. Hence the following equilibria are postulated:

$$\underset{\text{yellow}}{(ReO_2py_4)Cl} + HCl \rightleftharpoons \underset{\text{red}}{(ReO(OH)py_4)Cl_2}$$

$$\underset{\text{red}}{2(ReO(OH)py_4)Cl_2} + 5HCl \rightleftharpoons \underset{\text{green}}{(ReO(OH)py_4)(ReOCl_5)} + 4pyHCl + H_2O.$$

The compound formulated as $ReO(OH)Cl_2py_2$ by Murmann (57), obtained by boiling <u>trans</u>-$(ReO_2py_4)Cl$ in 1M. HCl is not $Re_2O_3Cl_4py_4$. As obtained above, the compound has an almost featureless infra-red spectrum and did not give consistent analytical results. The nature of this complex, or mixture is not known, although it is a nonconductor in acetonitrile.

Compounds of the type $ReO(OH)Cl_2L_2$ and $(Re(OH)_2Cl_2L_2)Cl$, (L= py, $\frac{1}{2}$en) were claimed by Murmann (57), suggesting a complete analogy between the two systems. That this is not so can readily be seen by the reaction of $(ReO_2L_4)^+$ with dilute hydrochloric acid. With L= $\frac{1}{2}$en, the reaction proceeds via the pink monoprotonated $(ReO(OH)en_2)^{2+}$. Whereas with L= py, the solution at no stage shows the bright red colouration due to $(ReO(OH)py_4)^{2+}$.

d) Reaction of $(ReO_2en_2)^+$ with HCl.

The nature of the reaction of trans-$(ReO_2en_2)Cl$ with acid has been fairly fully investigated, (57, 80, 81, 85) but further compounds have now been isolated. Over a period of time, the pink solution of trans-$(ReO(OH)en_2)^{2+}$ in 2M. HCl deposits green crystals of stoichiometry $Re_2O_3Cl_4en_2$, which react further with excess ethylenediamine to give trans-$(ReO_2en_2)Cl$.

The structure of the green complex is postulated to be similar to that of the pyridine complex, $(ReOCl_2py_2)_2O$ i.e. with an oxygen atom linking two octahedra (22) incorporating a linear Re-O-Re system. A weak band at 871 cm^{-1} is presumably due to the bridging oxygen (c.f. $(ReOCl_2py_2)_2O$, 876 cm^{-1} and $((ReCl_5)_2O)^{4-}$, 867 cm^{-1}). The terminal rhenium-oxygen stretch is in the expected region for a multiply bonded system, see Table 15. Murmann (57) formulates this compound as $ReO(OH)Cl_2en$, but unfortunately the compound's insolubility prevented a molecular weight from being determined.

The compound could not be prepared by any of the methods used for the pyridine analogue, nor could it be obtained from $Re_2O_3Cl_4py_4$ by reaction with ethylenediamine, since this resulted in the formation of yellow $(ReO_2en_2)^+$. No cleavage product was obtained with ethanol on refluxing for 6 days, or by heating in a sealed tube at 200°. The compound was completely insoluble in all common organic solvents, thus making molecular weight and conductivity measurements impossible.

After 2 days, the blue solution of trans-$(Re(OH)_2en_2)^{3+}$ in 10M. HCl deposited green crystals of oxotrichloroethylene-

diaminrhenium(V), $ReOCl_3en$. Care must be excercised in the preparation, for if the rhenium concentration is too low, no crystals separate out and if it is too high, the crystals are contaminated with ethylenediamine hydrochoride, enH_2Cl_2 (which can be removed by shaking with water). Since the yield of the reaction (w.r.t. rhenium) is almost 100%, the isolation and characterisation of enH_2Cl_2 indicates that the ratio en:Re is 1:1 in this compound, compared to 2:1 in the original starting material. Murmann (57) formulated this compound as $(Re(OH)_2Cl_2en)Cl$, but the infra-red spectrum and elemental analysis favour the above formulation. In fact Murmann's analytical data (57), fits the formulation $ReOCl_3en$ better than $(Re(OH)_2Cl_2en)Cl$. If $ReOCl_3en$ is heated in dilute HCl, hydrolysis occurs and $Re_2O_3Cl_4en_2$ is formed:

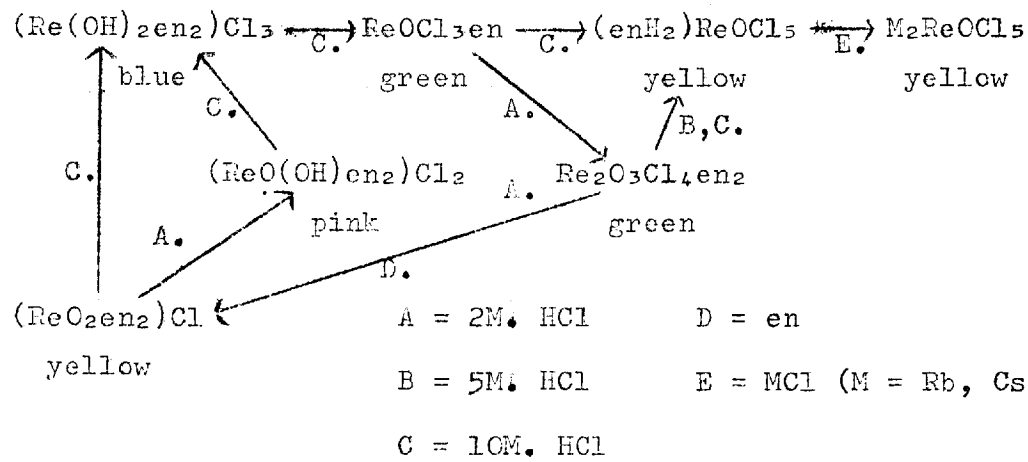
$$2ReOCl_3en + H_2O \longrightarrow Re_2O_3Cl_4en_2 + 2HCl.$$

This reaction occurs in any moist solvent in which $ReOCl_3en$ is partially soluble (e.g. MeOH, MeCN) - the liberated chloride ion is readily detected in MeOH.

On boiling in 5M. HCl, trans-$(ReO_2en_2)Cl$ gave firstly pink $(ReO(OH)en_2)^{2+}$, then insoluble green $Re_2O_3Cl_4en_2$; after about 40 minutes the latter dissolved to give a yellow solution. Addition of M^+ gave a precipitate of M_2ReOCl_5 (M = Rb, Cs). (see page 52).

The reactions of $(ReO_2en_2)^+$ with HCl are summarised in Figure 4.

FIGURE 4. Reactions of $(ReO_2en_2)^+$ with HCl.



These results do not invalidate the pseudo-first order kinetics observed by Murmann (57) for the reaction of $(Re(CH)_2en_2)^{3+}$ in concentrated HCl, but reformulation leads to the following equations:

$$(Re(OH)_2en_2)Cl_3 + 2HCl \xrightarrow{k_1} ReOCl_3en + enH_2Cl_2 + H_2O$$

$$ReOCl_3en + 2HCl \xrightarrow{k_2} enH_2ReOCl_5.$$

Very recently, new Russian work has appeared (85), which suggests that the compounds formulated above as $(ReO_2en_2)^+$, $(ReO(OH)en_2)^{2+}$ and $(Re(OH)_2en_2)^{3+}$ should be reformulated as $(Re(OH)_2(en\text{-}H)_2)^+$, $(Re(OH)_2(en\text{-}H)en)^{2+}$ and $(Re(OH)_2en_2)^{3+}$ respectively. A number of physical properties have been recorded; electrical conductivity, infra-red and visible spectra. Conductivity measurements do not distinguish between the two series of compounds.

For some reason, only that part of the infra-red spectrum between 4000 and 2400 cm^{-1} is given. In each case, it is concluded that the presence of a band in the region 3300-3550 cm^{-1} is proof of the presence of the O-H group. However,

it is well known that N-H also absorbs in this region (41e). This appears to have been ignored by Evteev (85), and more experimentation would be required in order to distinguish between the two. Certainly the infra-red spectrum in the range 1000-750 cm^{-1} is more distinctive and favours the original formulations of Lebedinskii et.al. (80). As previously stated, the rhenium-oxygen bond order in trans-dioxo complexes is 2 and the Re=O stretch in $(ReO_2en_2)Cl$ is at 769 cm^{-1}, however on protonation the bond order increases to 3 (as in the oxo-phosphine rhenium(V) compounds) and the Re=O stretch in, for example, $(ReO(OH)en_2)(ClO_4)_2$ is at 983 cm^{-1} (see Table 15). Were these compounds all bis(hydroxo) species (85), it would be impossible to interpret these differences.

Only in the case of "$(Re(OH)_2(en\text{-}H)_2)^+$" is the visible spectrum given. Bands are found at 300 mμ. and 440 mμ., although no extinction coefficients are given. It is difficult to believe that such fundemental colour changes occur solely due to the protonation of en-H.

On heating "$(Re(OH)_2(en\text{-}H)_2)Cl$" in concentrated HCl, Evteev (85) isolated $(ReOCl_5)^{2-}$, confirming our observations.

e) "Trioxoethylenediaminerhenium(VI)".

A compound trioxoethylenediaminerhenium(VI), ReO_3en was claimed to be one of the products obtained from reaction of tetrachlorobis(pyridine)rhenium(IV), $ReCl_4py_2$ with ethylene-diamine, (the other being $(ReO_2en_2)Cl$)(86) although no

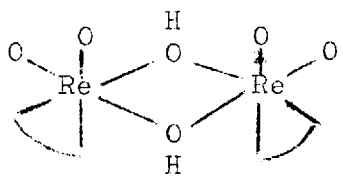
chemical analyses or properties, other than the diamagnetism, were given. It has also been claimed that trans-$(ReO_2en_2)Cl$ slowly hydrolyses to give an almost white compound, which was formulated as ReO_3en, although 4% chlorine was found in the sample (20).

Recently trioxodiethylenetriaminemolybdenum(VI), MoO_3dien has been prepared (87) and shown to have a cis-trioxo configuration (88) with an average Mo-O distance of 1.736 Å. Although the skeletal symmetry is C_{3v}, only one Mo-O stretching frequency could be seen in the infra-red spectrum, at 835 cm^{-1}, and it has therefore been assumed that there is accidental degeneracy of the A_1 and E modes (89). It is of interest to note that no such compounds were obtained with ethylenediamine or triethylenetetramine (87).

It was found that rhenium trioxide, ReO_3, (made by the dioxan reduction of perrhenic acid (90)) and ethylenediamine did not react, even when heated in a sealed tube at 200° for 16 hours. Thus direct combination proved to be impossible, hence it was decided to reinvestigate the hydrolysis of trans-$(ReO_2en_2)^+$.

A solution of $(ReO_2en_2)Cl$ in water was allowed to stand in a stoppered flask for 9 months. No white compound was obtained, in contrast to the observations of Lock (20), but large brown crystals separated out. Chemical analysis showed that they did not contain chlorine and that the stoichiometry was approximately that of ReO_3en. The compound was diamagnetic in the solid state at 25°, as measured on a Faraday

Balance, which would appear to discriminate against ReO_3en. Also since Re(VI) is a very unstable oxidation state with respect to hydrolysis, the likelihood of Re(VI) crystallising out in an aqueous medium is small. The mode of preparation suggests that Re(V) is the most likely oxidation state and since five co-ordination is not common, the six co-ordinate structure given below is favoured:



(= en

i.e. a cis-dioxo structure is postulated.

The compound is essentially a non-conductor in water (it is insoluble in all other inert solvents), and can be protonated by mineral acids. Addition of HCl to the yellow aqueous solution produces a red colouration, which is lost when the pH of the solution is raised. This is a reversible process.

The infra-red spectrum in the range 4000-600 cm^{-1} was superficially similar to that of the starting material, except that there was no band at 769 cm^{-1} (i.e. no trans-dioxo species was present), although there was a band at ca.820 cm^{-1}. This is additional evidence for the reassignment of the Re=O stretch in $(ReO_2en_2)Cl$, (see Table 6). The most striking feature of the spectrum is the presence of two strong bands at 920 and 898 cm^{-1}, which have no counterpart in the spectrum of $(ReO_2en_2)Cl$. These bands are considered to be the symmetric and asymmetric Re=O stretches respectively. The spectrum in the

range 600-400 cm^{-1} is relatively simple - $(ReO_2en_2)Cl$ has two bands at 578 cm^{-1} and 498 cm^{-1}, whereas this compound has the analogous bands at 545 cm^{-1} and 479 cm^{-1}. In addition there is a medium band at 472 cm^{-1}, which is tentatively assigned to a vibrational mode of the bridging 4-membered ring, probably the asymmetric Re-O stretch. The corresponding vibration in a wide range of comlexes containing the $(LCu\langle^{OH}_{OH}\rangle CuL)^{2+}$ cation (L= dipy, o-phen.) has been found in the range 478-498 cm^{-1} (91), in $(L_2Cr\langle^{OH}_{OH}\rangle CrL_2)^{4+}$ (L= o-phen.) at 551 cm^{-1} (92) and in $((NH_3)_4Co\langle^{OH}_{OH}\rangle Co(NH_3)_4)^{4+}$ at 535 cm^{-1} (93), and thus can be seen to be dependent on the metal atom concerned.

The infra-red data for a number of cis-dioxo molybdenum compounds has recently been summarised (94), and is given below in Table 9.

One would expect that cis-dioxo compounds would absorb at a greater frequency than the trans-dioxo, since in the former case there are greater possibilities for π-bonding, but at a lower frequency than the mono-oxo compounds (where the bond order is 3).

TABLE 9. Cis-dioxo metal oxygen stretching frequencies

Compound	Terminal M=O stretch sym.	asym.	Bridging M-O-M stretch	Reference
$(MoO_4)^{2-}$	936[a.]	895		41f
$MoO_2Cl_2(H_2O)_2$	963	938		b.
$(MoO_2F_4)^{2-}$	980	930		b.
$MoO_2Cl(\pi\text{-}C_5H_5)$	920	887		95
$MoO_2(oxine)_2$	925	899		96
$((MoO_2(C_2O_4)H_2O)_2O)^{2-}$	960	920	860	c.
$(MoO_2(\pi\text{-}C_5H_5))_2O$	920	898)		95
	930	850)		
	930	898	850	89
$(ReO_4)^-$	971[a.]	918		41f
$(ReO_2Br_2)^-$	935	875		14
$(ReO_2en(OH))_2$	920	898		
$(ReO_2Cl(Me_2SO)_2)_2$?	944	895		d.

a. - I.R. inactive

b. - W. P. Griffith personal communication.

c. - Crystal structure by F. A. Cotton, S. M. Morehouse, and J. S. Wood, Inorg. Chem., 1964, 3, 1603.

d. - See page 57

CHAPTER 4.

OXOPENTACHLORORHENATE(V).

a) Preparation.

The two previous methods for the preparation of the oxopentachlororhenate(V), $(ReOCl_5)^{2-}$ ion (97, 98), both involve addition of potassium iodide to perrhenic acid in hydrochloric acid and both result in the formation of dipotassium hexachlororhenate(IV) as the main product.

A better preparative method, similar to that for the oxopentachloromolybdate(V), $(MoOCl_5)^{2-}$ ion (99), is to dissolve freshly prepared $ReCl_5$ in 10M. HCl; addition of M^+ to this solution gives an immediate precipitate of M_2ReOCl_5, ($M^+ = Rb^+$, Cs^+, $C_9H_8N^+$, PPh_3H^+). With $M^+ = ((Ph)_4As)^+$ a yellow compound was obtained which decomposed in vacuo.

The ion was also obtained by allowing the blue acidic solution of trans-$(Re(OH)_2en_2)Cl_3$ to stand for some weeks, when yellow crystals of ethylenediaminium oxopentachlororhenate(V), $(enH_2)(ReOCl_5)$ were formed (see page 46). The caesium salt could be prepared from the latter and from bis(tetramethylammonium)oxopentachlororhenate(V), $(NMe_4)_2(ReOCl_5)$ by metathesis.

On boiling a solution of trans-$(ReO_2en_2)Cl$ in ca.5M. HCl, $(ReOCl_5)^{2-}$ and not $(Re(OH)_2Cl_4)^-$ as claimed (57) was formed. This result was shown by elemental analysis of the caesium salt and also by infra-red spectroscopy. No bands were visible in the O-H, or Re-OH stretching regions (3500-3000 cm^{-1} and 600-400 cm^{-1} respectively). The strong band at ca.950 cm^{-1},

assigned (57), as an O-H deformation mode, failed to shift on deuteration and is assigned by us as the Re=O stretch. Murmann (57) claims that protonation gives an O-H stretching band at 1600 cm^{-1}, this is incorrect - the only possibility is that the band is an H_2O (δ_2) bending mode i.e. either the compound is $(ReOCl_4H_2O)^-$ or moist $(ReOCl_5)^{2-}$. Our analytical results favour the latter, and this has been substantiated by independent workers (85). The $(Ph_4As)^+$ salt decomposed in vacuo and could not be prepared by us in a pure state.

The action of HCl gas on <u>trans</u>-$ReOCl_3(PPh_3)_2$ in benzene produces green triphenylphosphonium oxotetrachlorotriphenylphosphinerhenate(V), $(PPh_3H)(ReOCl_4PPh_3)$ (16). However, on passing HCl gas through a refluxing suspension of <u>trans</u>-$ReOCl_3(PPh_3)_2$ in tetrahydrofuran (T.H.F.), a pinkish compound of stoichiometry $(PPh_3H)_2(ReOCl_5).C_4H_8O$ was formed. A strong band at 1062 cm^{-1} and a weak one at 907 cm^{-1} are assigned to the asymmetric and symmetric ring stretches of the T.H.F. respectively (100).

$(PPh_3H)_2ReOCl_5$ and $(PPh_3H)_2ReOCl_5.C_4H_8O$, both originally pink, turned yellow after a day or two unless kept in vacuo. The product in each case was yellow $(PPh_3H)(ReOCl_4PPh_3)$ as shown by the appearance in the infra-red spectrum of a medium/strong band at <u>ca</u>.1090 cm^{-1} due to triphenylphosphine (as opposed to the triphenylphosphonium cation (101)). The solid state decomposition of $(PPh_3H)_2ReOCl_5$ is clean but the solvent in $(PPh_3H)_2ReOCl_5.C_4H_8O$ evidently stabilises the salt and only partial decomposition occurs. However the T.H.F. could be

removed by heating a suspension of the compound in acetone, or even 2M. HCl - the loss of HCl was noted when acetone was the solvent. The facile loss of HCl from triphenylphosphonium chlororhenates has been observed before (21).

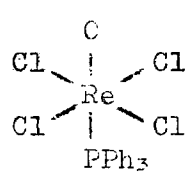
TABLE 10. Decomposition of triphenylphosphonium oxopentachlororhenates.

Compound	$\nu(cm^{-1})$	Compound	$\nu(cm^{-1})$	Assignment
$(PPh_3H)_2ReOCl_5$	2380	$(PPh_3H)_2ReOCl_5 \cdot C_4H_8O$	2424	P-H stretch
	1112		1113	P sensitive mode (q)[a]
			1062	asym. C_4H_8O ring stretch
	971		948	Re=O stretch
$(PPh_3H)(ReOCl_4PPh_3)$ (yellow)	2404	$(PPh_3H)(ReOCl_4PPh_3)$ (yellow)	2410	P-H stretch
	1114) 1092)		1113) 1093)	P sensitive modes (q) of the phenyl rings[a]
	970		968	Re=O stretch

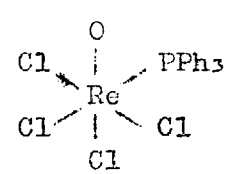
[a] Notation of D.H. Whiffen, J.C.S., 1956, 1350.

Thus it can be seen that the two decomposition products are identical.

Two isomers of $(PPh_3H)(ReOCl_4PPh_3)$ have thus been prepared, one green (16) and the other yellow. There are only two geometrical isomers of the anion, shown below:



(a)



(b)

Isomer (a), having the C_{4v} point group, should have 11 normal vibrations of species $4A_1 + 2B_1 + B_2 + 4E$ (treating the triphenylphosphine as a single unit and omitting site symmetry considerations) and should have 2 infra-red active Re-Cl stretching modes. Whereas isomer (b), with a C_s point group should have 15 normal vibrations of species $10A' + 5A''$, with 4 infra-red active Re-Cl stretches.

The green isomer was found to have Re-Cl stretches at 342, 325, 309 and 286 cm^{-1} whereas the yellow isomer has bands at 314 and 296 cm^{-1}. Thus the yellow isomer is considered to have structure (a).

This is in accord with the modes of preparation: addition of HCl to trans-$ReOCl_3(PPh_3)_2$ substitutes one of the PPh_3 groups for a Cl and thus results in the formation of the complex with the C_s point group (green (16)); the Cl lost from $(ReOCl_5)^{2-}$ would be expected to be the Cl trans to the oxygen, due to the strong trans effect of the oxo group, giving the complex with the C_{4v} point group (yellow).

When dimethylsulphoxide, (Me_2SO) was substituted for T.H.F., no salt formation occurred - green crystals of oxotrichlorotriphenylphosphinedimethylsulphoxiderhenium(V), $ReOCl_3$-PPh_3Me_2SO were obtained. The compound is diamagnetic in the solid state at 20°. The complex could also be obtained from green $ReO(OEt)Cl_2(PPh_3)_2$. $ReOCl_3PPh_3Me_2SO$ reacts with pyridine and ethylenediamine to give impure $(ReO_2py_4)Cl$ and $(ReO_2en_2)Cl$ respectively, but reaction with dipy. yields oxotrichloro2.2'-dipyridylrhenium(V), $ReOCl_3$dipy.

Both trans-$ReOCl_3(PPh_3)_2$ and green $ReO(OEt)Cl_2(PPh_3)_2$, on treatment with Me_2SO, in the absence of HCl, yield $(ReO_2Cl(Me_2SO)_2)_n$, which again is diamagnetic in the solid state at 20°. The compound dissolves in water to give a colourless solution, two equivalents of acid being liberated per unit formula weight (0.082 g. $ReO_2Cl(Me_2SO)_2$ ≡ 38.3 ml. 0.01N. NaOH). The most likely mode of dissolution would appear to be one accompanied by aerial oxidation:

$$ReO_2Cl(Me_2SO)_2 + H_2O + (O) \longrightarrow HReO_4 + HCl + 2Me_2SO$$

The molar conductance was 615 ohm^{-1} cm^2 per unit formula weight. Assuming both perrhenic and hydrochloric acids to be completely dissociated in aqueous solution, the theoretical molar conductance would be 831 ohm^{-1} cm^2. (The ionic conductances are H^+, 350; Cl^-, 76; ReO_4^-, 55) (102, 103). Thus the large ionic conductance of H^+ accounts satisfactorily for the observed molar conductance.

The preparation can be considered as a two stage one:

$$ReOCl_3(PPh_3)_2 + Me_2SO \overset{HCl}{\rightleftharpoons} ReOCl_3PPh_3Me_2SO + PPh_3 \quad \text{.....(1)}$$

or $ReO(OEt)Cl_2(PPh_3)_2 + Me_2SO + HCl \rightleftharpoons ReOCl_3PPh_3Me_2SO + EtOH + PPh_3$

$$ReOCl_3PPh_3Me_2SO + Me_2SO + H_2O \longrightarrow ReO_2Cl(MeSO)_2 + 2HCl + PPh_3 \quad \text{.....(2)}$$

Evidence for this scheme is that no $ReO_2Cl(Me_2SO)_2$ was formed if HCl was added to the reaction mixture or if calcium hydride dried benzene was used as the solvent in (2).

TABLE 11. A comparison of the infra-red spectra of some rhenium dimethylsulphoxide complexes with related compounds.

D[a]	$(ReO_2ClD_2)_2$		$ReOX_3PD$		$ReOX_3P_2$		P[b]	Assignments[c]
	di-μ-oxo Isomer(a)	di-μ-chloro Isomer(b)	X=Cl	X=Br	X=Cl	X=Br		
			1087 s.	1080 s.	1093 s.	1094 s.	1089 s.	P sensitive mode q.
			1074 sh.	1075 sh.	1075 sh.	1074 sh.		
1012 s.	1041 s.	1041 s.	1041 m.	1037 s.				
946 s.	1032 s.	1032 s.	993 vs.	990 vs.				CH_3 rock
921 m.	990 s.	990 s.						
887 w.	944 s.	969 m.						
			1031 m.	1030 sh.	1030 m.	1029 m.	1026 s.	ρ C-H in plane deformation.
			1001 s.	1000 s.	999 m.	999 m.	999 m.	Ring breathing mode
	969 m.	944 s	981 s.	980 s.	969 s.	980 vs.		Re=O stretch
		895 s.				971 sh.		
1055 vs.	907 vs.	907 vs.	1138 s.	1131 s.				S-O stretch
	895 s.		1129 s.	1122 s.				

TABLE 11. Continued.

D[a]	$(ReO_2ClD_2)_2$		$ReOX_3PD$		$ReOX_3P_2$		P[b]	Assignments[c]
	di-μ-oxo Isomer(a)	di-μ-chloro Isomer(b)	X=Cl	X=Br	X=Cl	X=Br		
			752 m.	751 m.	748 s.	746 s.	746 vs.	ν C-H deformation
						743 s.		
690 s.	726 m.	726 m.	735 sh.	735 sh.				Asymmetric C-S stretch
	720 m.	720 m.	729 s.	728 vs.				
			702 m.	702 m.	707 m.	706 m.		Out of plane ring
						699 w.		deformation
			692 s.	692 s.	693 s.	691 s.	693 vs.	
			535 vs.	534 vs.	522 vs.	524 vs.	514 vs.	
			528 sh.	527 sh.	507 vs.	506 s.	499 vs.	P sensitive mode y
					495 s.	498 s.	493 vs.	
			475 m.	474 m.	454 m.	450 w.	432 w.	P sensitive mode t
					443 m.		422 w.	
	474 sh.							Oxygen bridge
	471 s.							vibration ?

TABLE 11. Continued.

D^a	$(ReO_2ClD_2)_2$		$ReOx_3PD$		$ReOX_3P_2$		P^b	Assignments[c]
	di-μ-oxo Isomer(a)	di-μ-chloro Isomer(b)	X=Cl	X=Br	X=Cl	X=Br		
		474 sh.					)	
		471 s.	430 w.	429 w.			)	Me_2SO tortional
	460 s.	460 s.	424 w.	424 w.			)	mode
	458 s.	458 s.	418 w.	423 w.			)	

D= Me_2SO

P= PPh_3

a- From data in reference 104, which is confined to the range 4000-600 cm^{-1}. In fact Me_2SO is completely blank in the range 600-400 cm^{-1}.

b- E. Steger and K. Stopperka, Chem. Ber., 1961, 94, 3023.

c- Phosphine ring assignment notation due to D. H. Whiffen, J.C.S., 1956, 1350.

Unfortunately ($ReO_2Cl(Me_2SO)_2$) was not soluble enough in inert solvents to permit a molecular weight determination. An attempt to make the analogous bromides gave only $ReOBr_3PPh_3$-Me_2SO, oils being obtained instead of $ReO_2Br(Me_2SO)_2$.

There is a good deal of π-bond character in the sulphur oxygen bond in Me_2SO, the two most predominant canonical forms being:

$$\underset{(a)}{Me_2S = O} \qquad\qquad \underset{(b)}{Me_2S^+ - O^-}$$

Co-ordination via the oxygen atom would tend to make (b) predominant and via the sulphur, (a) predominant. Thus, the position of the sulphur oxygen stretching frequency gives an indication as to the mode of bonding, it being greater for sulphur bonded Me_2SO complexes than for oxygen bonded ones (104). Thus it is concluded that $ReOX_3PPh_3Me_2SO$ is a sulphur bonded complex and $(ReO_2Cl(Me_2SO)_2)n$ oxygen bonded, see Table 11.

However the complete assignment of the bands less than 1100 cm^{-1} is not unambiguous, hence in an endeavour to elucidate the nature of these bands, the spectra of $(Co(Me_2SO)_6)(ClO_4)_2$ and $PdCl_2(Me_2SO)_2$ were recorded over the range 1100-400 cm^{-1}, see Table 12. $(Co(Me_2SO)_6)(ClO_4)_2$ is an example of an oxygen bonded complex and $PdCl_2(Me_2SO)_2$ a sulphur bonded (104).

The strong band at 435 cm^{-1} in $(Co(Me_2SO)_6)^{2+}$ must be due to the co-ordinated Me_2SO. One possibility is that it is a Co-O stretch, but 435 cm^{-1} would seem to be rather high for this (although Cotton et.al. (105) have tentatively assigned bands at ca. 470 cm^{-1} in some molybdenum dimethylsulphoxide complexes as Mo-O stretches). In the oxygen bonded complexes

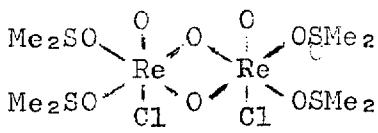
$MBr_2(Me_2SO)_2$, (M=Mg, Zn) there is a strong band at 443 cm^{-1} in both compounds (106). If this were an M-O stretch, one would have expected a considerable shift in the position of this band. The other possibility is that it is a torsional mode connected with the oxygen bonding (in sulphur bonded systems, it appears at a lower frequency and is much weaker).

TABLE 12. Infra-red spectra of $(Co(Me_2SO)_6)(ClO_4)_2$ and $PdCl_2(Me_2SO)_2$.

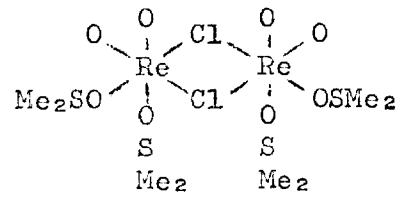
$(Co(Me_2SO)_6)(ClO_4)_2$[a]	$PdCl_2(Me_2SO)_2$[a]	Assignment
1080 vs. bd.		ν_3 mode of ClO_4^- (41f)
1026 sh.	1022 s.	
990 vs. bd.	994 w.	CH_3 rock
	946 m.	
	925 m.	
943 s. 934 sh.	1119 s.	S=O stretch
716 s.	731 m.	Asymmetric C-S stretch
680 m.	685 m.	Symmetric C-S stretch
623 s.		ν_4 mode of ClO_4^- (41f)
435 vs. bd.	416 m.	Me_2SO torsional mode?

a - prepared by the method of J.Selbin, W.E.Bull and L.H.Holmes, J. Inorg. Nuclear Chem., 1960, 16, 219.

The nature of $ReO_2Cl(Me_2SO)_2$ is uncertain, but the two most reasonable formulations would appear to be:



(a)



(b)

In formulation (a) there is a diμoxo system with a corresponding singlet Re=O stretch at 969 cm^{-1} and in (b) a diμchloro system containing a <u>cis</u>- dioxo group with corresponding Re=O stretches at 944 cm^{-1} and 895 cm^{-1}. It was impossible to distinguish between these two possibilities unambiguously, seeTable 11.

It was hoped that bands due to the bridging ring system in (a) could be seen. Unfortunately, there is only one fully substantiated transition metal complex containing such a system - $BaMo_2O_4(C_2O_4)_2.5H_2O$, which has been shown to contain $((MoO(C_2O_4)H_2O)_2O_2)^{2-}$ (107). However all the bands in the infra-red spectrum of this compound could be accounted for without any oxygen bridging mode - although the ν_{10} oxalate mode at 480 cm^{-1} is rather broad and could conceivably mask the oxygen bridge mode under the envelope. The bridging chloride vibrational mode in (b) would be expected to occur less than 300 cm^{-1}. Infra-red studies on some diμhydroxo copper species indicate that a band in the range 478 - 498 cm^{-1} could be assigned to a Cu-O asymmetric stretch (91). Although strictly speaking, these compounds are not analogous to (a), one would reasonably expect that vibrations due to a

diμoxo system would be not too far removed from this value.

The $(ReOCl_5)^{2-}$ ion was also formed on heating trans-$(ReO_2py_4)Cl$ in 5M. HCl, see page 43.

b) Magnetic properties.

Earlier workers (108) claimed that K_2ReOCl_5 was weakly paramagnetic, the explanation presumably being similar to that postulated for other $(ReO)^{3+}$ complexes; however recently Colton (109) found that Cs_2ReOCl_5 was paramagnetic with a "spin-only" value of the magnetic moment (μ = 2.85 B.M.) and a small value of the Weiss constant. This result could not be confirmed by us, although the salt is in fact paramagnetic. However the magnetism appears to depend on the exact method of preparation. The caesium salt prepared by Method A. (see experimental) obeys the Curie-Weiss Law, but gave large values of the Weiss Constant. The magnetic moment was field dependent, but at room temperature and H = 6.48×10^3 gauss, μ = 2.0 B.M. (I). Under the same conditions Cs_2ReOCl_5 prepared from method B. gave μ = 1.7 B.M. (II) and that prepared from Method C. gave μ = 1.0 B.M. (III). All three samples had satisfactory analyses, identical infra-red and reflectance spectra, butthe X-ray powder pattern of (III) was slightly different from those of the other two.

The electron spin resonance (e.s.r.) of the three powdered solids was examined at 20°. All three had a strong line centred at g= 2.011, $\Delta H_{max\ slope} \sim 70$ gauss, but in the spectrum of (I) a complex hyperfine structure was observed. For (II) and especially (III), the hyperfine structure broadened

considerably ($\Delta H_{max\ slope}$ ~650 gauss) and was centred at g~2.

Although similar magnetic anomalies were observed for Rb_2ReOCl_5, $(Me_4N)_2ReOCl_5$ was found to have a magnetic moment of between 0.6 and 0.8 B.M. over a large temperature and field range.

Since the observed magnetic moments are dependent on the field strength i.e. the complex is magnetically concentrated, the actual values probably do not have any strict physical significance and thus, although we are unable to draw any firm conclusions from this data, it is clear that differences in the crystal packing can cause somewhat different anti-ferromagnetic interactions. There is no evidence that the anomalies are due to ferromagnetic or anti-ferromagnetic impurities according to analyses, e.g. for iron and nickel.

c) Spectroscopic properties of $(MOX_5)^{2-}$.

The spectra of a number of (d^1) species with large axial asymmetry such as $(VO)^{2+}$, $(CrO)^{3+}$, and $(MoO)^{3+}$ have been observed (99, 110, 111, 112, 113, 114) in which an orbital energy scheme similar to that originally postulated by Ballhausen and Gray (111) for $(VO)^{2+}$ has been proposed (essentially the same as that given in Figure 1). This requires that three allowed ligand field bands should be visible in the case of, for example $(MoOCl_5)^{2-}$. However only two bands can be seen, the third ($^2A_1 \longleftarrow {}^2B_2$) being obscured by the first charge transfer band. The spectrum of $(MoOCl_5)^{2-}$ in 10M. HCl is essentially the same as the reflectance spectrum of solid $(NH_4)_2MoOCl_5$ (112),

but dilution of the $(MoOCl_5)^{2-}$ solution results in the extinction coefficient of the $(^2B_1 \leftarrow {}^2B_2)$ transition increasing markedly - a behaviour which has been ascribed to the formation of oxo-bridged dimers (114). Further evidence indicating the presence of dimers in dilute acid has been obtained from magnetic (115) and e.s.r. (113) studies.

Recently there has been some criticism of the charge transfer assignment in which it was concluded that metal chlorine π-bonding should be taken into consideration (99, 116), although e.s.r. studies on $(NH_4)_2MoOCl_5$ failed to reveal any hyperfine splittings due to the chlorine atoms (113, 117). However bromine hyperfine splittings have been seen in the frozen solution ($77^{\circ}K.$) spectra of $(MoOBr_5)^{2-}$ and $(WOBr_5)^{2-}$ and an unpaired spin density on the bromine atoms of between 4.3 and 5.8% has been estimated (118), which indicates the existence of a small amount of in-plane π-bonding.

The entire orbital energy scheme has been queried by Selbin et.al. (119, 120) on the basis of low temperature spectroscopic studies on a number of $(VO)^{2+}$ species, but other workers (121) disagree with these interpretations. Thus it can be seen that a good deal of confusion remains - even for these superficially simple (d^1) systems.

The position regarding $(ReOCl_5)^{2-}$ (d^2) is very complicated, since some of the characteristics of $(MoOCl_5)^{2-}$ are retained and some new ones appear. The reflectance spectrum of solid Cs_2ReOCl_5 is quite different from the solution spectrum obtained by dissolving freshly prepared $ReCl_5$ in 10M. HCl. Furthermore,

on lowering the HCl concentration the solution turned green and one of the bands increased in intensity (like $(MoOCl_5)^{2-}$ (114)), but two of the others passed through a minimum (see Table 13). The solution in 10M. HCl is paramagnetic, as measured on a Gouy balance at 20° (μ= 2.1 B.M.) and confirmed by the n.m.r. method (122).

TABLE 13. Spectroscopic data for oxorhenium(V) species.

Species	Solvent	Peak positions (mμ)(molar extinction coefficients in parentheses)[a]
"$(ReOCl_5)^{2-}$"	12M. HCl	1050(20); 750(17); 700sh.(15); 474(23); 400sh.(27).
	9.9M. HCl	700 sh.(12); 474(20); 405(25).
	6.9M. HCl	675(78); 474(16); 405(22).
	5.9M. HCl	675(85); 474(7); 405(22).
	5.0M. HCl	675(98); 474(8); 405(24).
	3.0M. HCl	675(92); 474(16); 405(30).
$(ReOBr_5)^{2-}$	acetone [b]	820(26); 535(65); 450(52).
$(ReOI_5)^{2-}$	acetone [b]	815(1.5-2); 525(350); 415(1840).

a - For "$(ReOCl_5)^{2-}$", the extinction coefficient is calculated as the quotient of the observed absorbance and the total concentration of rhenium in the supposed monomer/dimer equilibrium expressed as monomer.

b - Quinolinium salt.

The data for the bromo and iodo analogues (123) seems unreliable on a number of counts, principally that the values of the

extinction coefficients seem to be rather large to be due entirely to ligand field transitions. (Even for $(MoOBr_5)^{2-}$ there are two quite diametrically opposed assignments (99, 124)).

$(ReOCl_5)^{2-}$ was also obtained by allowing a solution of $(Re(OH)_2en_2)Cl_3$ in 10M. HCl to stand over a period of time, (see page 46). The spectroscopic changes of a solution of $(Re(OH)_2en_2)Cl_3$ in 10M. HCl were observed over a period of 15 days and the results tabulated below, together with those of related species.

TABLE 14. Changes in the visible spectrum of $(Re(OH)_2en_2)^{3+}$

Compound [a]	Band maxima (mμ).
$(Re(OH)_2en_2)^{3+}$	600; 820.
Spectrum after 2 days	ca.400 sh.; 470 sh.; 750; 1050.
Spectrum after 6 days	408; 475; 775; 1060.
Spectrum after 15 days	410; 474; 785; 1080.
$enH_2(ReOCl_5)$	407; 475; 780; 1100.
Cs_2ReOCl_5 (II). [b]	406; 474; ca.800; (1040?).
"$Cs(Re(OH)_2Cl_4)$" (57)	408; 480; 820.
Filtrate from the above Cs_2ReOCl_5 preparation	400; 470; 770; 1048.
$ReCl_5$ in 10M. HCl.	400 sh.; 474; 700 sh.; 750; 1050.

a - All measurements performed in 10M. HCl.

b - Cs_2ReOCl_5 is very sparingly soluble in 10M. HCl, leading to some uncertainty in the position of the bands.

The principal difference in the spectra of "$(ReOCl_5)$" derived from $(Re(OH)_2en_2)^{3+}$ and that derived from $ReCl_5$ is that the latter possesses a charge transfer band between 400 and 350 mμ. There is no conclusive proof that $(ReOCl_5)^{2-}$ exists in solution at all. An infra-red spectrum of the solution of $ReCl_5$ in 10M. HCl failed to show an Re=O stretch in the diagnostic region (see Table 15).

Colton (109) had claimed that dissolution of $ReCl_5$ in concentrated HCl gave a yellow/brown solution which subsequently turned green, and from which $(ReOCl_6)^{2-}$ could be obtained. We have been unable to confirm the formation of Re(VI) species, although the colour change was confirmed. Cs_2ReOCl_5 was the only product obtained by addition of Cs^+ to either the yellow solution, or the green solution, or a solution through which ozone had been passed for 5 hours, as confirmed by the identity of infra-red and reflectance spectra and chlorine analyses for the products. The colour change yellow to green was observed whilst the solution was under a nitrogen atmosphere and was very rapid when the pressure of the vapour above the solution was reduced. Furthermore, the yellow colour could be regenerated by passing HCl gas through the green solution. Partial conversion to the yellow form was achieved by addition of LiCl to the solution. Thus it would appear that the chloride ion concentration is critical and that no redox reaction is occurring. Thus species such as $ReCl_6^-$ or $ReCl_7^{2-}$ may be present in solution (no Re=O stretch in the infra-red), although these could not be isolated in the solid state.

The e.s.r. spectra of the two solutions at -140° were different and contained different degrees of hyperfine structure - there being no obvious relationship between the two spectra or between that of the caesium salt obtained by addition of Cs^+ to either of the two solutions. Unfortunately the signal broadened out at 20° and no single sextet (for ^{185}Re (37.07%) and ^{187}Re (62.93%), I = $\frac{5}{2}$) could be seen.

TABLE 15. Infra-red spectra of some $(ReO)^{3+}$ species.

Compound	Colour	Re=O in $(ReOCl_5)^{2-}$	Other stretching modes	m.p.
$ReOCl_3py_2$	green		970 (Re=O)	
$(ReO(OH)py_4)$-$(ReOCl_5)$	green	940	968 (Re=O)	
$(ReOCl_2en)_2O$	green		980 (Re=O)	195d.
$ReOCl_3en$	green		983, 967 (Re=O)	
Cs_2ReOCl_5	yellow	952		>310
Rb_2ReOCl_5	yellow	977, 956		
$(C_9H_8N)_2(ReOCl_5)$	yellow	950		
$enH_2(ReOCl_5)$	yellow	974		240d.
$(NMe_4)_2(ReOCl_5)$	orange	ca.950		>300
$ReOCl_3dipy$	brown		985 (Re=O)	
$(ReO(OH)py_4)$-Cl_2	red		973 (Re=O)	unstable
$(ReO(OH)py_4)$-$(ClO_4)_2$	purple		983 (Re=O)	explosive
$(ReO(OH)en_2)$-$(PtCl_6)$	fawn		987 (Re=O), 552 (Re-OH)	
$(Re(OH)_2en_2)_2$-$(PtCl_6)_3$	green		561 (Re-OH)	

CHAPTER 5.

HYDROLYSIS OF RHENIUM PENTACHLORIDE.

In addition to the usual disproportionation reaction, $3Re(V) \longrightarrow 2Re(IV) + Re(VII)$, (which occurs in alkali or an excess of water), there is the possibility of the reaction:

$$ReCl_5 + H_2O \rightleftharpoons (ReOCl_3) + 2HCl \rightleftharpoons H_2ReOCl_5.$$

With an excess of HCl present, the equilibrium is pushed over to form $(ReOCl_5)^{2-}$ as discussed above; the transient green colour noted by Colton (109) and also by us is probably due to $(ReOCl_3)$.

Dissolution of $ReCl_5$ in moist acetone (or T.H.F.) followed by addition of triphenylphosphine results in the formation of trans-$ReOCl_3(PPh_3)_2$ (Re=O stretch 969 cm^{-1}). From the resulting acetone solution trichlorotriphenylphosphinerhenium(III) bis(acetone), $ReCl_3PPh_3.2Me_2CO$ could be obtained. A possible reaction scheme is:

$$ReCl_5 + H_2O \longrightarrow (ReOCl_3) + 2HCl$$

$$(ReOCl_3) + 2PPh_3 \longrightarrow \text{trans-}ReOCl_3(PPh_3)_2$$

$$(ReOCl_3) + 2PPh_3 \xrightarrow{Me_2CO} ReCl_3PPh_3.2Me_2CO + PPh_3O$$

In support of this scheme small amounts of triphenylphosphine oxide were obtained from the mother liquors and the $ReCl_3PPh_3.2Me_2CO$ could be oxidised with molecular oxygen to green $ReOCl_3(PPh_3)_2$ (Re=O stretch 983 cm^{-1}). $ReCl_5$ dissolves in acetone to give a green solution, which on standing in air turns purple and then brown. At all stages trans-$ReOCl_3(PPh_3)_2$

could be obtained on addition of triphenylphosphine. ($ReOCl_3$) has not been isolated in the above reaction, nor from reaction of $ReCl_5$ with liquid sulphur dioxide (c.f. the reaction of $MoCl_5$ with liquid SO_2 to give $MoOCl_3$ (125)).

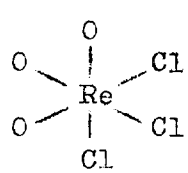
CHAPTER 6.

THE TRIOXOTRICHLORORHENATE(VII) ION.

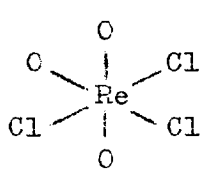
The vast majority of oxygen containing Re(VII) compounds can be considered to be perturbations of $(ReO_4)^-$ e.g. $(ReO_3N)^{2-}$, ReO_3X (X= F, Cl, Br), $(ReO_3S)^-$ and Re_2O_7; although both six co-ordinate $ReOF_5$ and five co-ordinate ReO_2F_3 have been described (126). However no compound of stoichiometry $(ReO_3X_3)^{2-}$ has been described, although Peacock (127) considered that the $(ReO_3F_3)^{2-}$ ion should be capable of existence, and both the isoelectronic $(WO_3F_3)^{3-}$ (128) and $(OsO_3F_3)^-$ (129) have been described.

Dissolution of perrhenic acid in concentrated HCl saturated with HCl gas produces a yellow solution from which CsCl precipitates a pale yellow solid of stoichiometry $Cs_2(ReO_3Cl_3)$ (130). The compound dissolves in water (or base) to give a clear solution with no black ReO_2 forming, indicating that a Re(VII) species is present. It turns white if exposed to the atmosphere.

There are two possible geometrical isomers:



(a)



(b)

Simplified group theory (omitting site symmetry considerations) would indicate that since isomer (a) has the C_{3v} point group, there should be 10 normal vibrations of the ion of species

$4A_1 + A_2 + 5E$ and that there should be two metal-oxygen and two metal-chlorine stretching modes active in both the infra-red and Raman spectra. Similarly, isomer (b) should have 15 normal vibrations, of species $6A_1 + A_2 + 4B_1 + 4B_2$ and that there should be three metal-oxygen and three metal-chlorine stretching modes active in both the infra-red and Raman spectra.

The infra-red spectrum consists of an extremely broad absorbtion centred at about 900 cm^{-1}, with a band width (width at half intensity) of about 100 cm^{-1}. In the metal-chlorine stretching region, bands were found at 314 sh., 320 vs., 334 m. and 370 m. (all in cm^{-1}). It is suggested that the shoulder at 314 cm^{-1} is an isotopic effect due to ^{37}Cl, thus it is expected that the ratio of the two frequencies should be inversely proportional to the square root of the atomic masses:

$$\left(\frac{37}{35}\right)^{0.5} = 1.03 \qquad \left(\frac{320}{314}\right) = 1.02$$

The agreement is quite good, and thus three bands remain which are assigned to rhenium-chlorine stretching modes, suggesting that isomer (b) with C_{2v} symmetry is the correct formulation. The assignment of the above three bands as Re-Cl stretches is not completely unambiguous, since O-Re-O deformation modes are known to occur in this region.

The Raman spectrum of the solid was examined using the mercury green line (5461 Å) as the exciting line. Unfortunately scattering effects made observations of the Re-Cl stretches impossible, but three weak bands could be seen in the Re-O

stretching region - 868±4, 910±4 and 940±4 cm^{-1}. Thus it is concluded that isomer (b) is the correct geometrical formulation.

The preparation of the analogous fluoride was attempted. However it was never obtained, even when liquid hydrogen fluoride was used as the solvent. (The Raman spectrum of a solution of sodium perrhenate in 15% hydrogen fluoride was that of the unperturbed $(ReO_4)^-$ ion). Addition of a solution of CsF in concentrated HF to a solution of perrhenic acid in concentrated HF with some liquid HF present did not give an immediate precipitate. If the mixture was kept cool, large white crystals separated out after about a week. Analytical results indicated that this compound was $CsReO_4$. In confirmation of this, no Re-F stretches could be seen in the infra-red spectrum and the X-Ray powder pattern was identical to that of an authentic sample of $CsReO_4$ obtained by addition of an aqueous solution of CsCl to an aqueous solution of perrhenic acid. Other cations such as $(Ph_4As)^+$ gave immediate precipitates of the corresponding perrhenate, or in the case of $(R_4N)^+$ or Rb^+ did not give any precipitates at all. In view of the fact that $(ReO_3Cl_3)^{2-}$ appears to exist, there seems to be no reason why the fluoride should not. The most likely explanation as to why the ion was not obtained is that the salts are too soluble relative to the corresponding perrhenate.

EXPERIMENTAL.

Simple elemental microanalyses were by the Microanalytical Laboratories of Imperial College and by Alfred Bernhardt Mikroanalytisches Laboratorium, Mulheim/Ruhr. Rhenium was determined as tetraphenylarsonium perrhenate and caesium as the tetraphenylborate. Infra-red spectra were recorded in nujol mulls on a Grubb Parsons Spectromaster unless otherwise stated. Electronic spectra were recorded in solution on a Perkin Elmer 350 Spectrophotometer. Magnetic measurements were carried out by the Gouy method, and in solution by the n.m.r. method (122), using a Varian 3400B. spectrometer operating at 56.45 Mc/s. unless otherwise stated. Melting points were determined on a Kofler hot stage and are corrected. Molecular weights were determined using a Mechrolab Osmometer operating at 37° in the solvent indicated, unless otherwise stated. Vapour phase chromatographs were obtained from a Perkin Elmer F 11 Gas Chromatograph. E.s.r. spectra were obtained on a Varian V 4502/15 Spectrometer. Solid state Raman spectra were obtained on a Carey 81 Raman Spectrometer using the mercury green (5461 Å) line as excitation, with a neodymium filter. Far infra-red spectra were recorded on a Grubb Parsons D.M.4 Spectrometer.

All reactions were carried out under an atmosphere of nitrogen unless otherwise stated.

Trans-oxotrichlorobis(triphenylphosphine)rhenium(V). (17)

Rhenium metal (3g.) was dissolved in excess 100 vol. hydrogen peroxide and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in 10M. HCl (7 ml.), and the solution added to a suspension of triphenylphosphine (25 g.) in glacial acetic acid (250 ml.). After stirring at room temperature for about $\frac{1}{2}$ hr., the product was filtered, washed with glacial acetic acid and ether and obtained as yellow/green microcrystals (12.2 g., 91%.). (Found: C, 52.3; H, 3.7; O, 1.9 calc. for $C_{36}H_{30}Cl_3OP_2Re$: C, 51.9; H, 3.5; O, 1.9%). The product thus obtained was suitable for most purposes, but not all. All traces of acetic acid could be removed by suspending the solid in ether, filtering and drying in vacuo. over phosphorus pentoxide.

Oxoethoxodichlorobis(triphenylphosphine)rhenium(V).(green isomer) (17)

Rhenium metal (3 g.) was dissolved in excess 100 vol. hydrogen peroxide and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in 10M. HCl (7 ml.) and the solution added to a suspension of triphenylphosphine (25 g.) in ethanol (250 ml.). The mixture was heated to the boiling point, and refluxed for ten minutes. The hot suspension was filtered and the green product was washed with ethanol and ether and obtained as microcrystals (12.1 g., 87%). (Found: C, 54.2; H, 4.4 calc. for $C_{38}H_{35}Cl_2O_2P_2Re$: C, 54.2; H,4.2%).

Oxoethoxodichlorobis(triphenylphosphine)rhenium(V). (grey/green isomer).

Rhenium metal (3 g.) was dissolved in excess 100 vol.

hydrogen peroxide and the solution evaporated to dryness. The perrhenic acid thus formed was dissolved in 1OM. HCl (6 ml.) and added to a suspension of triphenylphosphine (24 g.) in ethanol (300 ml.). The mixture was stirred at room temperature for four hours, filtered, washed with ethanol and ether and obtained as grey/green microcrystals (7.3 g., 54%). (Found: C, 54.3; H, 4.4%).

Oxoethoxodichlorobis(triphenylphosphine)rhenium(V). (purple isomer)

The grey/green isomer above (0.50 g.) was dissolved in a mixture of benzene (50 ml.) and ethanol (20 ml.) and refluxed for twenty hours. On cooling, purple crystals of the compound were deposited (0.23 g., 46%). (Found: C, 54.9; H, 4.6%). This isomer was also obtained on refluxing the green isomer in an ethanol/benzene mixture for three hours.

The infra-red spectra of the three isomers were examined in the range 900-1000 cm^{-1}.

Isomer	$\nu_{Re=O}$	$\nu_{\delta O-CH_2}$	Intensity ratio $\nu_{\delta O-CH_2} : \nu_{Re=O}$
green	949	908	1:1
grey/green	945	906	2.5:1
purple	945	905	2:1

Thus it seems reasonable to suppose that the grey/green isomer is not just a mixture of the green and purple isomers.

Decomposition of green $ReO(OEt)Cl_2(PPh_3)_2$.

A solution of green $ReO(OEt)Cl_2(PPh_3)_2$ (1 g.) in benzene (60 ml.) was shaken at 20° for four days. The insoluble

product was collected and washed with ether to give trans-$ReOCl_3(PPh_3)_2$ as prisms (0.3 g., 30%). (Found: C,51.7; H, 3.8 calc. for $C_{36}H_{30}Cl_3OP_2Re$: C, 51.9; H, 3.6%).

The infra-red spectrum of this compound was identical to that of an authentic sample.

Oxoalloxodichlorobis(triphenylphosphine)rhenium(V).

Trans-$ReOCl_3(PPh_3)_2$ (0.5 g.) was refluxed in benzene (30 ml.) and allyl alcohol (5 ml.) for 10 minutes producing a bright green solution. Addition of 30/40 petrol to the cold solution afforded the compound as green microcrystals similar in appearance to the starting material (0.39 g., 76%). (Found: C, 54.4; H, 4.0; O, 3.7, $C_{39}H_{35}Cl_2O_2P_2Re$ requires C, 54.8; H, 4.1; O, 3.8%).

The compound was very soluble in benzene.

Reaction of green $ReO(OEt)Cl_2(PPh_3)_2$ with acacH in benzene.

$ReO(OEt)Cl_2(PPh_3)_2$ (green isomer) (2 g.) was dissolved in benzene (30 ml.) and to this solution was added acacH (2 ml.). This mixture was refluxed for six hours and then evaporated down (in vacuo.) to about 15 ml. Filtration afforded large green crystals together with orange microcrystals. The large green crystals were hand picked from the remainder and their infra-red spectrum showed a strong absorbtion at 979 cm^{-1}, attributable to a rhenium oxygen stretching mode, whereas the orange compound was blank in this region. (Found for the green crystals C, 43.0; H, 3.6 calc. for $C_{23}H_{22}Cl_2O_3PRe$: C, 43.5; H, 3.5%) i.e. the green complex is $ReOCl_2acacPPh_3$. (Found for the orange crystals C, 55.9;

H, 4.3 calc. for $C_{41}H_{37}Cl_2O_2P_2Re$: C, 55.9; H, 4.2%) i.e. $ReCl_2acac(PPh_3)_2$. This is to be contrasted to the behaviour of purple $ReO(OEt)Cl_2(PPh_3)_2$ which under the same experimental conditions yields only the orange $ReCl_2acac(PPh_3)_2$. (24) (Found C, 55.9; H, 4.3; Cl, 8.0; O,4.0; P, 6,9 M 911 (ebullioscopic in benzene) $C_{41}H_{37}Cl_2O_2P_2Re$ requires C, 55.9; H, 4.2; Cl, 8.1; O, 3.6; P, 7.0% M 881)

Oxodibromo(pentane2-4dionato)triphenylphosphinerhenium(V) (24)

A solution of $ReO(OEt)Br_2(PPh_3)_2$ (2 g.) in benzene (50 ml.) was heated for about one minute in the presence of acacH (2 ml.) and poured into 30/40 petrol when a green precipitate was obtained. Usually the green crystals had to be separated from the orange material as above. The green product was reprecipitated by slow evaporation of its benzene solution and washed with ether to give the product as prisms (0.26 g., 15%). (Found: C, 38.7; H, 3.1; Br, 22.7 M, 660 (ebullioscopic in benzene) $C_{23}H_{22}Br_2O_3PRe$ requires C, 38.2; H, 3.1; Br, 22.1% M, 723).

Oxodi-iodo(pentane2-4dionato)triphenylphosphinerhenium(V).

An attempt was made to prepare this compound in a similar way to that of the bromide, but it has not yet been prepared pure, because of the similar solubility of the red product of the reaction.

Oxodichloro(pentane2-4dionato)phenyldiethylphosphinerhenium(V). (24)

This was prepared from $ReO(OEt)Cl_2(PPhEt_2)_2$ (12) in a similar manner to the chloride of the triphenylphosphine analogue above, and was obtained as prisms (20%). (Found: C, 33.8; H, 4.0; $C_{15}H_{22}Cl_2O_3PRe$ requires C, 33.5; H, 4.1%).

The compound was diamagnetic, like the triphenylphosphine analogue, but more soluble in organic solvents.

Dibromo(pentane2-4dionato)bis(triphenylphosphine)rhenium(III).

This was prepared from $ReO(OEt)Br_2(PPh_3)_2$ (4 g.) in a similar manner to that of the chloro complex described above and reprecipitated from hot benzene with 30/40 petrol and obtained as prisms (1.27 g. 30%). (Found: C, 50.5; H, 3.9; Br, 17.0; O, 4.0; P, 6.1 $C_{41}H_{37}Br_2O_2P_2Re$ requires C, 50.8; H, 3.9; Br, 16.5; O, 3.3; P, 6.4%).

Di-iodo(pentane2-4dionato)bis(triphenylphosphine)rhenium(III).

This was prepared from $ReO(OEt)I_2(PPh_3)_2$ (1.24 g.) in a similar manner to the chloro complex above and was obtained as needles (0.4 g., 31%). (Found: C, 45.9; H, 3.7 $C_{41}H_{37}I_2O_2P_2Re$ requires C, 46.3; H, 3.5%).

Dichloro(pentane2-4dionato)bis(phenyldiethylphosphine)rhenium(III).(24)

This was prepared in the same way as the above compounds, but starting with $ReO(OEt)Cl_2(PPhEt_2)_2$ (12) and was obtained as prisms (25%). (Found: C, 43.8; H, 5.4 $C_{25}H_{37}Cl_2O_2P_2Re$ requires C, 43.6; H, 5.4%).

The compound was more soluable in organic solvents than the triphenylphosphine analogue.

Chlorobis(pentane2-4dionato)triphenylphosphinerhenium(III).

Green $ReO(OEt)Cl_2(PPh_3)_2$ (3.33 g.) was refluxed in acacH (30 ml.) for 16 hours and cooled. The product was collected, refluxed in benzene for 16 hours exposed to the atmosphere, and the suspension allowed to cool. The orange product was filtered, washed with ether and obtained as prisms

(0.6 g., 22%). (Found: C, 49.0; H, 4.1; O, 9.3 M, 683 (chloroform) $C_{28}H_{29}ClO_4PRe$ requires C, 49.3; H, 4.3; O, 9.4% M, 682).

Di-μ-pentane2-4dionato-tetrachlorobis(pentane2-4dionato)-dirhenium(IV).

Green $ReO(OEt)Cl_2(PPh_3)_2$ (4.28 g.) was refluxed in acacH (40 ml.) for 50 hours and the mixture allowed to cool depositing the compound. The crude product was collected, reprecipitated from chloroform solution with 30/40 petrol and obtained as orange microcrystals (1.15 g., 25%). (Found: C, 26.5; H, 2.7; Cl, 15.4; O, 14.4; Re, (by difference) 41.0 M, 939 (chloroform); 909 (ebullioscopic in chlorobenzene) $C_{20}H_{28}Cl_4O_8Re_2$ requires C, 26.4; H, 3.1; Cl, 15.6; O, 14.1; Re, 40.8% M, 911).

The compound was virtually insoluble in all common organic solvents, only small amounts being recrystallisable from dichloromethane, acetic acid and trifluoroacetic acid.

Trichloroacetatotriphenylphosphine oxiderhenium (IV).

Green $ReO(OEt)Cl_2(PPh_3)_2$ (1 g.) was placed in a Carius tube with acacH (3 ml.). The tube was sealed and heated at 200° for 24 hours. The tube was allowed to cool, then opened and allowed to stand open to the atmosphere for one minute and then the contents were filtered. A mixture of blue microcrystals and large red crystals was obtained. The mixture was shaken in dichloromethane or chloroform, in which the blue compound was soluble. The red crystals were filtered off and the filtrate was allowed to evaporate at room

temperature depositing the compound as needles (0.21 g. 28%). (Found: C, 38.2; H, 3.1; Cl, 14.4; O, 7.0; P, 4.0; M, 678 (chloroform) $C_{20}H_{18}Cl_3O_3PRe$ requires C, 38.2; H, 2.9; Cl, 16.9; O, 7.6; P, 4.9% M, 630). m.p. 227-232°.

An attempt was made to purify the compound by adsorbing the dichloromethane solution on a silica column and then eluting with acetone, and allowing this solution to evaporate at room temperature. However, the analytical results were not much improved. (Found: C, 40.8; H, 3.0; Cl, 15.8; O, 7.6%).

The infra-red spectra in nujol and hexachlorobutadiene mulls is given below.

Band position	Assignment
1592 w.	C-C stretch in phenyl ring
1500 w.	Me deformation
1485 m.	C-C stretch in phenyl ring
1453 s.	Asymmetric C=O stretch
1437 vs.	C-C stretch in phenyl ring
1356 w.	Symmetric C=O stretch (?)
1144 s.	Co-ordinated P=O stretch
1119 s.)	
)	P-sensitive mode q.
1088 s.)	

The P-sensitive mode q was split when the spectrum was recorded in dichloromethane solution, and is thus not a solid state effect.

Tetra-μ-acetatodichloro dirhenium(III).

Green $ReO(OEt)Cl_2(PPh_3)_2$ (1 g.) was placed in a Carius tube with acacH (3 ml.). The tube was sealed and heated at 200° for 24 hours. The tube was allowed to cool, then opened and allowed to stand open to the atmosphere for one minute and then the contents were filtered. A mixture of blue microcrystals and large red crystals was obtained. The mixture was shaken in dichloromethane or chloroform, in which the blue compound was soluble. The large red crystals were filtered and washed with ether (0.21 g. 52%). (Found: C, 14.6; H, 1.7; O, 18.9 calc. for $C_8H_{12}Cl_2O_8Re_2$: C, 14.1; H, 1.8; O, 18.8%).

The compound was insoluble in all common organic solvents and had an infra-red spectrum identical to that of an authentic sample (40).

Tetra-μ-acetatodibromo dirhenium(III).

This was prepared as above starting from $ReO(OEt)Br_2(PPh_3)_2$ (but this time no blue compound was obtained), and obtained as red crystals (0.14 g. 34%). (Found: C, 12.9; H, 1.6; O, 17.0 $C_8H_{12}Br_2O_8Re_2$ requires C, 12.5; H, 1.6; O, 16.7%).

The bromo complex was slightly more soluble in organic solvents than was the chloro analogue.

Dichloro(1, 1, 1 trifluoropentane2-4dionato)bis(triphenylphosphine)rhenium(III).

A solution of green $ReO(OEt)Cl_2(PPh_3)_2$ (1 g.) and 1, 1, 1 trifluoropentane2-4dione (2 ml.) in benzene (40 ml.) was

heated under reflux for 15 minutes, cooled and 30/40 petrol added. The product was collected and reprecipitated from benzene with 30/40 petrol and obtained as needles (0.68 g. 61%). (Found: C, 53.2; H, 4.0 M, 838 (chloroform) 941 (benzene) $C_{41}H_{34}Cl_2F_3O_2P_2Re$ requires C, 52.7; H, 3.7% M, 934).

Dichloro(1, 1, 1, 5, 5, 5hexafluoropentane2-4dionato)bis-(triphenylphosphine)rhenium(III).

This was prepared and purified in the same way as above starting from green $ReO(OEt)Cl_2(PPh_3)_2$ (0.95 g.) and 1, 1, 1, 5, 5, 5hexafluoropentane2-4dione (2 ml.) in benzene (40 ml.) and obtained as microcrystals (0.79 g. 71%). (Found: C, 49.3; H, 3.2; F, 11.5; M, 986 (benzene) $C_{41}H_{31}Cl_2F_6O_2P_2Re$ requires C, 49.8; H, 3.1; F, 11.5 M, 989).

Dichloro (4, 4, 4trifluorol-2' thienylbutanel-3 dionato)-bis(triphenylphosphine)rhenium(III).

This compound was prepared and purified as above starting from green $ReO(OEt)Cl_2(PPh_3)_2$ (0.5 g.) and 4, 4, 4trifluorol-2' thienylbutanel-3dione (thenoyl trifluoracetone, T.T.A.) (0.25 g.) in benzene (30 ml.) and obtained as needles (0.26 g. 44%). (Found: C, 52.6; H, 3.6; S, 3.5 M, 1059 (chloroform) $C_{44}H_{34}Cl_2F_3O_2P_2ReS$ requires C, 52.7; H, 3.4; S, 3.2% M, 1002).

Trichloro(1-phenylbutanel-3dionato)triphenylphosphinerhenium(IV).

Green $ReO(OEt)Cl_2(PPh_3)_2$ (0.5 g.) was dissolved in benzene (40 ml.) containing 1-phenylbutanel-3dione (0.4 g.) and was refluxed for 15 hours. Additon of 30/40 petrol afforded

brown/red microcrystals of the complex. These were dissolved in benzene and reprecipitated with 30/40 petrol (0.11 g. 26%). (Found: C, 47.7; H, 3.4; O, 4.6; M, 756 (benzene) $C_{28}H_{24}Cl_3O_2PRe$ requires C, 47.0; H, 3.4; O, 4.5% M, 716).

The compound was soluble in most common organic solvents.

Dichloro(1-3diphenyl propanel-3dionato)bis(triphenylphosphine)-rhenium(III).

Green $ReO(OEt)Cl_2(PPh_3)_2$ (0.5 g.) was dissolved in benzene (50 ml.) containing 1-3diphenylpropanel-3dione (0.4 g.) and refluxed for 15 hours. To the clear green solution was added 30/40 petrol affording dark green microcrystals of the compound (0.4 g.). (Found: C, 57.7; H, 4.0; O, 3.0 M, 1961 (benzene) $C_{51}H_{41}Cl_2O_2P_2Re$ requires C, 60.9; H, 4.1; O, 3.2% M, 1004).

The compound was dissolved in benzene (giving a dichromatic solution) and allowed to run down an alumina column. 30/40 petrol was added to this solution affording dark green mycrocrystals, similar in appearance to the original crystals.

(Found: a) C, 61.4; H, 4.4; M, 4021 (benzene)

b) C, 61,5; H, 4.8; M, 5775 (benzene)).

Oxodichloro(salicylaldehydo)triphenylphosphinerhenium(V).

Trans-$ReOCl_3(PPh_3)_2$ (0.5 g.) was dissolved in refluxing benzene (50 ml.) for 16 hours. To the hot filtrate was added salicylaldehyde (0.15 g.). The mixture was refluxed for a further 10 minutes and allowed to cool and then filtered. 30/40 petrol was added to the filtrate yielding a green compound together with some brown material. This mixture was added to acetone (in which the brown compound is sparingly

soluble), filtered and to the clear filtrate was added 30/40 petrol affording olive green prisms (0.06 g. 15%). (Found: C, 46.1; H, 3.5; O, 7.4 M, 647 (acetone), 670 (chloroform), 1119 (benzene) $C_{25}H_{20}Cl_2O_3PRe$ requires C, 45.7; H, 3.1; O, 7.3% M, 657).

Di-μ-catecholatohexachlorobis(triphenylphosphine)dirhenium(V).

Trans-$ReOCl_3(PPh_3)_2$ (0.5 g.) was refluxed in benzene for 48 hours. To the hot solution was added a solution of catechol (0.13 g.) in benzene. Refluxing was continued for a further 10 minutes and the mixture was allowed to cool and then filtered. Addition of 30/40 petrol to the filtrate produced the compound as a brown microcrystals (0.11 g. 14%). (Found: C, 43.7; H, 2.7; O, 4.7 M, 1295 (benzene); 1324 (acetone) $C_{48}H_{38}Cl_6O_4P_2Re_2$ requires C, 43.5; H, 2.9; O, 4.8% M, 1326).

Oxotrichlorobis(pyridine)rhenium(V).

Trans-$ReOCl_3(PPh_3)_2$ (0.5 g.) was suspended in dichloromethane (20 ml.) and chlorine gas was passed through until a deep red solution was obtained. Pyridine was slowly added to the solution until it turned green. On boiling this solution, green microcrystals of the compound separated out. These were filtered and washed with ether (0.1 g. 44%). (Found: C, 25.8; H, 2.2; O, 3.5 $C_{10}H_{10}Cl_3N_2ORe$ requires C, 25.6; H, 2.1; O, 3.4%). The compound was insoluble in all inert solvents, but formed blue $ReO(OEt)Cl_2py_2$ on boiling in ethanol, and trans-$(ReO_2py_4)Cl$ on refluxing in moist pyridine.

Oxoethoxodichloro(2.2' dipyridyl)rhenium(V).

Green $ReO(OEt)Cl_2(PPh_3)_2$ (0.5 g.) was suspended in ethanol

(40 ml.). To this was added 2.2' dipyridyl (0.2 g.) and the mixture was heated, open to the atmosphere, just to the point of ebullition. At this stage a red/brown solution was obtained,, which on cooling turned dark blue, depositing the compound as a dark blue amorphous powder (0.02 g. 7%). (Found: C, 29.7; H, 2.7; N, 6.0 $C_{12}H_{13}Cl_2N_2O_2Re$ requires C, 30.3; H, 2.8; N, 5.9%).

Further refluxing did not increase the yield - rather the compound tended to decompose.

The principal bands in the infra-red spectrum are:

Band position (cm^{-1})	Assignment (131)
1600 m.	ring frequency
1446 s.	ring frequency
952 s.	Re=O stretch
916 s.	ϕO-CH_2
763 s.	out of plane ring hydrogen bending mode

Oxoethoxodichloro(1-10 phenanthroline)rhenium(V).

Green $ReO(OEt)Cl_2(PPh_3)_2$ (0.5 g.) was suspended in ethanol (30 ml.) to which was added 1-10 phenanthroline hydrate (0.2 g.). The mixture was heated, open to the atmosphere, for about 2 minutes giving a red solution. On cooling, the solution turned blue and deposited the compound as a blue powder. This was filtered and washed with ethanol and ether (0.08 g. 27%). (Found: C, 34.1; H, 3.0; N, 5.6; O, 6.5 $C_{14}H_{13}Cl_2N_2O_2Re$

requires C, 33.8; H, 2.6; N, 5.6; O, 6.4%).

The principal bands in the infra-red spectrum are:

Band position (cm^{-1})	Assignment (131)
1511 w.	ring frequency
1429 m.	ring frequency
1033 s.	?
958 s.	Re=O stretch
904 m.	δ O-CH_2
852 s.	out of plane central ring hydrogen bending mode
718 s.	out of plane heterocyclic ring hydrogen bending mode

Chlorotricarbonylbis(triphenylphosphine)rhenium(I).

Method A.

Trans-$ReOCl_3(PPh_3)_2$ (1 g.) was placed in a bomb with triphenylphosphine (1.2 g.) and powdered copper. Carbon monoxide at 150 atms. was admitted and the bomb was heated at 120° for 12 hours. The solid mass was extracted into dichloromethane. Addition of ethanol afforded the compound as white microcrystals. These were boiled in ether (to get rid of the last traces of triphenylphosphine), filtered and dried (0.99 g. 99%). (Found: O, 5.6 calc. for $C_{39}H_{30}ClO_3P_2Re$: O, 5.8%).

Method B.

This was essentially the same as Method A, substituting green $ReO(OEt)Cl_2(PPh_3)_2$ (1 g.) for the trans-$ReOCl_3(PPh_3)_2$.

The carbon monoxide pressure was 180 atms. (0.92 g. 94%) m.p. 185-189°. (Found: O, 6.0%).

Method C.

This was the same as above using $ReCl_4(PPh_3)_2$ (1 g.) and a carbon monoxide pressure of 165 atms. (0.94 g. 96%). (Found: O, 6.0%).

Chlorodicarbonylbis(triphenylphosphine)rhenium(I).

A suspension of green $ReO(OEt)Cl_2(PPh_3)_2$ (1 g.) in ethanol (10 ml.) was placed in a bomb. Carbon monoxide at 60 atms. was admitted and the bomb was heated at 110° for 18 hours. The contents of the bomb were then boiled in excess ethanol and filtered. The solid thus obtained was dissolved in hot dichloromethane, filtered, and the filtrate was allowed to evaporate slowly at room temperature depositing pink and green plates (0.22 g. 23%), these were hand separated and were found to have identical infra-red spectra: (carbonyl stretches 2041 vw.; 1934 vs.; 1880 vs. (cm^{-1})). A sample of the pink isomer was washed with ether and dried in vacuo. over phosphorus pentoxide. (Found: C, 57.0; H, 4.0; O, 3.9 calc. for $C_{38}H_{30}ClO_2P_2Re$: C, 56.9; H, 3.7; O, 4.0%).

Chloropentacarbonylrhenium(I).

Method A.

Freshly prepared $ReCl_5$ (0.77 g.) and ethanol (5 ml.) were placed in a bomb with carbon monoxide (80 atms.) and heated at 100° for 17 hours. The white crystals of the compound were filtered and washed with ether (0.6 g. 78%). (Found: C, 16.8; Cl, 10.0 calc. for C_5ClO_5Re: C, 16.6; Cl, 9.8% calc. for the

dimeric tetracarbonylchloride $C_8Cl_2O_8Re_2$: C, 14.4; Cl, 10.6%).

Method B.

This was repeated using $(ReCl_3)_3$ (0.3 g.) instead of $ReCl_5$ and with the same experimental conditions, white crystals were obtained with an identical infra-red spectrum to that of $Re(CO)_5Cl$ as prepared above (0.18 g. 50%).

The compound was a non-conductor in nitrobenzene at 22°.

Tetraethylammonium oxotetrachlorotriphenylphosphine oxiderhenate(V).

Trans-$ReOCl_3(PPh_3)_2$ was suspended in dichloromethane and chlorine gas was passed through until a red solution was obtained. This was reduced to a small volume by boiling, then excess ethanol was added producing a yellow solution to which was added a solution of $Et_4NCl.H_2O$ in ethanol, affording the compound as a pink amorphous powder. This was filtered and washed with ether. (Found: C, 41.3; H, 4.6; N, 2.1; O, 3.8 $C_{26}H_{35}Cl_4NO_2PRe$ requires C, 41.5; H, 4.6; N, 1.9; O, 4.3%). m.p. 192-195°.

The infra-red spectrum in the range 1160-970 cm^{-1} is given below with assignments (101):

Band position(cm^{-1})	Assignment
1151	P=O stretch
1122)) 1094)	P sensitive mode q
1029	β in plane C-H deformation
997	phenyl ring breathing mode
979	Re=O stretch

Oxotrichlorobis(triphenylphosphine oxide)rhenium(V).

Trans-$ReOCl_3(PPh_3)_2$ (0.5 g.) was suspended in dichloromethane and ozone was passed through the mixture until a bright green solution was obtained. This was allowed to evaporate at room temperature affording the compound as bright green plates (0.06 g. 12%). (Found: C, 50.1; H, 3.7 $C_{36}H_{30}Cl_3O_3P_2Re$ requires C, 50.0; H, 3.5%). The infra-red spectrum in the range 1130-980 cm^{-1} is given below with assignments (101):

Band position(cm^{-1})	Assignment
1124	P=O stretch
1092))	P sensitive mode q
1066)	
1029	β in plane C-H deformation
999	phenyl ring breathing mode
980	Re=O stretch

Nonachlorotris(triphenylphosphine)trirhenium(III) bis(acetone).

Freshly prepared $(ReCl_3)_3$ (0.3 g.) was shaken in acetone overnight at room temperature giving a bright red solution. To this solution was added triphenylphosphine (0.6 g.) in acetone, giving an almost immediate crystalline precipitate of the complex. The mixture was allowed to stand for one hour, filtered, washed with acetone and ether and dried in vacuo at 110° (0.4 g. 66%). (Found: C, 40.2; H, 3.4; Cl, (a) 17.9, (b) 18.9; O, 2.2 $C_{60}H_{57}Cl_9O_2P_3Re_3$ requires C, 40.5; H, 3.2; Cl, 17.9; O, 1.8%).

The chlorine analysis was determined

(a) oxygen flask ignition method

(b) alkaline hydrolysis.

Bis(trichloro)1,2bis(diphenylphosphino)ethane dirhenium(III).

Freshly prepared $(ReCl_3)_3$ (0.2 g.) was dissolved in acetone and to this solution was added acetone solution of 1,2bis(diphenylphosphino)ethane. The compound was obtained as a dark blue/purple suspension which coagulated on boiling (0.4 g. 60%). (Found: C, 31.6; H, 2.7 $C_{26}H_{24}Cl_6P_2Re$ requires C, 31.7; H, 2.4%). The compound is insoluble in all common organic solvents, making a molecular weight determination impossible and indicating probable polymerisation.

Tripotassium transdioxotetracyanorhenate(V).

This was prepared by the method of Wilkinson et.al. (132) by refluxing a methanolic solution of potassium cyanide and green $ReO(OEt)Cl_2(PPh_3)_2$.

Trans-dioxobis(ethylenediamine)rhenium(V)chloride dihydrate.

This was prepared by the method of Wilkinson et.al. (16) by refluxing green $ReO(OEt)Cl_2(PPh_3)_2$ with ethylenediamine. Deuteration was achieved by dissolution of the complex in heavy water (D_2O) and evaporating to dryness in vacuo. several times.

Trans-dioxotetrapyridinerhenium(V)chloride dihydrate.

A sample of trans-$ReOCl_3(PPh_3)_2$ was shaken in acetone, then refluxed in ether and filtered. In this way the starting material is freed from all traces of acetic acid. Then the procedure given by Wilkinson et.al. (16) was followed except

that 5 ml. of pyridine were used instead of 2 ml.

Trans-dioxotetrammineosmium(VI)dichloride.

Purple potassium osmate (prepared by the addition of a solution of osmium tetroxide in potassium hydroxide to ethanol (76)) was shaken in a saturated aqueous solution of NH_4Cl affording the compound as yellow microcrystals (133).

Deuteration was achieved by shaking potassium osmate in a saturated solution of ND_4Cl in D_2O. ND_4Cl was prepared by dissolution of NH_4Cl in D_2O and evaporating to dryness in vacuo. The product so obtained was redissolved in D_2O and the solution was again evaporated to dryness.

Trans-dioxotetramminerhenium(V)chloride.

Green $ReO(OEt)Cl_2(PPh_3)_2$ (0.5 g.) was suspended in ethanol (25 ml.) with 0.88 ammonia (3 ml.) and warmed for a few seconds until a yellow suspension was formed. The mixture was allowed to cool and the collected microcrystals were washed with ethanol and ether (0.11 g. 58%). (Found: H, 3.7; N, 17.8; O, 9.9 $ClH_{12}N_4O_2Re$ requires H, 3.8; N, 17.4; O, 9.9%).

The compound was insoluble in all common organic solvents.

The infra-red spectrum, with suggested assignments (41d) is given overleaf:

Band position (cm^{-1})	Assignment
3170 s. 3086 s.	N-H stretch
1630 m.	NH_3 degenerate deformation
1318 s. 1295 s.	NH_3 symmetrical deformation
855 m. sh. 835 s.	Re=O stretch
807 m. 744 s. bd.	NH_3 rock
434 m.	Re-NH_3 stretch

Trans-dioxotetramminerhenium(V)chloride hydrate.

Green $ReO(OEt)Cl_2(PPh_3)_2$ (0.2 g.) was heated in ethanol (10 ml.) and 0.88 ammonia (1 ml.) for 2 minutes. The russet compound was filtered and washed with ether (0.05 g. 62%). (Found: N, 16.5; O, 14.0 $ClH_{14}N_4O_3Re$ requires N, 16.5; O, 14.1%).

The infra-red spectrum of the sample was similar to that of the anhydrous salt. The compound was insoluble in all common organic solvents.

Trans-oxohydroxotetrapyridinerhenium(V) oxopentachlororhenate(V).

Trans-$(ReO_2py_4)Cl.2H_2O$ (0.1 g.) was dissolved in water (5 ml.) and 10M. HCl (5 ml.) was added. The solution was boiled for 30 minutes. Filtration yielded green microcrystals of the compound which were washed with water, ethanol and ether (0.02 g. 27%). (Found: C, 26.1; H, 2.2; N, 6.5;

O, 5.3 $C_{20}H_{21}Cl_5N_4O_3Re_2$ requires C, 26.2; H, 2.3; N, 6.1; O, 5.3%).

μ-Oxodioxotetrachlorobis(ethylenediamine)dirhenium(V).

Trans-$(ReC_2en_2)Cl.2H_2O$ (0.71 g.) was dissolved in ca.2M. HCl (50 ml.) to give a pink solution of trans-$(ReO(OH)en_2)Cl_2$. The solution was allowed to stand for a month during which time green needles of the compound were deposited. The product was collected, washed with acetone and ether (0.37 g. 62%). (Found: C, 7.4; H, 2.5; Cl, 20.4; N, 8.1; O, 7.5 $C_4H_{16}Cl_4N_4O_3Re_2$ requires C, 7.0; H, 2.4; Cl, 20.8; N, 8.2; O, 7.0%).

Oxotrichloroethylenediaminerhenium(V).

Trans-$(ReO_2en_2)Cl.2H_2O$ (0.13 g.) was dissolved in ca.10M. HCl (5 ml.) giving a blue solution of trans-$(Re(OH)_2en_2)Cl_3$. The solution was allowed to stand for 2 days when green crystals of the compound were deposited (0.12 g. 97%). (Found: C, 6.8; H, 2.3; Cl, 28.7; N, 7.6; O, 5.1 $C_2H_8Cl_3N_2ORe$ requires C, 6.5; H, 2.2; Cl, 28.9; N, 7.6; O, 4.4%).

Di-μ-hydroxotetroxobis(ethylenediamine)dirhenium(V).

Trans-$(ReO_2en_2)Cl.2H_2O$ (1.8 g.) was dissolved in water (30 ml.) and allowed to stand in a stoppered flask for 9 months, when brown crystals of the compound separated out. These were filtered and washed with acetone and ether (0.19 g. 7%). (Found: C, 8.7; H, 3.0; Cl, 0.0; N, 9.8; O, 16.3 $C_4H_{18}N_4O_6Re_2$ requires C, 8.1; H, 3.1; Cl, 0.0; N. 9.5; O, 16.3%).

Dicaesium oxopentachlororhenate(V).

Method A.

Freshly prepared $ReCl_5$ (0.50 g.) was dissolved in hot 12M. HCl (10 ml.) to give a yellow solution. Addition of CsCl (0.47 g.) in 12M. HCl (10 ml.) yielded yellow prisms of the compound, which were washed with ether saturated with HCl (0.72 g. 84%). (Found: Cl, 27.6; Cs, 41.1; O, 2.7 calc. for Cl_5Cs_2ORe: Cl, 27.5; Cs, 41.2; O, 2.5; Re, 28.8%).

Method B.

This was the method given by Murmann (57) for the prearation of "$Cs(Re(OH)_2Cl_4)$". Trans-$(ReO_2en_2)Cl.2H_2O$ (0.5 g.) was heated in 5M. HCl (20 ml.) to give a yellow solution to which a solution of CsCl in 5M. HCl was added. The compound was treated as above and obtained as yellow prisms (0.59 g. 75%). (Found: Cl, 28.2; Cs, 40.1; O, 2.3%).

Method C.

To a solution of $(Me_4N)_2(ReOCl_5)$ (0.60 g.) in 12M. HCl (20 ml.) was added excess CsCl in 12M. HCl. The crystals were removed and washed as before (0.57 g. 78%). (Found: O, 2.3; Re, 29.0%).

Dirubidium oxopentachlororhenate(V).

Substitution of RbCl in the above procedures yields the yellow crystalline rubidium salt.

Method A.

(Found: Cl, 32.5 Cl_5ORb_2Re requires Cl, 32.3; O, 2.9%). μ = 2.1 B.M.

Method B.

(Found: Cl, 32.9; O, 3.1%). μ = 2.2 B.M.

The compound was markedly more soluble in 12M. HCl than the caesium salt.

Bis(quinolinium) oxopentachlororhenate(V).

Substitution of quinoline for CsCl in Method A. yields the compound as pale yellow microcrystals. (Found: C, 33.9; H, 2.3; O, 2.6 $C_{18}H_{16}Cl_5N_2ORe$ requires C, 33.8; H, 2.5; O, 2.5%). The compound is fairly soluble in 12M. HCl but virtually insoluble in cold acetone.

Bis(triphenylphosphonium) oxopentachlororhenate(V).

Substitution of triphenylphosphine (0.12 g.) for CsCl in Method A. afforded the compound as pink microcrystals, which were dried in vacuo. over phosphorus pentoxide (0.16 g. 80%). (Found: C, 47.7; H, 3.8; O, 2.3 $C_{36}H_{32}Cl_5OP_2Re$ requires C, 47.7; H, 3.6; O, 1.8%).

Ethylenediaminium oxopentachlororhenate(V).

Trans-$(ReO_2en_2)Cl.2H_2O$ (0.73 g.) was dissolved in 10M. HCl to give a blue solution containing trans-$(Re(OH)_2en_2)Cl_3$. The solution was allowed to stand for a month, during which time yellow prisms were deposited. The crystals were collected and washed with ether saturated with HCl (0.46 g. 58%). (Found: C, 5.9; H, 2.3; Cl, 40.2; N, 6.3; O, 4.1 C_2H_{10}-Cl_5N_2ORe requires C, 5.4; H, 2.3; Cl, 40.2; N, 6.4; O, 3.6%).

On addition of ether to the filtrate, a white sublimable solid was obtained with an infra-red spectrum identical to that

of an authentic sample of enH_2Cl_2. Both compounds could be obtained by boiling the blue $(Re(OH)_2en_2)Cl_3$ for 2-3 hours.

Bis(tetramethylammonium) oxopentachlororhenate(V).

Rhenium metal (1 g.) was dissolved in 100 vol. hydrodgen peroxide and the resulting solution evaporated to dryness. The residual perrhenic acid was dissolved in 10M. HCl (25 ml.) and to the solution was added a solution of tetramethylammonium iodide in water. The mixture was stirred at 20° for 2 hours and filtered. Evaporation to dryness of the filtrate yielded the compound as orange prisms. (Found: C, 18.6; H, 4.7; O, 3.0 $C_8H_{24}Cl_5N_2ORe$ requires C, 18.2; H, 4.6; O, 3.0%).

Impure $(Me_4N)_2(ReOCl_5)$ was also obtained on shaking trans-$ReOCl_3(PPh_3)_2$ with Me_4NCl in dichloromethane for a week at 20°.

Bis(triphenylphosphonium) oxopentachlororhenate(V) tetrahydrofuran.

Trans-$ReOCl_3(PPh_3)_2$ (1 g.) was suspended in dry T.H.F. (80 ml.). Dry HCl gas was passed through the refluxing suspension for 3 hours during which time the colour changed to buff. The compound was filtered, washed with ether and dried in vacuo. over phosphorus pentoxide (0.78 g. 66%). (Found: C, 48.7; H, 4.2; Cl, 18.3; O, 3.6 $C_{40}H_{40}Cl_5O_2P_2Re$ requires C, 49.1; H, 4.1; Cl, 18.2; O, 3.3%).

Triphenylphosphonium oxotetrachlorotriphenylphosphinerhenate(V).

Method A.

$(PPh_3H)_2ReOCl_5$ was allowed to stand for 10 days open to the laboratory air during which time yellow microcrystals of the compound appeared. (Found: Cl, 16.7 $C_{38}H_{31}Cl_4OP_2Re$

requires C, 49.7; H, 3.6; Cl, 16.4; C, 1.8%).

Method B.

$(PPh_3H)_2ReOCl_5.C_4H_8O$ (0.1 g.) was suspended in 2M. HCl and the mixture heated for 5 minutes. The solid was filtered, washed with acetone and ether; affording yellow microcrystals (0.03 g. 34%). (Found: C, 50.0; H, 3.4; Cl, 17.0; C, 1.7%).

The compound was insoluble in all common organic solvents, thus making conductivity and molecular weight measurements impossible.

Oxotrichlorotriphenylphosphinedimethylsulphoxide rhenium(V).

Trans-$ReOCl_3(PPh_3)_2$ (0.5 g.) was suspended in benzene (50 ml.) and dimethylsulphoxide (1 ml.). Dry HCl gas was passed through the cold suspension during which time the trans-$ReOCl_3(PPh_3)_2$ went into solution in the benzene layer. After 2 days, large green crystals appeared at the liquid interface. These were collected and washed with ether (0.1 g. 26%). (Found: C, 37.2; H, 3.3; O, 5.2 $C_{20}H_{21}Cl_3O_2PReS$ requires C, 37.0; H, 3.3; O, 4.9%).

There were no infra-red bands in the P-H stretching region (ca.2400 cm^{-1}). The compound was also formed:

(a) on shaking trans-$ReOCl_3(PPh_3)_2$ (1 g.) in benzene (30 ml.), Me_2SO (1 ml.) and 10M. HCl (5 ml.) at 20° for 4 days (0.68 g. 87%). (Found: C, 36.8; H, 3.2%).

(b) on shaking green $ReO(OEt)Cl_2(PPh_3)_2$ (1 g.) in benzene (30 ml.), Me_2SO (1 ml.) and 10M. HCl (5 ml.) at 20° for 1 day (0.63 g. 82%). (Found: C, 37.2; H, 3.4%).

In both cases the compound was filtered, washed with acetone and obtained as green microcrystals.

Oxotrichloro2.2'dipyridylrhenium(V).

$ReOCl_3PPh_3Me_2SO$ (0.2 g.) was suspended in dichloromethane (30 ml.) to which was added a solution of dipy. (0.2 g.) in dichloromethane (5 ml.). The mixture turned brown immediately and was refluxed, open to the atmosphere, for $3\frac{1}{2}$ hours. The solution was evaporated down (at reduced pressure) to about a quarter of its original volume, depositing a brown solid which was filtered and washed with ether (0.12 g. 84%). (Found: C, 25.7; H, 1.8; O, 3.7 calc. for $C_{10}H_8Cl_3N_2ORe$ C, 25.8; H, 1.7; O, 3.5%).

The infra-red spectrum is clear between 985 cm^{-1} (Re=O stretch) and 767 cm^{-1} (out of plane ring hydrogen bending mode (131)). Both isomers of this stoichiometry have been claimed (134), one green and one purple, but no infra-red data was given.

On prolonged heating in ethanol, a blue solution was obtained which probably contained the blue species ReO(OEt)-Cl_2dipy.

Bis(dioxochlorobis(dimethylsulphoxide)rhenium(V)).

Trans-$ReOCl_3(PPh_3)_2$ (1 g.) or green ReO(OEt)$Cl_2(PPh_3)_2$ (1 g.) was shaken at 20° in benzene (25 ml.) and Me_2SO (1 ml.) for 20 hours. The green amorphous complex was collected, washed with ether and dried in vacuo. over phosphorus pentoxide (0.5 g. 100%). (Found: C, 11.5; H, 2.9; Cl, 8.7; O, 15.6; Re, 46.2; S, 14.6 $C_8H_{24}Cl_2O_8Re_2S_4$ requires C, 11.7; H, 2.9; Cl, 8.7; O, 15.6; Re, 45.4; S, 15.6%).

Oxotribromotriphenylphosphinedimethylsulphoxide rhenium(V).

$ReOBr_3(PPh_3)_2$ (1 g.) was shaken in benzene (25 ml.), Me_2SO (1 ml.) and conc. HBr (5 ml.) at 20° for 5 hours. The green solid was collected, recrystallised from dichloromethane, washed with ether and obtained as green plates (0.54 g. 67%). (Found: C, 30.6; H, 3.0; O, 4.2 $C_{20}H_{21}Br_3O_2PReS$ requires C, 30.7; H, 2.7; O, 4.1%).

Trans-oxotrichlorobis(triphenylphosphine)rhenium(V).

Freshly prepared $ReCl_5$ (0.5 g.) was dissolved in acetone. To this green solution was added triphenylphosphine (0.72 g.) in acetone. The mixture was shaken at 20° for $1\frac{1}{2}$ hours during which time the solution turned purple and yellow/green crystals of the compound were formed. These were collected and washed with ether (0.5 g. 44%). (Found: C, 52.4; H, 3.9 calc. for $C_{36}H_{30}Cl_3OP_2Re$ C, 51.9; H, 3.6%).

Trichlorotriphenylphosphinerhenium(III) bis(acetone) - isomer I.

Addition of ether to the purple mother liquors above yielded a purple tar. This was redissolved in acetone (5 ml.); ether (40 ml.) was added and the mixture was allowed to stand overnight depositing purple crystals of the compound. (This procedure may have to be performed several times to get a non tarry residue). The crystals were filtered, washed with ether and dried in vacuo. at 20° (0.24 g. 26%). (Found: C, 42.9; H, 4.0; O, 4.3; M, 681 (acetone) $C_{24}H_{27}Cl_3O_2PRe$ requires C, 43.0; H, 4.1; O, 4.8%; M, 671).

The carbonyl stretching frequency of the acetone could be seen at 1712 cm^{-1}.

Trichlorotriphenylphosphinerhenium(III) bis(acetone - isomer 2.

The purple crystals of isomer 1. were heated in vacuo. at 80° yielding green microcrystals of the compound - with a greatly increased total volume. (Found: C, 43.0; H, 4.2; O, 4.8%; M, 661 (acetone))

The carbonyl stretch is visible at 1712 cm^{-1}, and there is a complete absence of bands in the range 900-1000 cm^{-1}.

A solution of the compound in acetone was added to a solution of triphenylphosphine in acetone; oxygen was blown through the mixture and the mixture was allowed to stand for 3 weeks. A small amount of pale green precipitate was formed with a strong absorbtion at 983 cm^{-1}, suggesting $ReOCl_3(PPh_3)_2$ had been formed.

Dicaesium trioxotrichlororhenate(VII). (first prepared by N.P.Johnson).

Rhenium metal (2 g.) was dissolved in 100 vol. hydrogen peroxide and the solution evaporated to dryness. The residue (perrhenic acid) was dissolved in 10M. HCl (10 ml.) and the solution was saturated with HCl gas giving a yellow solution. To this was added a solution of CsCl (4 g.) in saturated HCl. The mixture was allowed to stand overnight. The yellow crystalline product was collected under an atmosphere of HCl, washed with 12M. HCl and dried in vacuo. over phosphorus pentoxide. (4.15 g. 58%). (Found: Cl, 17.1; Cs, 43.8; O, 7.8; Re, 30.6 $Cl_3Cs_2O_3Re$ requires Cl, 17.5; Cs, 43.8; O, 7.9; Re, 30.7%).

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