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Melvin Leitheiser

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REACTIONS OF
OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V)

BY

MELVIN LEITHEISER

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Chemistry, South Dakota
State University

1969

REACTIONS OF
OXOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V)

This thesis is approved as a creditable and independent investigation by a candidate for the degree Master of Science and is acceptable as meeting the thesis requirement for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser Date

Head, Chemistry Department Date

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ML

INTRODUCTION

While sealed tube reactions have been used extensively in the synthesis of other transition metal complexes (1), the method has seen limited use in synthetic rhenium chemistry. The first reaction reported was the preparation of tris(1,10 phenanthroline)rhenium(III) chloride (2).

The second reaction was an attempt to isomerize oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3\left[(C_6H_5)_3P\right]_2$, by refluxing it in chloroform (3). Instead of isomerization, oxodichloro(ethoxy)bis(triphenylphosphine)rhenium(V), $ReO(OC_2H_5)Cl_2\left[(C_6H_5)_3P\right]_2$ was produced; the ethoxy moiety came from an ethanol preservative in commercial chloroform. As temperature was sometimes important, the isomerization was also attempted in chloroform in a sealed tube at 120°C. The reaction unexpectedly gave compounds identified as tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4\left[(C_6H_5)_3P\right]_2$, and tetrachlorobis(triphenylphosphineoxide)rhenium(IV), $ReCl_4\left[(C_6H_5)_3PO\right]_2$. The unusual behavior of the oxotrichlorobis(triphenylphosphine)rhenium(V) in the sealed tube led to the current work. The purpose of this project was to make a systematic investigation of sealed tube reactions of several rhenium co-ordination compounds in different solvents at variable temperatures.

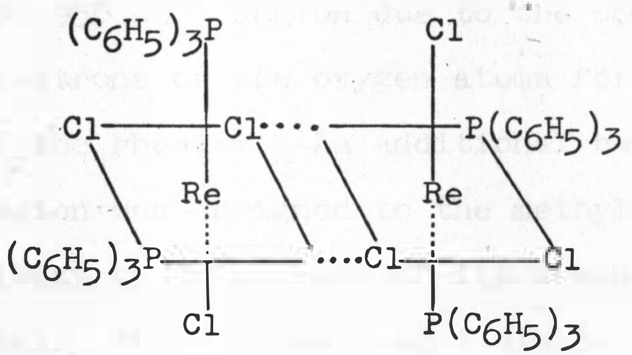
Complications arising in the recrystallization of one of the starting materials, oxotrichlorobis(triphenylphosphine)rhenium(V), led to an investigation of a series of reactions producing triphenylphosphonium salts of several rhenium anions.

HISTORICAL

The commerical supply of rhenium has limited the study of its chemistry until 1960 (4). Since then much work has been published in two related fields. Rhenium is one of the few metals capable of forming metal atom cluster compounds. This has led to the formation of many novel compounds. The other area that is being investigated is the co-ordination chemistry of rhenium monomeric species. A considerable amount of difficulty resulted in the interpretation of the monomeric chemistry because many of the species were found to be di- and trimeric.

The work presented in this thesis will be restricted to monomeric species stabilized by triphenylphosphine and triphenylphosphine oxide ligands. Since an excellent review article (5) exists that covers the entire field of rhenium chemistry, the Historical section will be limited to the compounds used in this work, namely oxotrichlorobis-(triphenylphosphine)rhenium(V), tetrachlorobis(triphenylphosphine)rhenium(IV), and oxotrichloro(triphenylphosphine)-triphenylphosphineoxiderhenium(V).

The first compound used in this study was prepared in 1960 by Freni and Valenti (6) which they formulated as trichlorobis(triphenylphosphine)rhenium(III), $ReCl_3[(C_6H_5)_3P]_2$(I). The compound was a nonelectrolyte, poorly soluble in alcohol or acetone, which indicated that the complex was dimeric and; therefore, octahedrally and coordinately saturated. The compound was diamagnetic as expected for low spin d^2 complexes(6).



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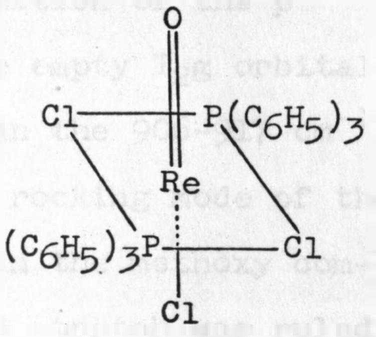


II

Reinvestigation of Freni and Valenti's work by Chatt and Rowe (7), and Johnson, Lock, and Wilkinson (8) indicated that the yellow compound I should be formulated as trans-oxotrichlorobis(triphenylphosphine)-rhenium(V), $ReOCl_3[(C_6H_5)_3P]_2$(II). This formulation was based on the consistently high elemental analysis as well as a strong infrared absorption band in the area of the accepted metal-oxygen double bond stretching frequency.

The infrared spectra of rhenium compounds were examined and it was found that compounds containing the rhenium-oxygen double bond had a strong absorption in the 958-985 cm^{-1} region (7). In complexes containing the trans oxygen-rhenium-alkoxy grouping, where the alkoxy was methyl, ethyl, methoxyethyl, or benzyl, the double bond stretching frequency was lowered to the 930-958 cm^{-1} region due to the competition of the p electrons of the oxygen atoms for the empty T_2g orbitals of the rhenium. An additional band in the 906-917 cm^{-1} region was assigned to the methylene rocking mode of the alkoxy group because of its absence in the methoxy complex. The rhenium-oxygen single bond stretch was ruled out because of the closeness to the rhenium-oxygen double bond stretching frequency. The singly bonded oxygen stretch probably occured in the 500-700 cm^{-1} region (7) (9).

In an attempt to resolve the early work, Chatt and Rowe (7) re-examined the four known reactions for preparing triphenylphosphine compounds of rhenium. The following table summarizes their findings.

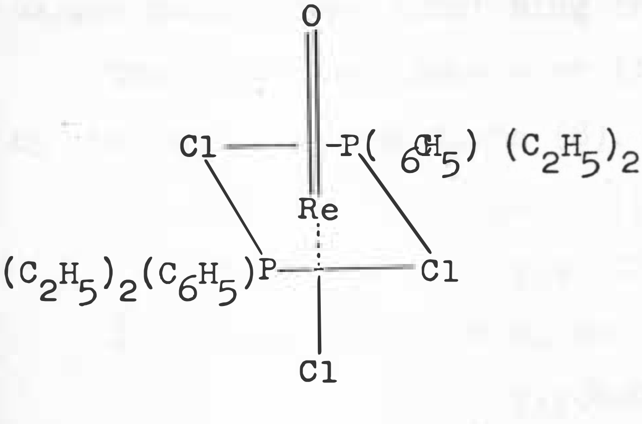
Table I. Re-examination of the Methods of Preparing Triphenylphosphine Compounds of Rhenium.

Reaction Number	Reactants	Reported Product	Reformulated Product
1.	Perrhenate ion Triphenylphosphine Hydrochloric Acid Ethanol	$ReCl_3[(C_6H_5)_3P]_2$ (6)	$ReOCl_3[(C_6H_5)_3P]_2$
2.	Rhenium Heptoxide Triphenylphosphine Hydrazine Dihydrochloride Ethanol	$ReCl_3[(C_6H_5)_3P]_2$ (6)	$ReO(OC_2H_5)Cl_2[(C_6H_5)_3P]_2$ *
3.	Rhenium Trichloride Triphenylphosphine Acetone or Ethanol	$ReCl_3(C_6H_5)_3P$ (6) (10)	$ReCl_3(C_6H_5)_3P$
4.	Trichlorotriphenylphosphinerhenium(III) Triphenylphosphine Chlorine Acetone	$ReCl_3[(C_6H_5)_3P]_2$ (10)	No product could be isolated **

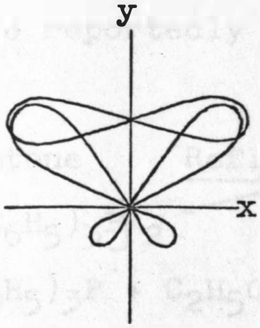
*This compound was later reformulated as $ReNCl_2[(C_6H_5)_3P]_2$ (11).

**Much discussion has resulted from this reaction. It has been claimed to form $ReCl_3[(C_6H_5)_3PO]_2$ (12).

Of the reformulated compounds, probably the most useful is the oxotrichlorobis(triphenylphosphine)rhenium(V), (II). The compound is found to be a good starting material for much of the co-ordination chemistry of rhenium. The compound may exist as three isomers. The trans configuration is assigned to (II) because of the low dipole moment of 2.5 Debye (7). The X-ray crystal structure of the similarly prepared oxotrichlorobis(diethylphenylphosphine)-rhenium(V), $ReOCl_3\left[(C_2H_5)_2(C_6H_5)P\right]_2$ (III) shows the compound to be trans (13). The crystal structure also indicates that the rhenium atom is above the octahedral plane and that the rhenium-oxygen bond distance is abnormally short. With this formulation the remaining two electrons in the 5d orbitals of the rhenium would be unpaired to give a paramagnetic compound, while the experimental results show the compound to be diamagnetic.



III



IV

In the octahedral d^2 system only one of the three nonbonding t_{2g} orbitals is required to accommodate the two nonbonding electrons. The remaining two t_{2g} orbitals are available for multiple $(d\pi\text{-}p\pi)$ bonding to the oxygen atom. The filled oxygen p orbitals donate electrons to the empty t_{2g} orbitals of the rhenium atom. This results in the bond containing considerable triple bond character as illustrated in IV. This can account for the short rhenium-oxygen bond distance and the rise of the rhenium atom above the plane of the octahedron. A similar effect occurs in the nitrogen containing rhenium compounds such as trichlorophenylimidobis(triphenylphosphine)rhenium(V), $ReCl_3(C_6H_5N)[(C_6H_5)_3P]_2$. The less electronegative nitrogen can donate its electrons even more readily than the oxygen to give more triple bond character. This is shown in the shift of the rhenium-nitrogen double bond stretching frequency some 90 cm^{-1} up field from the rhenium-oxygen double bond stretching frequency (11).

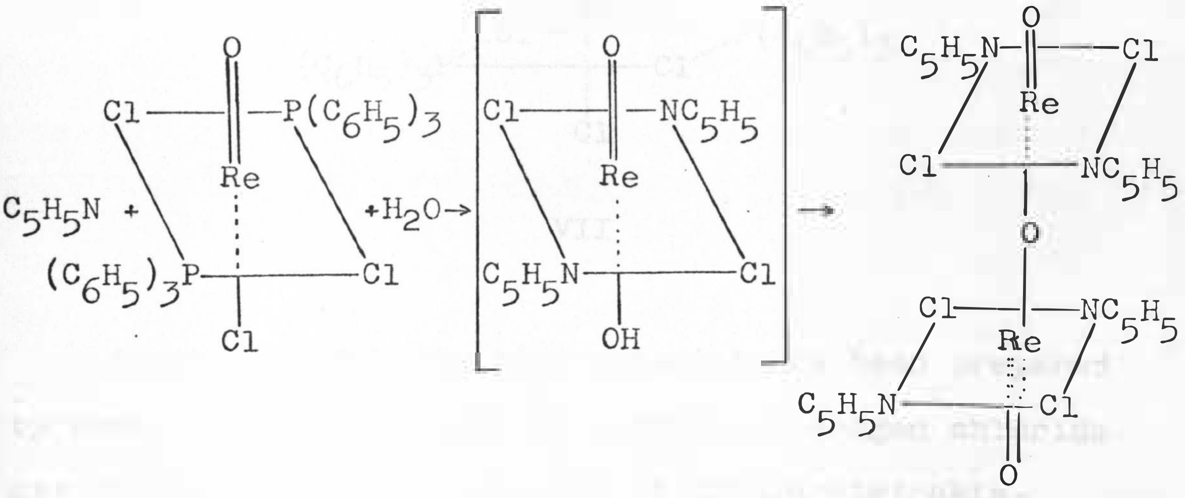
The other two isomers of (II) were reportedly made by the following reactions (8).

1. $\underline{\text{trans}}\text{-}ReOCl_3[(C_6H_6)_3P]_2$ + Acetone $\xrightarrow{\text{Reflux}}$ $\underline{\text{cis}}\text{-}ReOCl_3[(C_6H_5)_3P]_2$

2. $HReO_4 + HCl + N_2H_4\cdot 2HCl + (C_6H_5)_3P + C_2H_5OH \xrightarrow{\text{Reflux}} \underline{\text{cis}}\text{-}ReOCl_3[(C_6H_5)_3P]_2$

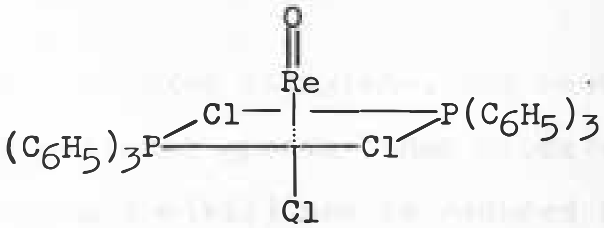
Dipole moments of these isomers have not been determined, so the assignment of the correct cis structure remains unresolved. The compounds are thought to be isomers because the elemental analysis is consistent for the structure. In addition, the rhenium-oxygen stretching frequency is shifted from 969 cm^{-1} in the trans isomer to 981 cm^{-1} for the product of reaction 1 and to 986 cm^{-1} for the product of reaction 2. No experimental work has been performed on these isomers because of the difficulty in obtaining the pure isomers.

While studying the reaction of pyridine and II, Johnson, Taha, and Wilkinson (14) produced μ-oxo-dioxo-tetrachlorotetrakis(pyridine)dirhenium(V), (VI). The



II V VI

compound was fairly stable and was an example in which the triphenylphosphine could be replaced by another ligand. The intermediate hydroxy species V could not be isolated. In an attempt to prepare the triphenylphosphine analog of VI, water was added to a dichloromethane solution of II. The resulting maroon solution failed to yield the desired product (8). The replacement of the _trans_ chlorine was not unexpected since the _trans_ alkoxy complexes had been formed. The _trans_ effect of the oxygen and the repulsions of the other groups on the plane cause the _trans_ chlorine to be labile as illustrated in VII.



VII

Another useful starting material has been prepared by Freni and Valenti (15) by bubbling hydrogen chloride gas through a benzene solution of trihydrotetrakis(triphenylphosphine)rhenium(III), $ReH_3\left[(C_6H_5)_3P\right]_4$. The red product formed was soluble in chloroform, benzene, and dichloromethane. The preparation was found to be quantitative in warm benzene. The infrared spectrum of the compound was similar to that for II except for the missing rhenium-oxygen double bond stretching frequency. The compound was formulated as tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4[(C_6H_5)_3P]_2$.

Several other methods for the preparation have been given in which the complex is a product in some of the reactions of II (16) (17). The yield rarely exceeds 40 per cent. The complex results when solutions of I are heated to relatively high temperatures (120°C) via the following reaction.

$$3\ ReOCl_3[(C_6H_5)_3P]_2 \rightarrow 2\ ReCl_4[(C_6H_5)_3P]_2 + ReO_3Cl + (C_6H_5)_3P$$

When II was refluxed in xylene, the amount of the red product was somewhat greater than expected; however, the trioxochlororhenium(VII) may be reduced by the liberated triphenylphosphine to II with repetition of the cycle (17). When excess triphenylphosphine was added, the yield of the tetrachlorobis(triphenylphosphine)-rhenium(IV) became almost quantitative by the following reaction.

$$ReO_3Cl + 2\ HCl + 3\ (C_6H_5)_3P \longrightarrow ReOCl_3[(C_6H_5)_3P]_2 + (C_6H_5)_3PO + H_2O$$

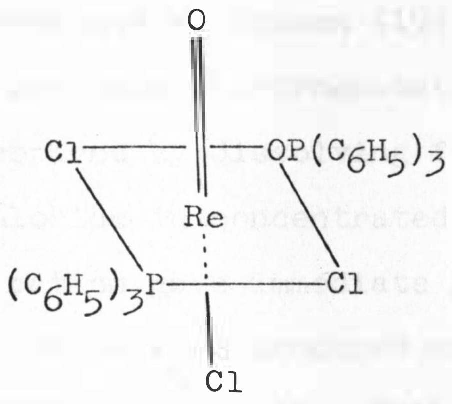
A summary of the reactions of tetrachlorobis(triphenylphosphine)rhenium(IV) are given in Table II.

Table II. Reactions of Tetrachlorobis(triphenylphosphine)-rhenium(IV).

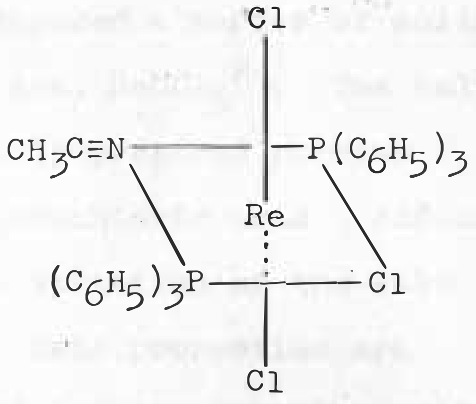
1. $ReCl_4\ [(C_6H_5)_3P]_2$ + pyridine $\longrightarrow ReCl_4(py)(C_6H_5)_3P$
2. $ReCl_4\ [(C_6H_5)_3P]_2$ + acetylacetone $\longrightarrow Re_2Cl_4(Acac)_4$
3.* $ReCl_4\ [(C_6H_5)_3P]_2$ + RCOOH $\longrightarrow Re_2Cl_3(RCO_2)_2\ [(C_6H_5)_3P]_2$

*R is an alkyl group

The only reported preparation of oxotrichloro-(triphenylphosphine)triphenylphosphineoxiderhenium(V), VIII, was by Wilkinson and Rauchias (18) in 1967. The compound was isolated from the mother liquor of dichloromethane solutions of IX. They reported that the compound could be best prepared by passing a current of air through a suspension of trichloro(acetonitrile)bis(triphenylphosphine)rhenium(III) in boiling benzene for twenty minutes. The acetonitrile was allowed to distill off as the azeotrope. The conditions were critical and oxidation was inhibited by the free nitrile. The infrared spectrum showed bands for triphenylphosphine oxide at 1119 cm^{-1} and 1064 cm^{-1} as well as a band at 1090 cm^{-1} due to the triphenylphosphine.



VIII



IX

It was found that the triphenylphosphine oxide could be replaced by a number of components as shown in Table III.

Table III. Reactions of Oxotrichloro(triphenylphosphine)-triphenylphosphineoxiderhenium(V).

1. $ReOCl_3(C_6H_5)_3P(C_6H_5)_3PO + Acac^{*} \rightarrow ReOCl_2(Acac)(C_6H_5)_3P$

2. $ReOCl_3(C_6H_5)_3P(C_6H_5)_3PO + bipy^{**} \rightarrow ReOCl_3(bipy)$

3. $ReOCl_3(C_6H_5)_3P(C_6H_5)_3PO + (C_2H_5)_2(C_6H_5)P \rightarrow ReOCl_3[(C_2H_5)_2(C_6H_5)P]_2$

*Acac is acetylacetone

**bipy is 2,2' bipyridyl

Grove and Wilkinson (19) prepared a series of salts of the oxopentachlororhenate(V) ion, $ReOCl_5^{2-}$. The salts were prepared by dissolving freshly prepared rhenium pentachloride in concentrated hydrochloric acid. Addition of the cation gave immediate precipitation of the salt. Several salts were produced and their properties are summarized in Table IV. Both triphenylphosphonium salts were unstable and lost a mole of hydrogen chloride gas in the solid state to give a yellow triphenylphosphonium oxotetrachlorotriphenylphosphinerhenate(V).

Table IV. Characteristics of Oxopentachlororhenate(V) Salts.

Compound	$\nu(Re{=}O)cm^{-1}$	Color
Cs_2ReOCl_5	952	yellow
Rb_2ReOCl_5	977,956	yellow
$(enH)_2{}^*ReOCl_5$	974	yellow
$(C_9H_8N)_2ReOCl_5$	950	yellow
$[N(CH_3)_4]_2ReOCl_5$	951	orange
$[(C_6H_5)_3PH]_2ReOCl_5$	971	pink
$[(C_6H_5)_3PH]_2ReOCl_5 \cdot C_4H_8O$	948	pink
$[ReO(OH)py^{\#}_4]ReOCl_5$	940,968	pale green

*en is ethylenediamine and #py is pyridine

Recently the oxopentachlororhenate(VI) ion, $ReOCl_5^{1-}$, has been prepared by the addition of chloride ions to solutions containing oxotetrachlororhenium(VI), $ReOCl_4$ (9). Other workers (20) (21) (22) who used hydrochloric acid as the source of the chloride ion have reported different products. Atmospheric hydrolysis of the oxopentachlororhenate(VI) ion produced the linear μ-oxo-dioxooctachlorodirhenate(VI) ion. The rhenium oxygen double bond stretch was found at 970 cm^{-1} and the bridging mode was assigned to a 730 cm^{-1} band (9).

EXPERIMENTAL

Infrared Spectra

The spectra of all complexes were obtained as potassium bromide wafers or as nujol mulls. The instrument used was a model 521 Perkin-Elmer grating spectrophotometer. Preliminary infrared analyses were performed on a Beckman IR-5.

Triphenylphosphine

The triphenylphosphine was obtained from Alfa Inorganics, Inc. and was used as received.

Ammonium Perrhenate

The ammonium perrhenate was used as received from the S. W. Shattuck Chemical Company.

Dichloromethane

The dichloromethane was obtained from Fisher Scientific Company and was used without further purification. The dichloromethane that gave the oxygen bridged compound was obtained from Eastman Organic Chemicals.

Chloroform

The chloroform was obtained from Mallinckrodt Chemical Works. The chloroform contained 0.75 per cent ethanol as a preservative. Pure dry chloroform was obtained by the method of Wiberg (23).

2-Butanone

The 2-butanone was used as received from the Matheson Company.

Toluene

The toluene was used as received from E. H. Sargent Company.

Xylene

The xylene was purchased from Merck and Company, Inc. and was used without further purification.

Hydrogen Chloride

The hydrogen chloride was generated by refluxing concentrated hydrochloric acid and passing the vapor through a calcium chloride drying tube.

Analyses

Some carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., while the remaining carbon, hydrogen, chlorine, and rhenium analyses were performed by the analysts at South Dakota State University. Chlorine was determined gravimetrically with the Parr Bomb method of Beamish (24), while rhenium was analyzed spectrophotometrically by the α-furildioxime method (25).

Oxotrichlorobis(triphenylphosphine)rhenium(V).

The compound was prepared using a modification of the method of Chatt and Rowe (7). To a 100 ml round bottom flask equipped with a reflux condenser were added 0.50 g (1.9 mmole) ammonium perrhenate, 5 ml (5 mmole) of concentrated hydrochloric acid, and 20 ml of ethanol. The ammonium perrhenate dissolved in 15 minutes, and 3.10 g (12 mmole) of triphenylphosphine, dissolved in 25 ml of hot ethanol, was added. After a momentary series of color changes from green to yellow, a yellow solid precipitated. The mixture was refluxed for ten minutes. The complex was then isolated by filtration, washed with hot ethanol, and dried with diethyl ether to give 1.50 g (96 per cent) of yellow powder.

The 1.50 g of yellow powder was recrystallized from dichloromethane to give 1.30 g (84 per cent) green crystals.

Anal. Calcd. for $C_{36}H_{30}P_2ReOCl_3$: C, 51.99; H, 3.61;
Found C, 51.24; H, 3.62;

The infrared spectrum of the compound contained bands characteristic of co-ordinated triphenylphosphine and a strong band at 981 cm^{-1} and shoulder at 969 cm^{-1} assigned to the rhenium-oxygen double bond stretch.

The doublet indicated that the recrystallized product was a mixture of isomers. Consult the Appendix for the complete spectrum.

Tetrachlorobis(triphenylphosphine)rhenium(IV).

The compound was made with a modification of the procedure given by Rouschias and Wilkinson (17). The reaction flask was a 500 ml, three neck, round bottom flask equipped with a reflux condenser and a gas inlet tube. The gas inlet tube was placed beneath 50 ml of propanoic acid which contained 4.04 g (4.8 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V) and 4.0 g (15 mmole) of triphenylphosphine. The mixture was refluxed and dry hydrogen chloride gas was bubbled through the mixture for two hours. The solution's color slowly changed from yellow to deep red with a deep red solid suspended in it. The mixture was then filtered and the red product was dried with diethyl ether to give 3.78 g (93 per cent) of deep red powder. The red powder was recrystallized from chloroform to give 3.02 g (75 per cent) of red crystals. Consult the Appendix for the complete infrared spectrum.

Anal. Calcd. for $C_{36}H_{30}P_2ReCl_4$: C, 50.76; H, 3.53;

Found C, 50.40; H, 3.42;

Oxotrichloro(triphenylphosphine)triphenylphosphineoxide-rhenium(V).

To a 500 ml Erlenmeyer flask was added 250 ml of benzene and 1.09 g (1.3 mmole) of oxotrichlorobis-(triphenylphosphine)rhenium(V). To a 150 ml beaker containing 60 ml of benzene and 30 g of anhydrous calcium chloride was added 10 ml of 40 per cent formaldehyde solution. The benzene, saturated with formaldehyde, was then separated from the calcium chloride by filtration and added to the 500 ml Erlenmeyer flask. The solution color changed from green to blue and a blue solid precipitated in a few minutes. The solid was isolated by filtration, washed with ethanol, and dried with diethyl ether to yield 0.91 g (83 per cent) of blue powder. The blue powder was recrystallized from dichloromethane to give 0.74 g (68 per cent) of turquoise crystals. Anal. Calcd. for $C_{36}H_{30}P_2ReO_2Cl_3$: C, 51.00; H, 3.54; Re, 22.0; Found C, 51.41; H, 3.54; Re, 21.8;

The compound can also be made from dichloromethane solutions by an analogous procedure; however, the compound is soluble in dichloromethane and the resulting blue solution must be concentrated in order to obtain the product. The infrared spectrum shows bands for both co-ordinated triphenylphosphine at 1090 cm^{-1} and triphenylphosphine oxide at 1145 cm^{-1}, 1117 cm^{-1}, and 1064 cm^{-1}, as well as the rhenium-oxygen double bond stretch at 962 cm^{-1}. Consult the Appendix for the complete spectrum.

μ-oxo-dioxotetrachlorotetrakis(triphenylphosphine)dirhenium(V).

In a recrystallization process, 1.03 g (1.2 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V) was dissolved in 300 ml of dichloromethane which contained some unknown substance. The initial green solution changed to violet after standing for 30 minutes. Concentration of this solution on a hot plate to 30 ml and the addition of 20 ml of hexane gave 0.57 g (55 per cent) of gray crystals.

Anal. Calcd. for $C_{72}H_{60}P_4Re_2O_3Cl_4$: C, 53.66; H, 3.75;
Found C, 52.75; H, 3.79;

The compound was recrystallizable from the dichloromethane containing the unknown substance. All other solvents tried resulted in the decomposition of the complex. The infrared spectrum contained a strong band at 945 cm^{-1} assigned to the rhenium-oxygen double bond stretch. Consult the Appendix for the complete spectrum. Table V gives a summary of the experiments performed in an attempt to identify the unknown substance.

Table V. Table of Attempts to Identify the Nature of the Unknown Substance Found in the Dichloromethane.

1.* CH_2Cl_2 (with unknown substance) + $ReOCl_3[(C_6H_5)_3P]_2 \longrightarrow$

$Re_2O_3Cl_4[(C_6H_5)_3P]_4$

2. CH_2Cl_2 (Distilled) + $ReOCl_3[(C_6H_5)_3P]_2 \longrightarrow$

$Re_2O_3Cl_4[(C_6H_5)_3P]_4$

3. CH_2Cl_2 (Distilled from $CaCl_2$) + $ReOCl_3[(C_6H_5)_3P]_2 \longrightarrow$

$Re_2O_3Cl_4[(C_6H_5)_3P]_4$

4. CH_2Cl_2 (3A Molecular sieves) + $ReOCl_3[(C_6H_5)_3P]_2 \longrightarrow$

$ReOCl_3[(C_6H_5)_3P]_2$

5. CH_2Cl_2 (Passed down alumina column) + $ReOCl_3[(C_6H_5)_3P]_2 \longrightarrow$

$ReOCl_3[(C_6H_5)_3P]_2$

6. CH_2Cl_2 (Distilled from P_4O_{10}) + $ReOCl_3[(C_6H_5)_3P]_2 \longrightarrow$

$ReOCl_3[(C_6H_5)_3P]_2$

7.# $ReOCl_3[(C_6H_5)_3P]_2 + CH_2Cl_2 + H_2O \longrightarrow$ Maroon solution

8. $ReOCl_3[(C_6H_5)_3P]_2 + CH_2Cl_2 + H_2CO \longrightarrow ReOCl_3[(C_6H_5)_3P]\text{-}(C_6H_5)_3PO$

9. $ReOCl_3[(C_6H_5)_3P]_2 + CH_2Cl_2 + NH_3 \longrightarrow$ Red gel

10. $ReOCl_3[(C_6H_5)_3P]_2 + CH_2Cl_2 + CH_3CHO \rightarrow ReOCl[(C_6H_5)_3P]\text{-}C_2H_4O$

11. $ReOCl_3[(C_6H_5)_3P]_2 + CH_2Cl_2 + SO_2 \longrightarrow ReOCl_3[(C_6H_5)_3P]_2$

12. $ReOCl_3[(C_6H_5)_3P]_2 + CH_2Cl_2 + HCl_{(g)} \rightarrow [(C_6H_5)_3PH]_2ReCl_6$

*Preparation of μ-oxo-dioxotretachlorotetrakis(triphenylphosphine)rhenium(V).

#The following reactions use normal dichloromethane in an attempt to add the missing component.

Oxochlorotriphenylphosphineethanalrhenium(III).

When 0.51 g (0.61 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V) was dissolved in 30 ml of dichloromethane and 10 ml of ethanal added, a purple solution resulted after 30 minutes. The purple solution was concentrated on a rotary evaporator to 15 ml and was allowed to stand for 3 hours. The resulting purple crystals were recrystallized from dichloromethane-ethanal to give 0.24 g (70 per cent) of purple product.

Anal. Calcd. for $C_{20}H_{19}PReOCl$: C, 44.07; H, 3.61;
Found C, 43.93; H, 3.64;

The infrared spectrum contained a strong band at 1629 cm^{-1} assigned to the co-ordinated ethanal as well as a strong band at 972 cm^{-1} characteristic of the rhenium-oxygen double bond stretch. Consult the Appendix for the complete spectrum.

Oxoethoxydichlorobis(triphenylphosphine)rhenium(V).

In an attempt to recrystallize μ-oxo-dioxotetrachlorotetrakis(triphenylphosphine)rhenium(V), 0.51 g (0.32 mmole) was dissolved in 100 ml of dichloromethane which contained 10 ml of ethanol. The solution, concentrated on a hot plate, yielded 0.32 g (61 per cent) of violet crystals.

Anal. Calcd. for $C_{38}H_{35}P_2ReO_2Cl_2$: C, 54.16; H, 4.16;
Found C, 53.11; H, 3.85;

The infrared spectrum of this compound was identical with that of an authentic sample of oxodichloroethoxybis(triphenylphosphine)rhenium(V).

Bis(triphenylphosphonium) Hexachlororhenate(IV) Bisdichloromethane and Bis(triphenylphosphonium) Hexachlororhenate(IV).

To a 125 ml Erlenmeyer flask were added 0.43 g (0.51 mmole) of oxotrichlorobis(triphenylphosphine) rhenium(V) and 40 ml of dichloromethane. Hydrogen chloride gas was rapidly bubbled through the solution for 15 minutes at room temperature. The excess oxotrichlorobis(triphenylphosphine)rhenium(V) dissolved and gave a pale yellow solution. The flask was stoppered and allowed to stand for 20 hours. The solution deposited 0.32 g (75 per cent) of large pale green crystals. Anal. Calcd. for $C_{38}H_{36}P_2ReCl_{10}$: C, 41.83; H, 3.30; Cl, 29.9; Found C, 41.46; H, 3.70; Cl, 29.4;

The 0.32 g of the pale green crystals were dissolved with difficulty in 350 ml of dichloromethane by refluxing the mixture in a 500 ml round bottom flask. The resulting yellow solution was filtered and concentrated on a hot plate until crystallization began. The solution yielded 0.27 g (63 per cent) of small pale green crystals.

Anal. Calcd. for $C_{36}H_{32}P_2ReCl_6$: C, 46.70; H, 3.45; Cl, 23.0; Found C, 46.13; H, 3.69; Cl, 23.4;

As proof of the structure, the compound, bis(triphenylphosphonium) hexachlororhenate(IV), was also prepared by dissolving 0.58 g (0.57 mmole) of bis(tetraphenylarsonium) hexachlororhenate(IV) in 80 ml of dichloromethane in a 250 ml round bottom flask. To the solution was added 0.53 g (1.78 mmole) of triphenylphosphonium chloride. The solution was concentrated on a rotary evaporator to 30 ml. After the addition of 15 ml of hexane, the solution was allowed to stand for 5 hours. The resulting pale green crystals were isolated by filtration. Recrystallization from dichloromethane yielded 0.43 g (81 per cent) of product.

Anal. Calcd. for $C_{36}H_{32}P_2ReCl_6$: C, 46.70; H, 3.45; Cl, 23.0; Found C, 46.35; H, 3.68; Cl, 23.3;

When hydrogen chloride gas was bubbled through a 2-butanone solution of oxotrichlorobis(triphenylphosphine)rhenium(V), a brown powder was obtained. The powder was washed with ethanol to give a pale green solid. The infrared spectrum of this compound showed it to be bis(triphenylphosphonium) hexachlororhenate(IV).

The infrared spectra of these compounds were identical. The spectra contained a moderate band at

2438 cm^{-1} indicative of the phosphorus-hydrogen stretch and a band at 864 cm^{-1} indicative of the phosphorus-hydrogen bending mode. Consult the Appendix for the complete infrared spectrum.

Bis(triphenylphosphonium) Oxopentachlororhenate(V) Tetrahydrofuran.

This compound was prepared with a modification of the method given by Grove and Wilkinson (19). Hydrogen chloride gas was added for 15 minutes to a 50 ml Erlenmeyer flask that contained 0.25 g (0.30 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V) and 35 ml of tetrahydrofuran. The excess oxotrichlorobis(triphenylphosphine)rhenium(V) dissolved during the addition of hydrogen chloride gas to give an orange solution which deposited an orange solid. The mixture was stoppered and allowed to stand for 10 hours. The mixture was then filtered and yielded 0.17 g (68 per cent) orange powder.

Anal. Calcd. for $C_{40}H_{40}P_2ReO_2Cl_5$: C, 49.13; H, 4.10; Cl, 18.1; Found C, 48.63; H, 4.31; Cl, 17.4; The infrared spectrum of the compound agreed with that reported in the reference (19).

Bis(triphenylphosphonium) Oxopentachlororhenate(V) Dichloroform.

The compound was made by passing hydrogen chloride gas through 0.25 g (0.30 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V) suspended in 30 ml of chloroform. Rapid addition of hydrogen chloride gas caused the excess oxotrichlorobis(triphenylphosphine)rhenium(V) to dissolve. The resulting orange solution was stoppered and allowed to stand for 6 hours. The solution deposited 0.16 g (64 per cent) of orange powder.

Anal. Calcd. for $C_{38}H_{32}P_2ReOCl_{11}$: C, 39.98; H, 2.95; Cl, 32.1; Found C, 40.07; H, 2.86; Cl, 31.8;

Attempts to recrystallize the compound from dichloromethane, chloroform, and benzene yielded in each case *trans*-oxotrichlorobis(triphenylphosphine)rhenium(V). The infrared spectrum of bis(triphenylphosphonium) oxopentachlororhenate(V) dichloroform contained a band at 2410 cm^{-1} indicative of the phosphorus-hydrogen stretch and a broad band at 870 cm^{-1} assigned to the phosphorus-hydrogen bending mode. The spectrum also contained a broad band at 790 cm^{-1} assigned to the carbon-chlorine stretch (34).

Triphenylphosphonium oxotetrachlorotriphenylphosphine-rhenate(V).

The compound was prepared using a modification of the procedure of Johnson, Taha, and Wilkinson (14). Hydrogen chloride gas was bubbled through a mixture of 0.20 g (0.24 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V) and 25 ml of benzene in a 50 ml Erlenmeyer flask for 15 minutes. The excess oxotrichlorobis(triphenylphosphine)rhenium(V) dissolved upon the addition of the hydrogen chloride gas, and a green solid began to precipitate during the addition. The mixture was stoppered, allowed to stand for 15 hours, filtered, and yielded 0.15 g (75 per cent) of green powder.

Anal. Calcd. for $C_{36}H_{31}P_2ReOCl_4$: C, 49.71; H, 3.57; Cl, 16.4; Found C, 49.26; H, 3.56; Cl, 16.5;

The reaction of oxotrichlorobis(triphenylphosphine)-rhenium(V) with hydrogen chloride gas in hexane gave the same green powder. Although the oxotrichlorobis(triphenylphosphine)rhenium(V) was apparently insoluble in hexane, the compound formed after the mixture was allowed to stand for one month.

Anal. Calcd. for $C_{36}H_{31}P_2ReOCl_4$: C, 49.71; H, 3.57; Cl, 16.4; Found C, 49.44; H, 3.85; Cl, 16.7;

The same green powder was obtained through reactions similar to the benzene reaction in the solvents toluene and xylene. The infrared spectrum of this compound agreed with that reported in the reference (14).

Sealed Tube Reactions

The following reactions were performed in pyrex glass tubes approximately 15 mm x 18 cm. The tubes were constructed as shown in Figure 1. The tubes were sealed by placing the tube in an ice bath to the level of the solution in the tube. After the tubes were sealed at A they were placed in an explosion proof metal case and

Figure 1

put in an oven at 120°C. The tubes were opened by placing a scratch on the constricted area, B, of the tube and by applying pressure. The tube had to be cooled before opening to prevent the possibility of the solution boiling out of the tube due to a sudden release of pressure.

Tetrachlorobis(triphenylphosphine)rhenium(IV) and Tetrachlorobis(triphenylphosphineoxide)rhenium(IV).

To a reaction tube were added 0.43 g (0.51 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V) and 16 ml of chloroform. The tube was sealed and placed in an oven for 7 hours. The solution's color changed from green to brown during the reaction. The tube was removed from the oven, cooled, opened, and the contents were placed in a flask and stoppered. After 12 hours the solution had deposited 0.21 g (49 per cent) of a pale green crystalline solid. The solid was dissolved in chloroform and concentrated until crystallization began. The solution yielded 0.16 g (37 per cent) of a pale green crystalline solid. Consult the Appendix for the infrared spectrum.

Anal. Calcd. for $C_{36}H_{30}P_2ReO_2Cl_4$: C, 48.88; H, 3.40; Cl, 16.1; Found C, 48.63; H, 3.45; Cl, 16.7;

The mother liquor from the sealed tube was passed down an acid washed alumina column. A red band separated immediately and was eluted from the column. Identification of the red compound was made by comparison of its infrared spectrum with that of an authentic sample of tetrachlorobis(triphenylphosphine)rhenium(IV).

Anal. Calcd. for $C_{36}H_{30}P_2ReCl_4$: C, 50.76; H, 3.53;
Found C, 49.91; H, 3.19;

When tetrachlorobis(triphenylphosphine)rhenium(IV) and oxotrichloro(triphenylphosphine)triphenylphosphineoxiderhenium(V) were used under similar reaction conditions, only tetrachlorobis(triphenylphosphineoxide) rhenium(IV) was isolatable. The yields were 25 and 52 per cent respectively.

Table VI gives the amounts of the products isolated from the sealed tube reaction of oxotrichlorobis(triphenylphosphine)rhenium(V) in the chloroform sealed tube.

Table VI. Per cent of Products Isolated from the Sealed Tube Reactions of Oxotrichlorobis(triphenylphosphine)rhenium(V) with Chloroform.

Time (hours)	1	3	5	7	9	11
$ReCl_4\left[(C_6H_5)_3P\right]_2$ (per cent)	22	13	4	4	2	0
$ReCl_4\left[(C_6H_5)_3PO\right]_2$ (per cent)	10	28	42	78	92	96

The reaction of oxotrichlorobis(triphenylphosphine)-rhenium(V) was also performed under a helium atmosphere with ethanol-free chloroform for 11 hours. In this case the per cent yield of tetrachlorobis(triphenylphosphineoxide)rhenium(IV) decreased to 74 per cent and the amount of tetrachlorobis(triphenylphosphine)rhenium(IV) increased to 8 per cent.

Bis(methyltriphenylphosphonium) Hexachlororhenate(IV).

A tube containing 0.52 g (0.63 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V), 1 g (3.8 mmole) triphenylphosphine, and 17 ml of chloroform was placed in an oven at 120°C. After 18 hours 0.37 g (71 per cent) of large pale green crystals were recovered from the tube. The green crystals were recrystallized from dichloromethane-diethyl ether to give 0.34 g (65 per cent) of a pale green crystalline solid.

Anal. Calcd. for $C_{38}H_{36}P_2ReCl_6$: C, 47.85; H, 3.77; Cl, 22.4; Found C, 48.17; H, 3.96; Cl, 22.4;

The remaining orange solution was concentrated on a hot plate and deposited 0.05 g (9 per cent) of tetrachlorobis(triphenylphosphine)rhenium(IV) identified by comparison of its infrared spectrum with that of an authentic sample.

Similar reaction conditions using tetrachlorobis-(triphenylphosphine)rhenium(IV) and oxotrichloro(triphenylphosphine)triphenylphosphineoxiderhenium(V) gave the same green crystals.

The identity of the product, bis(methyltriphenylphosphonium) hexachlororhenate(IV), was verified by adding 0.5 g (1.3 mmole) of methyltriphenylphosphonium iodide in 30 ml of ethanol and 0.1 g (0.12 mmole) of bis-(tetraphenylarsonium) hexachlororhenate(IV) dissolved

in 30 ml of dichloromethane to a 250 ml round bottom flask. The solution was concentrated to 20 ml on a rotary evaporator. The pale green crystals that resulted were recrystallized from dichloromethane to give 0.09 g (73 per cent) of pale green crystals.
Anal. Calcd. for $C_{38}H_{36}P_2ReCl_6$: C, 47.85; H, 3.77;
Cl, 22.4; Found C, 47.45; H, 3.57; Cl, 22.4;

When 0.42 g (0.50 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V), 17 ml of pure dry chloroform, 1 g (3.8 mmole) triphenylphosphine, and 3 ml of butanol were reacted in a tube, 0.35 g (70 per cent) of the same pale green crystals resulted. The crystals were recrystallized from dichloromethane-diethylether.
Anal. Calcd. for $C_{38}H_{36}P_2ReCl_6$: C, 47.85; H, 3.77;
Cl, 22.4; Found C, 48.46; H, 3.79; Cl, 22.4;
Similar results were obtained when ethanol and propanol were added to the pure chloroform. The infrared spectrum contained bands at 1320 cm^{-1}, 1110 cm^{-1}, and 784 cm^{-1} indicative of the methyltriphenylphosphonium ion. Consult the Appendix for the complete infrared and NMR spectra.

Dichloromethyltriphenylphosphonium Pentachlorotriphenylphosphineoxiderhenium(IV) and Dichloromethyltriphenylphosphonium Chloride.

The reaction tube contained 1.0 g (3.8 mmole) of triphenylphosphine, 0.53 g (0.64 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V), and 17 ml of ethanol-free chloroform. The tube was sealed and placed in an oven at 120°C for 15 hours. The solution deposited 0.37 g (70 per cent) of pale green crystals which were isolated by filtration. The crystals were recrystallized from dichloromethane-hexane to give 0.30 g (57 per cent) of pale green crystals. Consult the Appendix for the infrared spectrum.

Anal. Calcd. for $C_{37}H_{31}P_2ReOCl_7$: C, 45.00; H, 3.14; Cl, 25.2; Found C, 44.80; H, 2.95; Cl, 24.4;

The mother liquor from the sealed tube was concentrated to 10 ml. After the addition of 50 ml of hexane to the solution, a white crystalline solid developed. The white product was isolated by filtration and recrystallized from ethanol. Consult the Appendix for the infrared spectrum.

Anal. Calcd. for $C_{19}H_{16}PCl_3$: C, 60.00; H, 4.24; Cl, 27.6;
Found C, 60.43; H, 4.52; Cl, 27.9;

Tetraphenylarsonium Pentachlorotriphenylphosphineoxiderhenate(IV).

To a 250 ml round bottom flask was added 0.43 g (0.45 mmole) of dichloromethyltriphenylphosphonium pentachlorotriphenylphosphineoxiderhenate(IV) dissolved in 60 ml of dichloromethane. A solution containing 0.71 g (1.70 mmole) of tetraphenylarsonium chloride dissolved in 50 ml of ethanol was added to this solution. The resulting solution was concentrated to 25 ml on a rotary evaporator and 10 ml of hexane was added. The 0.40 g (87 per cent) of pale green crystals was isolated by filtration. The compound was recrystallized from dichloromethane to give 0.35 g (77 per cent) of pale green crystals.

Anal. Calcd. for $C_{42}H_{35}AsPReOCl_5$: C, 49.20; H, 3.48; Cl, 17.3; Found C, 48.82; H, 3.42; Cl, 16.8;

The infrared spectrum contained bands for triphenylphosphine oxide at 1144 cm^{-1} and 1116 cm^{-1}. Consult the Appendix for the complete infrared spectrum.

Dichlorotris(triphenylphosphineoxide)acetonerhenium(III).

A reaction tube containing 0.63 g (0.76 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V) and 17 ml of dry acetone was heated for 15 hours. When the tube was removed from the oven, it contained a mixture of a black residue and a brown solution. The filtrate was passed down an acid washed alumina column. The purified green solution was concentrated on a hot plate to about 7 ml. Large dark blue crystals, 0.25 g (40 per cent) resulted after standing two weeks.

Anal. Calcd. for $C_{57}H_{51}P_3ReO_4Cl_2$: C, 59.60; H, 4.46;
Found C, 60.04; H, 4.69;

The infrared spectrum contained a band at 1690 cm^{-1} for co-ordinated acetone. Consult the Appendix for the complete spectrum.

Trichlorotriphenylphosphineoxiderhenium(III).

A tube containing 1.12 g (1.3 mmole) of oxotrichlorobis(triphenylphosphine)rhenium(V) and 18 ml of 2-butanone was heated for 24 hours. The resulting bluish-green solution was concentrated to 8 ml on a hot plate. A blue solid precipitated with the addition of excess hexane. The solid was dissolved in chloroform and the solution was passed down an acid washed alumina column. A blue band separated on the column and was collected. The blue solution was again concentrated on a hot plate. The solid was precipitated with hexane, dissolved in chloroform, and the solution was passed down an alumina column. The blue band was collected and the solution was recrystallized four times from chloroform-diethyl ether to give 0.43 g (53 per cent) of dark blue crystals.

Anal. Calcd. for $C_{18}H_{15}PReCl_3$: C, 37.96; H, 2.56; Cl, 18.4; Found C, 37.97; H, 2.68; Cl, 18.0;

The compound was also prepared by heating 0.61 g (0.73 mmole) of tetrachlorobis(triphenylphosphine)-rhenium(IV) and 17 ml of 2-butanone in a standard reaction tube for 20 hours. The contents of the tube were then concentrated to 7 ml and a blue solid was precipitated with hexane. The blue solid was dissolved in chloroform and the solution was passed down an acid washed alumina column. The resulting blue solution was passed down an alumina column a second time and the blue band again collected. The solution was concentrated to 8 ml and 5 ml of diethyl ether was added. The blue crystals that resulted were recrystallized five times from chloroform-diethyl ether to give 0.25 g (55 per cent) of dark blue crystals.

Anal. Calcd. for $C_{18}H_{15}PReOCl_3$: C, 37.96; H, 2.56; Cl, 18.4; Found C, 38.75; H, 2.32; Cl, 17.9;

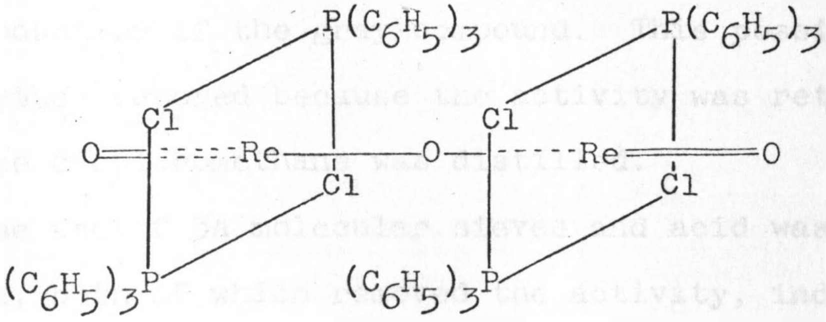
The infrared spectrum of the compound contained no bands in the carbonyl region, but did contain bands for co-ordinated triphenylphosphine oxide at 1152 cm^{-1}, 1119 cm^{-1} and 1070 cm^{-1}. Consult the Appendix for the complete infrared spectrum.

RESULTS AND DISCUSSION

As stated in the Introduction, the purpose of this work was to study the sealed tube reactions of several rhenium compounds in different solvents. The initial recrystallization of one starting material, oxotrichlorobis(triphenylphosphine)rhenium(V), resulted, not in recrystallization, but in the formation of a new complex.

On the basis of certain features of the infrared spectrum and the elemental analyses, three possible structures were considered for the compound. The first of these, oxodichloroethoxybis(triphenylphosphine)rhenium(V), was eliminated because the new compound had an additional band at 1100 cm^{-1} and reversed peak intensities at 945 cm^{-1} and 907 cm^{-1} (7). The second, oxodichlorohydroxobis(triphenylphosphine)rhenium(V), was ruled out because the band at 907 cm^{-1}, which could be attributed to the rhenium-hydroxyl bending mode, was not accompanied by a band for the oxygen-hydrogen stretching mode in the 3500-3700 cm^{-1} region (26). The preparation of the hydroxyl species was reported in the literature (8), but attempts to repeat this work were unsuccessful.

The gray compound, μ-oxo-dioxotetrachlorotetrakis(triphenylphosphine)dirhenium(V), is now tentatively assigned the structure X on the basis of the strong bands at 945 cm^{-1} and 907 cm^{-1} assigned to the rhenium-oxygen double bond stretch, and an additional band at 720 cm^{-1} due to the rhenium-oxygen-rhenium bridge (9). The compound is probably formed through an intermediate hydroxyl species.



X

Since the gray compound was one of the few rhenium-oxygen bridged species known, it was desirable to find the component present in the solvent responsible for its formation. All attempts; mass spectroscopy, gas chromatography, infrared spectroscopy, and Karl Fischer reagent; to identify the unknown substance present in the dichloromethane indicated that the only impurity was water. The concentration of water present was determined to be 0.003 per cent. Oxotrichlorobis(triphenylphosphine)rhenium(V) was recovered unchanged from dichloromethane to which 0.003 per cent of water had been added. Higher concentrations of water resulted in the decomposition of the oxotrichlorobis(triphenylphosphine)rhenium(V). To determine if the dichloromethane also contained some metal ion which might act as an acid or catalyst, several metal ions were added to the experimentally produced dichloromethane without the production of the gray compound. This possibility was further removed because the activity was retained when the dichloromethane was distilled.

The use of 3A molecular sieves and acid washed alumina, both of which removed the activity, indicated that the substance was a small polar molecule such as ammonia, water, formaldehyde, or hydrogen chloride. Addition of ammonia gas to dichloromethane which contained oxotrichlorobis(triphenylphosphine)rhenium(V) produced a red gel. Addition of formaldehyde produced a compound identified as oxotrichloro(triphenylphosphine) triphenylphosphineoxiderhenium(V), while addition of hydrogen chloride gas produced bis(triphenylphosphonium) hexachlororhenate(IV) bisdichloromethane.

All of the experiments led to the following conclusion. Although the water must be present for the formation of μ-oxo-dioxotetrachlorotetrakis(triphenylphosphine)dirhenium(V),there must be some other substance, for which there is no chemical evidence, that in some way catalyzes the reaction.

Attempted recrystallization of the gray compound from chloroform and acetone produced cis-oxotrichlorobis(triphenylphosphine)rhenium(V) and oxotrichloro-(triphenylphosphine)triphenylphosphineoxiderhenium(V) respectively. The reaction with chloroform containing ethanol produced oxodichloroethoxybis(triphenylphosphine)-rhenium(V). The implications of this phase of the research indicates further work is desirable; however, investigation stopped when the supply of impure dichloromethane was exhausted.

Phosphonium Salts

The reaction of hydrogen chloride with oxotrichlorobis(triphenylphosphine)rhenium(V) in dichloromethane, in an attempt to reproduce μ-oxo-dioxotetrachlorotetrakis-(triphenylphosphine)dirhenium(V), led to the study of the same reaction in other solvents. The reactions are particularly interesting since the only change in the reaction conditions was the solvent; however, it should be emphasized that the concentration of hydrogen chloride differs with solvent.

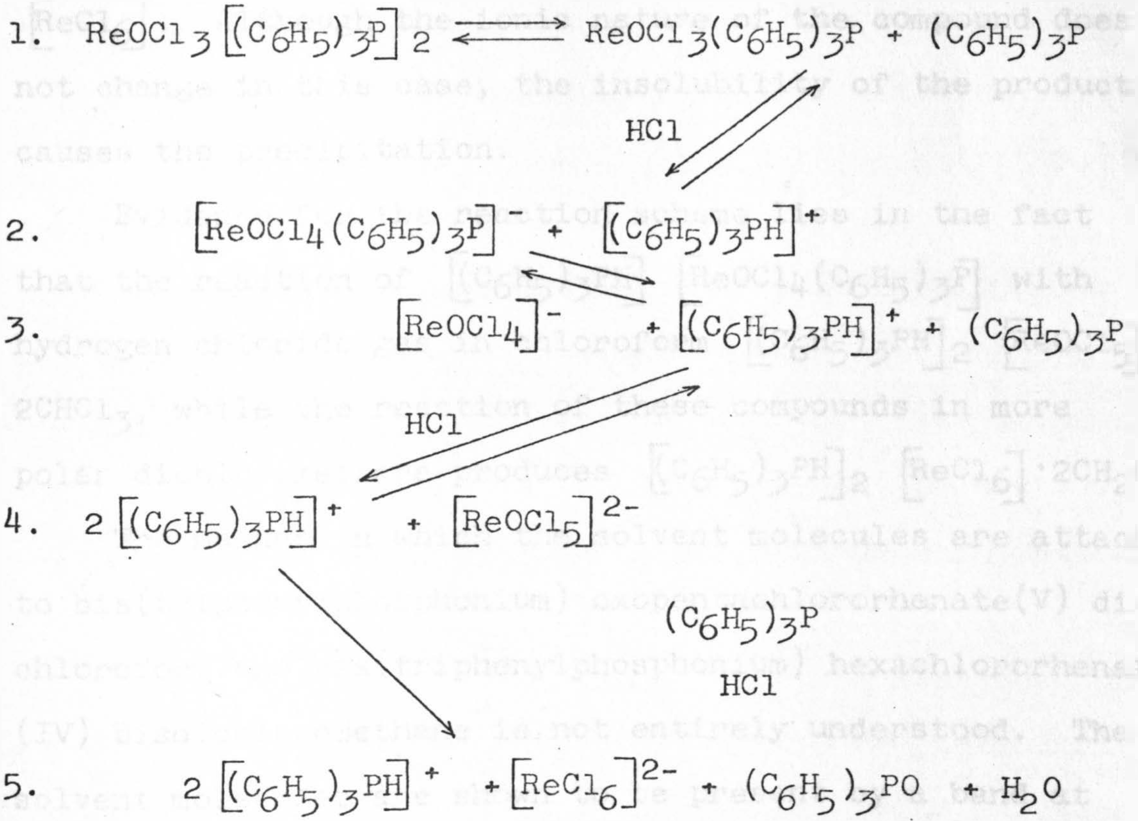
As shown in Table VII, a definite trend was established between polarity of the solvent and the product formed. In general, solvents with dipole moments of

Table VII. Summary of the Solvent Effects on the Products Produced in a Hydrogen Chloride Solution.

Solvent	Product	Dipole Moment (Debye units) (27)
Benzene (8)	$[(C_6H_5)_3PH]$ $[ReOCl_4(C_6H_5)_3P]$	0
Xylene	$[(C_6H_5)_3PH]$ $[ReOCl_4(C_6H_5)_3P]$	0
Hexane	$[(C_6H_5)_3PH]$ $[ReOCl_4(C_6H_5)_3P]$	0
Toluene	$[(C_6H_5)_3PH]$ $[ReOCl_4(C_6H_5)_3P]$	0.36
Chloroform	$[(C_6H_5)_3PH]_2$ $[ReOCl_5]\cdot 2CHCl_3$	1.02
Tetrahydrofuran (19)	$[(C_6H_5)_3PH]_2$ $[ReOCl_5]\cdot C_4H_8O$	1.6
Dichloromethane	$[(C_6H_5)_3PH]_2$ $[ReCl_6]\cdot 2CH_2Cl_2$	1.6
Ethanol	$[(C_6H_5)_3PH]_2$ $[ReCl_6]$	1.69
2-butanone	$[(C_6H_5)_3PH]_2$ $[ReCl_6]$	2.45

nearly zero Debye produced triphenylphosphonium oxotetrachlorotriphenylphosphinerhenate(V), while solvents with dipole moments in the range of 1-1.6 Debye produced bis-(triphenylphosphonium) oxopentachlororhenate(V), and more polar solvents (greater than 1.6 Debye) produced bis-(triphenylphosphonium) hexachlororhenate(IV). The upper limit on the last reaction is at least 2.89 Debye since it has recently been shown that the reaction in acetone produces the hexachlororhenate(IV) ion. The hydrogen chloride gas causes the acetone to condense and the reaction of this with the triphenylphosphonium ion produces bis(1,1-dimethyl-3-oxybutyltriphenylphosphonium) hexachlororhenate(IV) (28).

It is generally accepted (18) that in the replacement reactions of oxotrichlorobis(triphenylphosphine) rhenium(V) the complex must dissociate. The reaction of hydrogen chloride gas with the dissociated components will produce the various phosphonium salts. A plausible reaction scheme for the formation of the phosphonium salts would involve the following steps.



1. $ReOCl_3[(C_6H_5)_3P]_2 \rightleftharpoons ReOCl_3(C_6H_5)_3P + (C_6H_5)_3P$

HCl

2. $[ReOCl_4(C_6H_5)_3P]^- + [(C_6H_5)_3PH]^+$

3. $[ReOCl_4]^- + [(C_6H_5)_3PH]^+ + (C_6H_5)_3P$

HCl

4. $2[(C_6H_5)_3PH]^+ + [ReOCl_5]^{2-}$

$(C_6H_5)_3P$

HCl

5. $2[(C_6H_5)_3PH]^+ + [ReCl_6]^{2-} + (C_6H_5)_3PO + H_2O$

The different products, shown in Table VII, are formed in steps 2, 4, or 5 in the above reaction scheme. The ionic character of $[(C_6H_5)PH]$ $[ReOCl_4(C_6H_5)_3P]$ causes it to precipitate immediately from nonpolar solvents and no further reaction occurs. The product, $[(C_6H_5)_3PH]$-$[ReOCl_4(C_6H_5)_3P]$, is soluble in more polar solvents (1-1.6 Debye) so further reaction with hydrogen chloride gas gives $[(C_6H_5)_3PH]_2$ $[ReOCl_5]$. At this stage, the compound is too ionic for the solvent and precipitation occurs. The same process occurs in the more polar solvents (greater than 1.6 Debye) to produce $[(C_6H_5)_3PH]_2$-$[ReCl_6]$. Although the ionic nature of the compound does not change in this case, the insolubility of the product causes the precipitation.

Evidence for the reaction scheme lies in the fact that the reaction of $[(C_6H_5)_3PH]$ $[ReOCl_4(C_6H_5)_3P]$ with hydrogen chloride gas in chloroform $[(C_6H_5)_3PH]_2$ $[ReOCl_5]\cdot$-$2CHCl_3$, while the reaction of these compounds in more polar dichloromethane produces $[(C_6H_5)_3PH]_2$ $[ReCl_6]\cdot 2CH_2Cl_2$.

The manner in which the solvent molecules are attached to bis(triphenylphosphonium) oxopentachlororhenate(V) dichloroform and bis(triphenylphosphonium) hexachlororhenate(IV) bisdichloromethane is not entirely understood. The solvent molecules are shown to be present by a band at 790 cm^{-1} in the infrared spectra of these compounds corresponding to the carbon-chlorine stretch (29). Repeated attempts to prepare these compounds with different stoichiometries have failed. In complexes of the type $[R_3PH]_2\ [ReCl_6]$ it has been shown that the molar conductivity is somewhat less than expected. This decrease is probably due to the bonding of the phosphorus-hydrogen to the rhenium-chlorine (16). If the hydrogen of the phosphorus can bond to the chlorine of the rhenium, it is also possible that the hydrogen can bond to the chlorine of the solvent. This postulation is born out in the fact that the number of attached solvent molecules corresponds to the number of triphenylphosphonium ions. This type of bonding is shown to take place in iron nitriles, where the chloroform hydrogen bonds to the nitrile nitrogen (30).

Reactions with Aldehydes

As formaldehyde was considered a possible impurity in the dichloromethane, its reaction with oxotrichlorobis-(triphenylphosphine)rhenium(V) was studied. The compound, oxotrichloro(triphenylphosphine)triphenylphosphineoxide-oxiderhenium(V) was also made by the procedure of Rauchias and Wilkinson (18).

Three regions of the infrared spectrum have been used to distinguish between triphenylphosphine and triphenylphosphine oxide complexes. In the 1050-1150 cm^{-1} region triphenylphosphine has a strong band at 1090 cm^{-1}

assigned to the X-sensitive mode, while triphenylphosphine oxide has bands at 110 cm^{-1} assigned to the X-sensitive mode (31) and 1140 cm^{-1} assigned to the phosphorus-oxygen stretch (32). Triphenylphosphine oxide complexes also give a strong band at 720 cm^{-1}. In the 470-570 cm^{-1} region triphenylphosphine complexes have bands at 524 cm^{-1}, 508 cm^{-1}, and 496 cm^{-1}, while triphenylphosphine oxide complexes give bands at 553 cm^{-1}, 539 cm^{-1}, and 532 cm^{-1} (3). The infrared spectrum of the formaldehyde reaction product in these three regions indicates the presence of a mixed triphenylphosphine-triphenylphosphine oxide complex.

The reaction with formaldehyde is a fast efficient method of preparation of the complex. Triphenylphosphine, from the dissociated oxotrichlorobis(triphenylphosphine)rhenium(V) apparently reacts with the formaldehyde to give triphenylphosphine oxide which can coordinate to give the compound. No explanation can be given for the formation of the mixed triphenylphosphine-triphenylphosphine oxide instead of a pure triphenylphosphine oxide complex.

The reaction of ethanal in a dichloromethane or benzene solution of oxotrichlorobis(triphenylphosphine) rhenium(V) produced a purple crystalline solid, oxochlorotriphenylphosphine(ethanal)rhenium(III). A shift of

120 cm^{-1} in the infrared spectrum indicates that the ethanal is strongly bonded to the rhenium through the carbonyl. Attempts to reproduce this work have failed. Since the compound was produced from two different solvents, the possibility of impure solvents is reduced. The other possibility is the ethanal; however, the same bottle was utilized for both unsuccessful and successful experiments. When a different bottle of ethanal was tried, the reaction again ended in failure. Different concentrations of the ethanal did not give the product. The reactions with higher aldehydes in dichloromethane and benzene failed to give a product.

Sealed Tube Reactions with Chloroform

Since only a cursory investigation of the reaction of oxotrichlorobis(triphenylphosphine)rhenium(V) with chloroform had been performed (3), it was decided that a more extensive study should be conducted. The products obtained agreed with those reported, but the amounts of products were found to be time dependent as shown in Table VI. The formation of tetrachlorobis(triphenylphosphine)rhenium(IV) at short reaction times can be explained by disproportionation of the rhenium(V) species as described on page 11. However, the production of tetrachlorobis(triphenylphosphineoxide)rhenium(IV) at the expense of tetrachlorobis(triphenylphosphine)rhenium(IV) with increased time requires the additional variable, temperature.

The effect of temperature on the reaction is illustrated in the following experiments. In a five hour timed study, the sealed tube reaction of oxotrichlorobis(triphenylphosphine)rhenium(V) at 110°C produced mainly tetrachlorobis(triphenylphosphine)rhenium(IV), while the reaction at 130°C produced the triphenylphosphine oxide complex exclusively. No reaction occurs between tetrachlorobis(triphenylphosphine)rhenium(IV) and triphenylphosphine oxide in boiling chloroform, while the reaction in a sealed tube at elevated temperature gives tetrachlorobis(triphenylphosphineoxide)rhenium(IV). Thus the increased temperature of the sealed tube will cause the liberated triphenylphosphine oxide, page 11, to replace the triphenylphosphine in the tetrachlorobis(triphenylphosphine)rhenium(IV) to give tetrachlorobis(triphenylphosphineoxide)rhenium(IV). The amount of triphenylphosphine oxide formed requires more oxygen than can be obtained from the oxotrichlorobis(triphenylphosphine)-rhenium(V). Probable sources of additional oxygen are the air in the tube, the ethanol in the chloroform, and the air dissolved in the chloroform. To study the effect of excess oxygen, ethanol-free chloroform was used and the tube was sealed in a helium atmosphere. When the tube was heated at 120°C for 11 hours, 8 per cent of tetrachlorobis(triphenylphosphine)rhenium(IV) and 78 per cent of tetrachlorobis(triphenylphosphineoxide)-rhenium(IV) were recovered, as compared to 0 and 96 per cent in commercial chloroform. This indicates that some of the oxygen comes either from the air or the ethanol in the sealed tube.

The formation of tetrachlorobis(triphenylphosphineoxide)rhenium(IV) results from the replacement of the triphenylphosphine by the triphenylphosphine oxide. In an attempt to suppress this reaction, excess triphenylphosphine was added to the reaction tube. Instead of obtaining a greater yield of tetrachlorobis(triphenylphosphine)rhenium(IV), pale green bis(methyltriphenylphosphonium) hexachlororhenate(IV) was formed.

Since this product was unexpected and highly suspect because of the existence of a methyl group, it was desirable to have a second method of synthesis to check the formulation of the cation. The alternate method was a simple double displacement reaction of bis(tetraphenylarsonium) hexachlororhenate(IV) and methyltriphenylphosphonium iodide. The bis(ethyltriphenylphosphonium) hexachlororhenate(IV) salt was also produced from its ions. The infrared spectra of bis(methyltriphenylphosphonium) hexachlororhenate(IV), prepared by the two different methods, were identical. The possibility of the ethyl derivative was eliminated due to the absence of a doublet at 901 cm^{-1} and 889 cm^{-1} in the infrared spectrum. As further proof the nuclear magnetic resonance spectra of methyltriphenylphosphonium iodide and bis(methyltriphenylphosphonium) hexachlororhenate(IV) were, except for concentration shifts, superimposable.

In order to determine the origin of the methyl group in the methyltriphenylphosphonium ion, the reaction of oxotrichlorobis(triphenylphosphine)rhenium(V) was performed in ethanol-free chloroform. An entirely new product, dichloromethyltriphenylphosphonium pentachlorotriphenylphosphineoxiderhenate(IV) was formed. The formation of this product in the absence of ethanol indicated that the methyl group came from the ethanol. The mechanism for the reaction; however, is unknown.

A literature search revealed that the pentachlorotriphenylphosphineoxiderhenate(IV) ion had not been reported, although the analogous triphenylphosphine ion had been produced (33). To prove the existence of this anion moiety, tetraphenylarsonium pentachlorotriphenylphosphineoxiderhenate(IV) was prepared by the reaction of dichloromethyltriphenylphosphonium pentachlorotriphenylphosphineoxiderhenate(IV)and tetraphenylarsonium chloride. Retention of the bands indicative of coordinated triphenylphosphine oxide by the tetraphenylarsonium salt proves the formulation of the anion to be correct.

The dichloromethyltriphenylphosphonium ion was isolated from the mother liquor of the reaction as the chloride salt. A literature survey indicated that this compound has not been synthesized. The analogous compound, dibromomethyltriphenylphosphonium bromide, was made by reacting triphenylphosphine and bromoform at 150°C (34). The reaction in chloroform should occur at a higher temperature than that for bromoform. Since the reaction occured at 120°C, the rhenium is clearly acting as a catalyst (35). To further emphasize the point, no reaction occurs between triphenylphosphine and chloroform in a sealed tube at 120°C.

Since the source of the methyl group was the ethanol, it was thought that the replacement of the ethanol by other alcohols would result in the formation of additional alkylphosphonium cations. Propanol, butanol, and 2-methylbutanol were added to the ethanol-free chloroform, but the reaction gave only the bis(methyltriphenylphosphonium) hexachlororhenate(IV).

Sealed Tube Reactions with Ketones

The sealed tube reactions with ketones produced triphenylphosphine oxide complexes exclusively. The reaction of acetone and oxotrichlorobis(triphenylphosphine)rhenium(V) produced dichlorotris(triphenylphosphineoxide)acetonerhenium(II). A shift of 30 cm^{-1} to 1690 cm^{-1} for the carbonyl stretching frequency in the infrared spectrum indicated that the acetone was coordinated through the carbonyl. This complex is the first example of a rhenium(II) compound containing monodentate ligands (36). The low yield of this compound is a result of at least two factors. The more important is that the only source of triphenylphosphine oxide is the oxotrichlorobis(triphenylphosphine)rhenium(V). Secondly, the brown component of the solution is lost on the alumina column.

The reaction of 2-butanone with oxotrichlorobis(triphenylphosphine)rhenium(V) or tetrachlorobis(triphenylphosphine)rhenium(IV) produced trichlorotriphenylphosphineoxiderhenium(III). On the basis of the chemistry of rhenium(III) complexes, mononuclear, dinuclear, and trinuclear species are possible (5). The visible spectra of known rhenium(III) complexes have been shown to be diagnostic for dinuclear and trinuclear species.

Dinuclear species have bands in the visible spectrum at 14,000 cm^{-1}, 32,000 cm^{-1}, and 40,000 cm^{-1}, while trinuclear complexes contain bands in the 12,300-13,300 cm^{-1} and 17,500-19,400 cm^{-1} regions (5). The trichlorotriphenylphosphineoxiderhenium(III) absorbs at 16,400 cm^{-1}, 17,700 cm^{-1}, and 23,800 cm^{-1}. Thus, the dinuclear and trinuclear species can be ruled out because of the lack of agreement between the reported and observed bands. The molecular weight, determined to be 469, gives further evidence that the compound is actually a mononuclear species.

A reaction outline for the formation of trichlorotriphenylphosphineoxiderhenium(III) would appear to be as follows. The oxotrichlorbis(triphenylphosphine)-rhenium(V) dissociates in solution to give oxotrichlororhenium(V) and triphenylphosphine. The liberated triphenylphosphine can either combine directly with the oxygen which is bonded to the rhenium or it may abstract the oxygen to form triphenylphosphine oxide. The resulting triphenylphosphine oxide can then co-ordinate with the rhenium species to give the product.

SUMMARY

The work presented in this thesis clearly illustrates three points. The first is the effect of the solvent on the reactions, the second is the effect of temperature on reactions, and the third is the catalytic ability of rhenium complexes.

The effect of the solvent was illustrated in the formation of the different phosphonium salts with the hydrogen chloride gas in different solvent. In this case it was found that the polarity of the solvent caused the difference in the products formed. This point was further illustrated in the sealed tube reactions. In many cases the only change in the reaction conditions was the solvent.

Of the solvents and complexes used in the sealed tubes, only oxotrichlorobis(triphenylphosphine)rhenium(V) and chloroform react at the boiling point of the solvent. With the increase in temperature of the sealed tube, all of the rhenium complexes and solvents studied react. In many cases the product obtained is entirely unexpected.

The sealed tube reactions gave two examples in which the rhenium complex was acting as a catalyst. The rhenium catalyzed the reaction of the triphenylphosphine with the solvent and the preservative, ethanol, in the solvent.

Although triphenylphosphine oxide complexes are well known with other transition metals, relatively few are known with rhenium. The sealed tube reactions presented in this work give examples in which one, two, and three triphenylphosphine oxide ligands are complexed with the rhenium. One of the compounds formed is the first example of a rhenium(II) complex containing monodentate ligands.

APPENDIX

The infrared absorption spectra are given in the following Tables. All the spectra are from potassium bromide wafers unless otherwise indicated. The relative intensities are given as follows

vw - very weak
w - weak
m - medium
s - strong
vs - very strong
shld. - shoulder

The potassium bromide used in obtaining the spectra showed bands at 3435 cm^{-1} and 1630 cm^{-1} which are probably due to the presence of water.

Table VIII. Infrared Absorption Maxima for Oxotrichlorobis(triphenylphosphine)rhenium(V).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3040	vw	981	vs
1880	vw	969	m
1805	w	920	w
1581	w	770	vw
1568	s	746	shld.
1479	shld.	739	vs
1438	vs	700	shld.
1431	shld.	685	vs
1380	w(broad)	611	w
1181	w	537	vs
1157	w	509	s
1089	vs	500	s
1066	shld.	452	m
1022	w	429	w
995	m	418	shld.
		310	s

Table IX. Infrared Absorption Maxima for Tetrachlorobis(triphenylphosphine)rhenium(IV).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3058	w	1028	w
1960	vw	998	m
1810	vw	969	vw
1585	w	919	vw
1570	w	845	vw
1482	s	770	shld.
1433	vs	743	s
1387	vw	725	shld.
1335	shld.	700	shld.
1315	w	690	vs
1188	m	612	w
1158	w	539	vs
1132	vw	509	m
1118	vw	498	shld.
1089	s	451	m
1070	shld.	321	s

Table X. Infrared Absorption Maxima for Oxotrichloro(triphenylphosphine)triphenylphosphineoxiderhenium(V).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3057	m	1025	w
2950	shld.	997	m
2920	m	962	vs
2845	m	871	w
2790	vs	752	shld.
1900	vw	739	vs
1810	vw	717	s
1591	w	702	shld.
1570	shld.	688	vs
1481	s	611	w
1434	ws	569	vs
1401	vw	531	vs
1320	shld.	510	shld.
1317	w	492	s
1290	vw	480	shdl.
1185	w	450	vw
1158	shld.	438	w
1140	s	380	vw
1110	s	345	vw
1090	s	295	s
1070	shld.		

Table XI. Infrared Absorption Maxima of μ-oxo-dioxotetrachlorotetrakis(triphenylphosphine)dirhenium(V).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3050	vw	1117	shld.
2900	vs(broad)	1090	vs
1960	vw	1067	shld.
1890	vw	1025	m
1815	vw	995	m
1770	vw	969	w
1582	w	957	shld.
1567	w	943	vs
1480	vs	909	s
1460	vs	889	shld.
1430	vs	845	w
1373	vs	798	vw
1310	w	742	vs
1270	shld.	720	m
1184	m	703	shld.
1157	w	689	vs

Table XII. Infrared Absorption Maxima of oxochlorotriphenylphosphineethanalrhenium(III).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3050	w	1024	vw
1629	s	994	m
1580	vw	972	vs
1565	vw	917	s
1479	s	770	shld.
1431	vs	744	shld.
1400	vw	745	s
1362	w	705	s
1320	shld.	689	vs
1311	w	650	w
1278	vw	601	s
1210	w	571	s
1180	w	541	vs
1155	vw	510	s
1109	s	499	m
1091	vs	450	w
1060	w	380	w
		342	m

Table XIII. Infrared Absorption Maxima of Oxodichloroethoxybis(triphenylphosphine)rhenium(V) (in nujol).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3050	w	1185	s
2900	vs(broad)	1157	w
1960	vw	1107	vs
1897	vw	1092	vs
1817	w	1072	vs
1773	vw	1027	s
1671	vs(broad)	997	s
1584	m	970	w
1569	m	947	s
1480	vs	906	vs
1455	vs	850	m
1430	vs	791	vs
1372	vs	758	s
1342	m	740	vs
1315	w	720	vw
1270	shld.	702	s
		690	vs

Table XIV. Infrared Absorption Maxima for Bis(triphenylphosphonium) Hexachlororhenate(IV).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3060	shld.	1318	w
3050	w	1261	w
3020	shld.	1185	vs
2910	vw	1163	w
2427	m	1109	vs
2380	shld.	1022	vw
1980	vw(broad)	994	m
1905	vw	863	s
1821	vw	745	vs
1585	m	719	s
1570	shld.	688	vs
1481	s	610	vw
1438	vs	499	vs
1392	vw	429	w
1333	w	293	vs

Table XV. Infrared Absorption Maxima of Bis(triphenylphosphonium) Oxopentachlororhenate(V) Dichloroform.

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3050	vw	1162	w
2950	shld.	1110	vs
2920	m	1025	w
2850	m	996	w
2410	w	945	vs
1583	vw	870	m(broad)
1560	vw	755	shld.
		742	vs.
1481	m	719	m
1460	vw	688	vs
1439	vs	660	shld.
1375	vw	525	w
1343	vw	500	vs
1315	vw	429	w
1211	w	299	vs

Table XVI. Infrared Absorption Maxima for Tetrachlorobis(triphenylphosphineoxide)rhenium(IV).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3045	m	994	s
2912	m	970	shld.
1962	vw	920	vw
1890	w	885	w
1820	w	770	shld.
1770	vw	752	m
1585	s	745	s
1481	s	721	vs
1432	vs	685	vs
1380	w(broad)	610	w
1333	m	552	s
1310	m	535	vs
1180	shld.	452	m
1156	shld.	441	m
1115	vs	435	m
1070	vs	395	vw
1024	s	389	vw
		308	vs

Table XVII. Infrared Absorption Maxima of Bis(methyltriphenylphosphonium) Hexachlororhenate(IV).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3040	w	996	m
2980	w	901	vs
2909	w	887	vs
1583	w	784	m
1500	shld.	750	shld.
1480	m	739	vs
1445	vs	714	s
1390	w	684	vs
1335	m	520	shld.
1320	m	505	vs
1300	shld.	480	shld.
1185	w	440	w
1150	w(broad)	380	vw
1110	vs	295	vs

Table XVIII. Nuclear Magnetic Resonance Spectrum of Bis-(methyltriphenylphosphonium) Hexachlororhenate(IV).

(τ) Value	Relative Intensity
3.19	15
8.47	1.5
8.69	1.5

Table XIX. Infrared Absorption Maxima of Dichloromethyltriphenylphosphonium Pentachlorotriphenylphosphineoxiderhenate(IV).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3043	w	888	w
1584	w	820	vw
1480	s	810	vw
1437	vs	763	shld.
1356	w	744	s
1334	vw	722	vs
1310	vw	700	shld.
1234	vw	690	shld.
1180	shld.	684	vs
1150	s	664	shld.
1112	vs	610	vw
1090	s	549	shld.
1063	s	539	vs
1023	m	530	shld.
996	m	512	w
899	w	500	w
		477	vw

Table XX. Infrared Absorption Maxima of Tetraphenylarsonium Pentachlorotriphenylphosphineoxiderhenate(IV).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3049	w	901	w
1580	vw(broad)	889	w
1478	s	739	vs
1433	vs	720	s
1332	w	682	vs
1310	w(broad)	609	vw
1180	shld.	549	s
1145	shld.	533	s
1129	s	520	shld.
1116	s	475	s
1075	vs	465	s
1018	w	458	shld.
992	s	342	m
		299	vs

Table XXI. Infrared Absorption Maxima for Dichlorotris(triphenylphosphineoxide)acetonerhenium(II).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3040	vw	1115	vs
2910	vw	1084	m
1691	m	1065	shld.
1582	w	1022	w
1500	shld.	993	w
1480	w	746	m
1450	m	719	vs
1432	vs	689	vs
1310	vw	548	vs
1230	vw		
1180	shld.	538	shld.
1145	vs	460	vw
		350	shld.
		334	s

Table XXII. Infrared Absorption Maxima of Trichlorotriphenylphosphineoxiderhenium(III).

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3050	vw	1024	w
1890	vw	997	m
1810	vw	970	shld.
1581	vw	900	vw
1569	vw	840	vw
1480	s	798	vw
1460	w	750	s
1432	vs	720	vs
1375	w	690	vs
1330	shld.	550	vs
1312	w	539	vs
1298	w	515	w
1182	m	460	w
1152	shld.	420	w
1119	s	390	vw
1088	s	354	s
1070	shld.	330	vs
		310	shld.

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