Aspects of the Inorganic Chemistry of Rhenium

A Thesis submitted

by

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Abstract

By heating trans-oxotrihalogenobis(triphenylphosphine)-rhenium(V) with a variety of carboxylic acids or their anhydrides were isolated not only the known compounds $ReX_4(PPh_3)_2$ and $Re_2Cl_2(R.CO_2)_4$, but also the new series of carboxylato-complexes, $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$, $Re_2OX_5(R'CO_2)(PPh_3)_2$ and $Re_2Br_2(R.CO_2)_4$ (X = Cl or Br, R = alkyl, R' = alkyl or aryl). The relative proportions of these compounds depend, inter alia, on the duration of heating, the amount of oxygen present, and the strength of the acid used. Convenient preparative routes to the compounds $ReCl_4(PPh_3)_2$ and $Re_2Cl_2(R.CO_2)_4$ are described.

The monomeric rhenium(III) complexes, $ReX_3(RCN)(PPh_3)_2$ (R = alkyl; X = Cl, Br) have been prepared in high yield by heating trans-$ReOX_3(PPh_3)_2$ with triphenylphosphine and an alkanonitrile; other monomeric rhenium(III) complexes may be obtained from them by ligand substitution, while aerial oxidation gives $ReOCl_3(PPh_3O)$-PPh_3. The nitrile complexes are oxidised rapidly by halogenated compounds of the type $R'CY_3$ (R' = any group, Y = Cl or Br) to $ReX_3Y(PPh_3)_2$ or $ReX_2Y_2(PPh_3)_2$.

Rhenium pentachloride is reduced by nitriles to tetrachloro-bis(alkanonitrile)rhenium(IV). The oxidation product is an organic chlorocompound. New rhenium(IV) complexes were obtained by substitution or by addition of nucleophiles to the coordinated nitrile group. Addition of primary aromatic amines gives

complexes of amidines, and of alcohols complexes of imidate esters. Reduction of the complex $ReCl_4(MeCN)_2$ gives the tetrachlorobis-(acetonitrile)rhenate(III) ion. Malononitrile reacts with trans-$ReOCl_3(PPh_3)_2$ to give trichloro[4-(dicyanomethylene)azetid-2-imine] bis(triphenylphosphine)rhenium(III).

The properties and structure of the new compounds and the mechanism of the reactions are discussed.

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INTRODUCTION

Rhenium, first detected by X-ray spectroscopy by Noddack, Tacke and Berg in 1925 (1) was the last of the stable elements to be discovered. Extensive geochemical work by the discoverers established its abundance in the lithosphere as 0.001 p.p.m., the least among the metals (2). The element is siderophile and would be expected to concentrate in the earth's core, but even in iron meteorites (0.6 p.p.m.) it is less abundant than osmium, iridium and gold (3). Rhenium concentrates in pegmatites and pneumatolytic rocks, especially in molybdenites associated with copper, which can attain a maximum of 0.3% of rhenium, and which provide the only commercial source (4). A distinct mineral species, dzhezkazganite $CuReS_4$, has recently been identified in the copper deposits of Kazakhstan (5,6), and ReS_2 may occur in the Mansfeld copper shales (6) It appears that in sedimentary rocks rhenium is dispersed in molybdenum sulphides when the amount of molybdenum is high, but otherwise crystallises out as $CuReS_4$ (7). Despite its scarcity, rhenium accumulates as a by-product of the molybdenum industry as the volatile heptoxide, and is actually available at a cost less than that of most of the platinum metals.

The chemistry of rhenium resembles that of technetium

and, to a much lesser degree, that of molybdenum and osmium. Apart from some similarities in formal stoicheiometry and in the carbonyls, it bears little relation to that of its congener, manganese. All the oxidation states from -I to VII are known, but the -I, 0 and I states are virtually confined to organometallic compounds, and the divalent state is very rare (8). Rhenium(III), Re(IV) and Re(V) show a strong tendency to form coordination compounds, a large number of which are now known (8). Despite rapid advances in the last 5 years many gaps still remain in our knowledge of the chemistry, and most of the work to be described will be concerned with the behaviour of rhenium in these oxidation states. Both Re(V) and Re(VI) are unstable towards disproportionation to Re(IV) and Re(VII) but, whereas Re(V) can be stabilised by various ligands, Re(VI) apparently cannot, and very few compounds of Re(VI) have actually been prepared. The reactions of the hexachloride and of the oxyhalides $ReOX_4$ in non-aqueous solvents have been hardly investigated and certainly merit further attention. Rhenium(VII) shows little tendency to form complexes, and its chemistry is dominated by the very stable perrhenate ion to which most other species are readily hydrolysed. Rhenium forms no simple or aquated cations in any of the oxidation states.

The stereochemistry of Re(IV) and Re(V) is predominantly octahedral. Notable exceptions are the halides, the five-coordinate complexes $ReOX_4^-$ (9) and $ReNX_2(PPh_3)_2$ (10,11), and

the eight-coordinate ions $Re(CN)_8^{3-}$ (12) and $[Re(diars)_2Cl_4]^+$ (13). The structural chemistry of Re(III), by contrast, is quite varied, and has been studied intensively since 1963 (8). A number of distinct structural types are now recognised:

(a) Mononuclear complexes, mostly of the octahedral types $ReX_2(LL')_2^+$ and ReX_3L_3. The well-established members of the former type are $ReX_2(diphos)_2^+$ (X = Cl, Br) (14,18) and $ReX_2(diars)_2^+$ (X = Cl, Br, I) (15); and of the latter type $ReCl_3(PEt_2Ph)_3$ and $ReCl_3(PEt_2Ph)(diphos)$ (14), $ReX_3(thiourea)_3$ (X = Cl, Br) (16), and the β-diketone complexes $ReX_2(DD')(PPh_3)_2$ and $ReX(DD')_2(PPh_3)$ (DD' = β-diketone; X = Cl, Br, I) (17). In addition, the complexes $ReX_3(RCN)(PPh_3)_2$ (X = Cl, Br; R = alkyl or aryl), $ReCl_3py_2(PPh_3)$, $ReCl_3py_3$, and $ReCl_3(LL')(PPh_3)$ (LL' = dipy, benzil, phenquin) will be described in the present work (19). Cotton has repeatedly stressed the scarcity of complexes of the neutral type (16,18) but he apparently overlooked the β-diketone complexes and, when the new complexes are also included, it becomes evident that Re(III) often assumes an octahedral stereochemistry. The anion $ReCl_4(RCN)_2^-$ will be described later, and the complexes claimed to be $ReI_3[P(OR)_3]_3$ (R = aryl) (20), $Re(CN)_6^{3-}$ (12), and $Re(OH)_3(CN)_3^{3-}$ (21) should also belong to this class. Only a few mononuclear compounds in which rhenium is not six-coordinate have been reported. They include $Re(CO)X_2(diars)_2^+$ (X = Br, I) (22), $ReH_3(PPh_3)_4$ (23), $ReCl_3(PPh_3O)_2$ (24), and $ReCl_3(R.CO_2H)_2$ (25). Contrary

to early reports, Re(III) never assumes fourfold coordination.

(b) Dinuclear complexes with a direct metal-metal bond of which $Re_2Cl_8^{2-}$ is the formal prototype (16,18,26-29). Two $ReCl_4$ units are held together only by a (quadruple) Re—Re bond in an eclipsed configuration (26). Some of the chlorine atoms can be replaced by other ligands, for example by bridging carboxylate groups in $Re_2Cl_2(R.CO_2)_4$ (25,27), and the coordination number of each rhenium atom can increase from five to six. Related is the Re(II) - Re(III) complex Re_2Cl_5(dithiahexane)$_2$ whose crystal structure shows the absence of bridging groups (30), and the Re(II) - Re(III) carboxylates $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ to be described may be similar. Highly insoluble substances of stoicheiometry $ReCl_3L$ and $ReCl_3LL'$ of uncertain structure have been obtained from $Re_2X_8^{2-}$ (X = Cl, Br) and various neutral ligands (16,18).

(c) Trinuclear complexes based on the $Re_3X_9L_3$ prototype, where the ligands L may be anionic (halide, NO_3^-, SCN^-) or neutral (PR_3, PR_3O, R_2SO, RCN, py, etc.), and where some or all of the ligands L may be absent, to give $Re_3X_9L_2$, Re_3X_9L, and ultimately the trihalides Re_3X_9 (X = Cl, Br, I) (31,32). Extensive crystallographic studies have shown the structure to be based, in each case, on an equilateral triangle with a rhenium atom at each apex carrying one terminal halogen above and one below the plane of the triangle, and with a ligand L, when it is present, in the plane. Each pair of rhenium atoms

is bridged by a halogen, also in the plane. The ligands L are held loosely, and the six terminal halogens are labile, so that mixed complexes may be prepared (31-33). In addition, related compounds with bidentate terminal ligands are known (34). Unlike the mono- and dinuclear compounds which can be obtained in many ways, the trinuclear compounds have been obtained, directly or indirectly, from the trihalides (31).

No nitrile complexes of rhenium had been reported prior to the commencement of this work and only one investigation of carboxylate complexes had been published (25). Since nitrile complexes of other metals are often convenient preparative intermediates, a detailed study of the reactions of rhenium compounds with nitriles was undertaken. Two series of such complexes were obtained, trivalent $ReX_3(RCN)(PPh_3)_2$ (X = Cl, Br; R = alkyl or aryl) (19) and tetravalent $ReCl_4(RCN)_2$ (35), from which several new complexes of Re(III), Re(IV) and Re(V) could be prepared by ligand substitution or by redox reactions. Of particular interest was the observation of reactions of the coordinated nitrile group itself with nucleophiles BH to form complexes of imido derivatives R·C(:NH)B (35), a reaction expected, but apparently seldom reported, for nitrile complexes of other transition metals. The trinuclear compound $Re_3Cl_9(RCN)_3$ has recently been obtained by others (34). From the reactions of trans-$ReOCl_3(PPh_3)_2$ with carboxylic acids or anhydrides

three series of carboxylato complexes were isolated, namely orange $Re_2X_2(R.CO_2)_4$, green $Re_2OX_5(R.CO_2)(PPh_3)_2$, and purple $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ (X = Cl, Br) (36). The orange complexes have since been investigated thoroughly by other workers (16,27), but the apparently unusual structure of the purple complexes remains unsettled and awaits further study by X-ray techniques.

It has become apparent that not only free, but even coordinated triphenylphosphine (PPh_3) can reduce Re(V), probably through initial dissociation. This explains the diverse reactions of the well-studied preparative intermediate, trans-$ReOCl_3(PPh_3)_2$ (14,24), which are sensitive to the experimental conditions, and which often lead to mixtures of products. Trans-$ReOCl_3(PPh_3)_2$ not only can react by ligand substitution, but can also disproportionate to Re(IV) and Re(VII), and (following substitution) can be reduced by its own PPh_3 to Re(III). Formally, the redox reaction is a direct exchange of oxygen between $ReOCl_3$ and PPh_3, and does not seem to involve a Re(IV) intermediate. This is in spite of the exceptional stability of the complex $ReCl_4(PPh_3)_2$ which was obtained repeatedly, by us and by others (23,37), from systems containing PPh_3. In substitution reactions, the first PPh_3 group of bisphosphine complexes can be readily replaced (e.g. by pyridine), but the second PPh_3 group is held rather tenaceously. With these principles in mind the various reactions of the phosphine complexes are

readily understood, and will be discussed more fully later.

Several books on rhenium have appeared recently, dealing chiefly with the extraction (38) and metallurgy (39,40) of the element, and with the chemistry of its compounds (41-43). The last three works supersede earlier monographs on the chemistry. Reference 43 is the most up to date, covering the literature up to June 1965, and a detailed review of recent work extends the coverage to the autumn of 1966 (8).

CHAPTER I.

THE REACTION OF trans-$ReOCl_3(PPh_3)_2$ WITH CARBOXYLIC ACIDS AND ANHYDRIDES

The readily available trans-oxotrichlorobis(triphenylphosphine)rhenium(V), trans-$ReOCl_3(PPh_3)_2$ (14,24), or the related alkoxo compounds, $ReOCl_2(OR)(PPh_3)_2$ (14,24), have proved convenient starting materials for the preparation of a variety of rhenium compounds by interaction with phosphines and arsines (37), amines (10,24), pyridine (44), β-diketones (17), dimethyl sulphoxide (45), hydrogen chloride (24,45), sodium borohydride (46), and lithium aluminium hydride (47). Not only Re(V) but lower-valent compounds can thus be produced. The only carboxylate complexes of rhenium then known were obtained in low yield from the expensive trichloride (25). We therefore investigated the reaction of trans-$ReOX_3(PPh_3)_2$ (X = Cl, Br) with carboxylic acids and their anhydrides with a view to preparing the known complexes by a more convenient route, and to obtaining further carboxylate complexes. Mixtures of products resulted, and were initially separated by paper chromotography and repeated fractional crystallisation from organic solvents. Once pure material became available and the solubilities in various solvents were determined, the separation methods described in the experimental section could be adopted. The unexpected

stoicheiometry found for some of the products necessitated the use of several different acids before the results could be considered reliable.

The reaction conditions.

By heating trans-$ReOCl_3(PPh_3)_2$ with carboxylic acids ($R.CO_2H$) at ca. 120° (e.g. in boiling toluene) in the absence of oxygen, we obtained red tetrachlorobis(triphenylphosphine)-rhenium(IV), $ReCl_4(PPh_3)_2$, and a series of purple complexes of the type $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$. In air, under similar conditions, dark green complexes of the type $Re_2OCl_5(R.CO_2)(PPh_3)_2$ were obtained in addition. The reactions were very slow, so that the concentration of $ReCl_4(PPh_3)_2$ rose slowly to a maximum after 3 to 6 hr. heating, then fell slowly to zero in a further 12 to 24 hr., whereas that of the carboxylate complexes rose steadily. On prolonged heating in air, the purple compounds were oxidised to brown products, and under nitrogen, reacted with more carboxylic acid to give orange complexes of the type $Re_2Cl_2(R.CO_2)_4$ described by Taha and Wilkinson (25). This introduced complications in the separation of the new complexes, and it is not generally advisable, from a preparative point of view, to heat for more than 12 hr. For any given acid, the ratio of the amounts of the green to the purple complex formed in air increased with the strength of the acid. Thus, pivalic acid (pK_a, 5.03) gave the purple complex only, aliphatic acids with two hydrogen

atoms in the α-position (pK_a, 4.82-4.85) gave both types of complexes in roughly equal amounts, and acetic (pK_a, 4.75) and phenylacetic (pK_a, 4.32) acids gave more of the green complex than of the purple. Only green $Re_2OCl_5(R.CO_2)(PPh_3)_2$ was obtained from aromatic acids (benzoic pK_a, 4.19; anisic pK_a, 4.47) in air and no purple complex was obtained even under nitrogen, but this might not have been due to the effect of acid strength alone. Both $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ and $Re_2OCl_5(R.CO_2)$-$(PPh_3)_2$ could be obtained directly by substituting $ReCl_4(PPh_3)_2$ for trans-$ReOCl_3(PPh_3)_2$ in the above reactions, the other main products being triphenylphosphine oxide and hydrogen chloride. No analogous compounds could be obtained from trans-$ReOCl_3(PPh_3)_2$ and trifluoracetic, α-chloropropionic, p-nitrobenzoic, or crotonic acids, or from $ReOCl_3(AsPh_3)_2$ and acetic acid.

The complex $ReCl_4(PPh_3)_2$.

The compound $ReCl_4(PPh_3)_2$, previously obtained by different methods by Freni and Valenti (23) and by Chatt et al. (37), was the primary isolable product and was formed by disproportionation of trans-$ReOCl_3(PPh_3)_2$. The reaction could be arrested at this stage if carried out in an atmosphere of hydrogen chloride, and yields then approached the theoretical for the well-known disproportionation (41):

$$3Re(V) \longrightarrow 2Re(IV) + Re(VII).$$

The presence of carboxylic acid was not essential and dispro-

portionation also occurred, albeit less cleanly, in pure boiling xylene under hydrogen chloride,[*] presumably according to the equation:

$$3ReOCl_3(PPh_3)_2 \longrightarrow 2ReCl_4(PPh_3)_2 + ReO_3Cl + 2PPh_3 \qquad (1)$$

Estimated yields of $ReCl_4(PPh_3)_2$ often exceeded somewhat that required by equation (1). This was probably because part of the Re(VII) species was reduced by the liberated triphenylphosphine back to trans-$ReOCl_3(PPh_3)_2$, a reaction known to occur with hydrochloric acid solutions of perrhenic acid (24):

$$ReO_3Cl + 2HCl + 3PPh_3 \longrightarrow ReOCl_3(PPh_3)_2 + POPh_3 + H_2O \qquad (2)$$

Indeed, the conversion, of trans-$ReOCl_3(PPh_3)_2$ to $ReCl_4(PPh_3)_2$ became quantitative when an excess of triphenylphosphine was added; in effect resulting in a reduction of Re(V) to Re(IV).

Tetrachlorobis(triphenylphosphine)rhenium(IV) may be prepared by heating trans-$ReOCl_3(PPh_3)_2$ with triphenylphosphine in boiling propionic acid for 2 hr. in an atmosphere of hydrogen chloride. The physical properties of the compound thus obtained agreed with those reported by Freni and Valenti (23). The solid and its solutions in inert solvents were stable to oxygen, aqueous acids, and hydrogen peroxide in the cold, but were hydrolysed by base. In air, oxidative decomposition began at

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[*] When the hydrogen chloride was omitted, only the decomposition products $[(ReCl_3PPh_3)_x$?] of $ReCl_4(PPh_3)_2$ were isolated. Acid was generally found to retard decomposition of most compounds described in this chapter.

ca. 80° and was rapid at 120°, unless acid was present. In vacuo the solid was stable up to ca. 220°, but lost triphenylphosphine above this temperature, leaving a green residue [probably impure $(ReCl_3PPh_3)_x$], which finally turned black at 300°. When $ReCl_4(PPh_3)_2$ was boiled with pyridine (Py) for 10 min. it gave orange tetrachloro(pyridine)(triphenylphosphine)rhenium(IV), $ReCl_4(Py)PPh_3$, in good yield. The compound $Re_2Cl_4(acac)_4$, first obtained by refluxing the green isomer of $ReOCl_2(OEt)(PPh_3)_2$ with acetylacetone(acac H) for 50 hr. (17), was obtained by refluxing $ReCl_4(PPh_3)_2$ with acetylacetone for 1 hr. In the presence of hydrogen chloride, $ReCl_4(PPh_3)_2$ did not react on heating with carboxylic acids or their anhydrides.

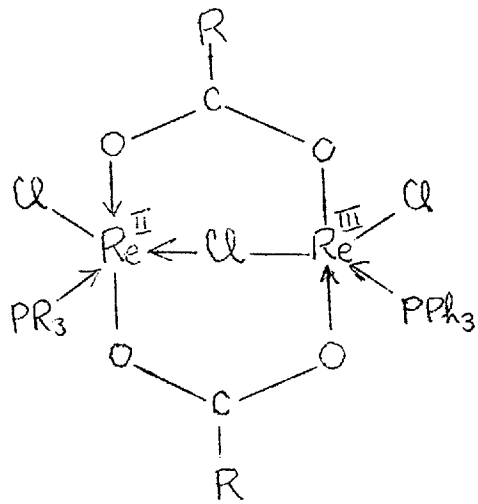
The most convenient method of preparation of $ReCl_4(PPh_3)_2$ is from the reaction of $ReCl_3(MeCN)(PPh_3)_2$ and carbon tetrachloride which will be described later. The yield from rhenium metal is only slightly lower than in the disproportionation reaction, but the purity is higher and obviates recrystallisation. The complex was also obtained from $ReCl_4(RCN)_2$ and PPh_3, and as a by-product of the reaction of $ReCl_3(RCN)(PPh_3)_2$ with α-diketones, and it is clearly of high stability in systems containing PPh_3.

The complexes of the type $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$.

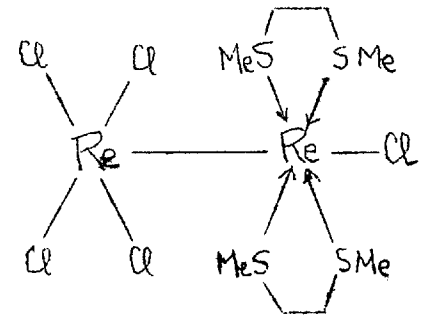
Elementary analyses and molecular-weight measurements on the purple compounds were consistent with the formulation

$Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ for R = Et, $n-C_3H_7$, $Me_2CH.CH_2$, Me_3C, $MeCH_2.CHMe$, $n-C_5H_{11}$, $n-C_7H_{15}$, $n-C_{11}H_{23}$, $Ph.CH_2$, and cyclohexyl. The presence of two carboxylate residues per molecule was demonstrated directly in the case R = $n-C_{11}H_{23}$ by isolating lauric acid quantitatively on hydrolysis. Freshly prepared solutions in nitrobenzene were non-conducting. Proton magnetic resonance (n.m.r.) spectra were consistent with the presence of phenyl groups and alkyl residues. Infrared spectra in the region 4000-600 $cm.^{-1}$ could be interpreted on the basis of absorptions by triphenylphosphine (48) and bidentate carboxylate groups (49). In particular, the characteristic absorptions of monodentate carboxylate, Re=O (24), Re-H (50), -OH, $-OH_2$, $-CO_2H$, P=O, and P-H functions were not observed. On the basis of these facts, the purple compounds may be assigned any one of a number of structural formulae, in all of which rhenium has an effective oxidation state of 2.5. We originally suggested structure I for the complexes, and this was criticized by Cotton (16) on the grounds that it is unlikely that a chlorine atom and two carboxylate groups would bridge simultaneously. Extensive work since that time demonstrated the stability of Re-Re bonds in the dinuclear Re(III) compounds, and a crystal structure determination on the Re(II)-Re(III) compound $Re_2Cl_5(dithiahexane)_2$ (16,30) established its structure as II. In the light of this work additional structures such as III and IV can be assigned to the carboxylate complexes, but only X-ray crystallography can rigorously

distinguish between them. Structure III is the most consistent with the known stereochemical preferences of Re(III).



I



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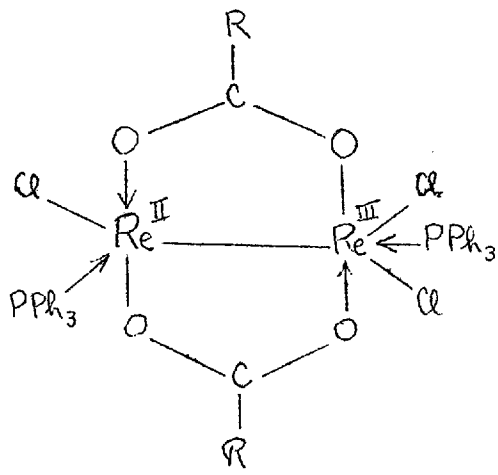
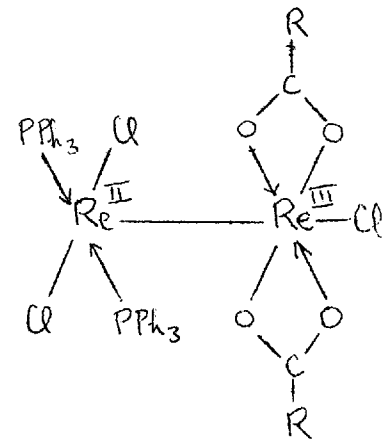


III



IV

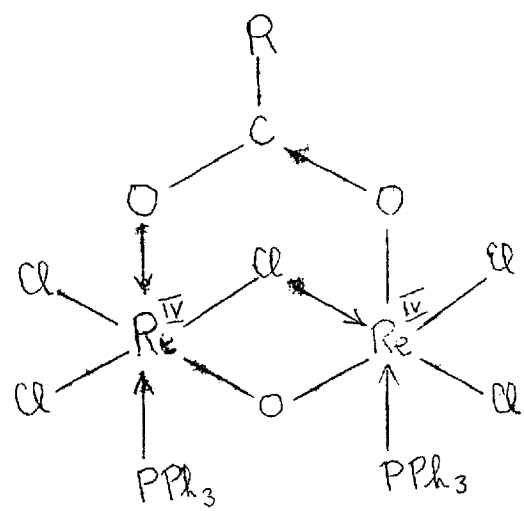
The compounds were obtained in large, dark purple crystals, giving vivid purple solutions in organic solvents. The absorption spectra in the visible region were practically identical for all members of the series. Solubilities increased with increasing length of the alkyl chain so that, whereas the acetate was insoluble in alkanes, alcohols, ethers, etc., the laurate was readily soluble in most organic solvents. The compounds were feebly paramagnetic and, when corrected for the diamagnetism of the ligands, susceptibilities correspond to an effective magnetic moment of 2·0 B.M. for the solids and 1.4 B.M. in solution. The solid compounds were stable indefinitely in air, but decomposed slowly in solution unless sealed under nitrogen, and were also decomposed by alumina. Decomposition was slow (i.e. several hours) even at 80°, and was retarded by acid (HCl, $R.CO_2H$). In solution, the compounds were rapidly oxidised in the cold by halogens (including iodine), chloric, perchloric, and nitric acids, and slowly or on heating by peroxides, ketones, nitro-compounds, stannic chloride, etc. the primary product in each case was an unstable blue compound [Re(III)?], which either decomposed spontaneously or was oxidised further to green, yellow [Re(V)?], and finally colourless [Re(VII)] products. When heated for several days with carboxylic acid in the absence of oxygen, the purple compounds were converted into orange $Re_2Cl_2(R.CO_2)_4$.

The Complexes of the Type $Re_2OCl_5(R.CO_2)(PPh_3)_2$.

Elementary analyses, molecular weight measurements, and n.m.r. studies on the green compounds were consistent with the formulation $Re_2OCl_5(R.CO_2)(PPh_3)_2$ for R = Me, Et, $Me_2CH.CH_2$, $MeCH_2.CHMe$, $n\text{-}C_7H_{15}$, $n\text{-}C_9H_{19}$, $n\text{-}C_{11}H_{23}$, $n\text{-}C_{15}H_{31}$, $Ph.CH_2$, Ph, and p-MeO.C_6H_4. Solutions in nitrobenzene were non-conducting The caprate ($R = n\text{-}C_9H_{19}$) gave one molar equivalent of capric acid on hydrolysis. Infrared spectra in the region 4000-600 $cm.^{-1}$ were similar to those of the purple complexes, and could be interpreted completely on the basis of absorptions by triphenylphosphine and bidentate carboxylate groups. Since the characteristic absorptions of Re=O, -OH, $-OH_2$, CO, and P=O functions were absent, the oxygen atom which does not form part of the carboxylate group can only be bridging. One chlorine atom must also be assumed to be bridging if both metal atoms are to have the same coordination. A number of geometrical isomers satisfy these requirements, in each of which both rhenium atoms are tetravalent and six co-ordinate. Structure V is the most plausible on chemical and other grounds. The solids had a diamagnetism approximating to that calculated from Pascal's constants and hence magnetic interactions, not necessarily via a metal-metal bond, evidently occur between the two rhenium atoms.

The compounds were obtained in dark-green hexagonal

prisms or needles giving vivid blue solutions in organic solvents. Absorption spectra in the visible region revealed at least three intense (presumably charge transfer) bands, independent of the nature of R. Solubilities increased with increasing organic character, except for aromatic members which were decidedly less soluble than even the acetate. The solids were stable in air up to their melting points and resisted all aqueous reagents (including caustic alkali) even at 100°. They dissolved freely in thionyl chloride without decomposition, and solutions in inert solvents did not react with chlorine, bromine, peroxides, $\alpha\alpha'$-dipyridyl, etc., but gave orange substances when heated with pyridine. Solutions in aprotic solvents turned bright green when shaken with strong acid (nitric, perchloric) and the original blue colour was restored at once on addition of Brønsted base



V

(water, alcohols, ethers), probably owing to reversible protonation of the oxo bridge.

The compounds were adsorbed tenaciously on Grade III alumina as a purple band and could be eluted only with strong acid. Purple substances, possibly of similar structure, were found in solution on addition of strong base (alkali alkoxides, amines with $pK_a > 10.6$). The reaction was initially reversed by even weak acid, but on standing with base further irreversible changes took place. A purple crystalline solid was isolated from the reaction of $Re_2OCl_5(Me.CO_2)(PPh_3)_2$ and sodium methoxide but this was probably different from the purple species in solution since it did not generate the parent complex when acidified. Its infra-red spectrum differed from that of the parent complex only in the presence of a strong band in the Me—O stretching region at 1014 $cm.^{-1}$ (54,55), and its solutions in nitrobenzene were non-conducting Analyses and molecular weight measurement were consistent with the formula $Re_2OCl_4(OMe)(Me.CO_2)(PPh_3)_2$. The compound showed the same chemical inertness as $Re_2OCl_5(Me.CO_2)$-$(PPh_3)_2$ itself, and likewise developed a green colouration reversibly with strong acids. It is therefore reasonable to assume that one chlorine atom in $Re_2OCl_5(Me.CO_2)(PPh_3)_2$ was replaced by a methoxy group with retention of the basic structure.

No reaction occurred when $Re_2OCl_5(Me.CO_2)(PPh_3)_2$ was heated with acetic acid to reflux under nitrogen for several days.

Other reactions.

When heated with acid anhydrides, trans-$ReOCl_3(PPh_3)_2$ gave the same compounds as with the corresponding acids, but more rapidly and less cleanly. With acetic anhydride, but not with the higher anhydrides, a canary yellow salt [Λ_0 = 25 mhos $cm.^2 mole^{-1}$ for a molecular weight of 900, indicating a uni-univalent electrolyte in nitrobenzene (56)] could be isolated in addition. The same salt was obtained by heating $ReCl_4(PPh_3)_2$ with anhydride, and the reaction was completely inhibited by hydrogen chloride. The nature of the yellow substance is not clear. Analyses correspond to an empirical formula between $ReCl_5(PPh_3)_2$ and $ReCl_5(PPh_3)_2(C_2H_3O)$ with the presence of oxygen uncertain, and the magnetic moment of 3.7 B.M. suggests tetravalent rhenium. The presence of phosphine groups of two kinds is indicated by a multiplicity of bands in the P-sensitive vibration regions (48) of the infra-red spectrum (see experimental section) which otherwise reveals no strongly absorbing groups. It is not possible to assign a structure to this substance without further work, but it may be some kind of phosphonium salt of the anion $ReCl_5(PPh_3)^-$, derived from PPh_3Cl_2 and acetic anhydride. When it is heated with acetic anhydride it gives $Re_2Cl_2(Me.CO_2)_4$.

The only solid product obtained on heating trans-$ReOCl_3(PPh_3)_2$ with aliphatic anhydrides under nitrogen for more than 12 hr. was a complex of the type $Re_2Cl_2(R.CO_2)_4$. These compounds,

hitherto available only through uneconomical routes (25-27), could thus be prepared in fair yield (50-60% overall from rhenium metal), and could prove useful intermediates for the preparation of dirhenium(III) octachloride ions $[Re_2Cl_8)^{2-}]$ by heating with hydrochloric acid (26).

Trans-oxotribromobis(triphenylphosphine)rhenium(V), trans-$ReOBr_3(PPh_3)_2$, reacted with carboxylic acids under the usual conditions to give red $ReBr_4(PPh_3)_2$ and green $Re_2OBr_5(R.CO_2)(PPh_3)_2$ but no compounds analogous to $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ could be isolated. In so far as they were investigated, the properties of these compounds were similar to those of their chloro-analogues.

The new series of orange complexes $Re_2Br_2(R.CO_2)_4$ * was obtained from trans-$ReOBr_3(PPh_3)_2$ and aliphatic anhydrides under the same conditions as $Re_2Cl_2(R.CO_2)_4$, and the compounds are assumed to have similar structures (25,27).

Solutions of $Re_2Cl_2(C_3H_7.CO_2)_4$ in organic solvents were reduced by zinc or cadmium amalgam in the strict absence of oxygen. The orange colour of the solution was discharged and small, almost colourless crystals began to separate. When even traces of air were admitted, the solution at once turned green and the crystals redissolved. Even in the solid state the reduced species

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* One member of this series (R = Me) was obtained previously by Grove from $ReOBr_3(PPh_3)_2$ and acacH at high temperatures (57), and many more have recently been prepared by Cotton (27).

was extremely sensitive to oxidation and could not be isolated pure. The reaction certainly merits further investigation as the product presumably contains rhenium in one of the rare lower oxidation states. When $Re_2Cl_2(Me.CO_2)_4$ was heated in a stream of hydrogen, it was reduced directly to the metal.

Mechanism of the reactions. - The detailed course of the reactions described is not clear, but a few observations may be made. The $ReCl_4(PPh_3)_2$ formed in situ according to equation (1) is the precursor of all the carboxylate complexes. Although $Re_2OCl_5(R.CO_2)(PPh_3)_2$ has the same formal oxidation state as $ReCl_4(PPh_3)_2$, it was not obtained when oxygen was rigorously excluded and probably arises by aerial oxidation of a lower-valent intermediate (Y). The intermediate cannot be $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ since this substance did not give $Re_2OCl_5(R.CO_2)(PPh_3)_2$ under a variety of oxidising conditions. Rather we suggest, with some reserve, that Y is the precursor of both complexes, and is itself formed by reduction of the $ReCl_4(PPh_3)_2$. It could then either absorb oxygen to give green $Re_2OCl_5(R.CO_2)(PPh_3)_2$, or be reduced further to purple $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$, with the two competing reactions dependent on acid strength. Although disproportionation reactions cannot be ruled out, we believe that the reducing species is triphenylphosphine, itself being oxidised to dichlorotriphenylphosphorane, PCl_2Ph_3. In carboxylic acid, this reacts at once according to the equation:

$$PCl_2Ph_3 + 2R.CO_2H \rightarrow POPh_3 + (R.CO_2)_2O + 2HCl \qquad (3)$$

but persists longer in pure anhydride, thus leading to various by-products. Even in the absence of oxygen, triphenylphosphine oxide and not triphenylphosphine was isolated from the reaction mixture, and this could only have been formed by solvolysis of PCl_2Ph_3. The compounds $Re_2Cl_2(R.CO_2)_4$, formed at the later stages of the reaction, are possibly derived from $Re_2Cl_3(R.CO_2)_4$. They were indeed obtained from the latter on heating with carboxylic acid, but it is difficult to see how the apparent oxidation involved comes about.

The formation of a Re(II) - Re(III) compound under mildly reducing conditions is surprising, but is in accord with the "reduction" of $Re_2Cl_8^{2-}$ by dithiahexane. It is possible that Re(III) can in fact disproportionate to Re(II), Re(IV) and Re(VII) under appropriate conditions, as has been reported in the old literature (41).

CHAPTER II.

THE PREPARATION AND REACTIONS OF THE COMPLEXES $ReX_3(RCN)(PPh_3)_2$ (X = Cl, Br).

The previously known reactions of trans-$ReOCl_3(PPh_3)_2$ and the new reactions with carboxylic acids and anhydrides were discussed in Chapter I. By heating the same compound with alkanonitriles (RCN) under nitrogen we obtained trichloro(alkanonitrile)bis(triphenylphosphine)rhenium(III), $ReCl_3(RCN)(PPh_3)_2$, in 30 - 35% yield, and we isolated $ReOCl_3(PPh_3O)(PPh_3)$ from the (aerially oxidised) mother liquors. When the reaction was carried out in the presence of additional free triphenylphosphine, the yield of $ReCl_3(RCN)(PPh_3)_2$ rose to 90%. The compounds, which are crystalline and easily purified, are thus readily available in 80% yield from the metal, and provide the most direct route to monomeric complexes of trivalent rhenium.

By ligand substitution reactions of $ReCl_3(R.CN)(PPh_3)_2$ we obtained the monomeric complexes $ReCl_3py_2(PPh_3)$, $ReCl_3py_3$, and $ReCl_3(LL')(PPh_3)$ (LL' = benzil, phenquin, $\alpha\alpha'$-dipyridyl). The bromo-complexes $ReBr_3(R.CN)(PPh_3)_2$ could be obtained from trans-$ReOBr_3(PPh_3)_2$ in the same way as the chloro-complexes, but the ethoxo-compound $ReOCl_2(OEt)(PPh_3)_2$ was not reduced, and $ReCl_3(R.CN)(PPh_3)_2$ did not react with alcohols. $ReCl_3(Ph.CN)(PPh_3)_2$ was formed by exchange from benzonitrile and the acetonitrile complex.

Properties and structure of the complexes $ReX_3(R.CN)(PPh_3)_2$. - The compounds were obtained as orange-yellow (X = Cl) or orange (X = Br) leaflets or needles, readily soluble in dichloromethane (27 g./l. at 25°, λ 433 mμ, ε 1800 for R = Me and X = Cl; 18 g./l. at 25°, λ 466 mμ, ε 2500 for R = Me and X = Br), less so in benzene and acetonitrile, and insoluble in alcohols and ethers. The solubility rose considerably with the size of the alkyl chain (ca. 300 g./l. in dichloromethane for R = $n\text{-}C_7H_{15}$ and X = Cl). The solids were stable indefinitely in air, but decomposed slowly in solution. Fresh solutions in nitrobenzene were practically non-conducting and gave no precipitate with silver nitrate in acetonitrile. The corrected susceptibilities of the solids (R = Me; X = Cl, Br) at 23° corresponded to an effective magnetic moment of 1.60 B.M., similar to that of the known octahedral complexes of rhenium(III) (17,58). The complex $ReCl_3(MeCN)(PPh_3)_2$ exists in two crystalline modifications which differ slightly in colour and in the splitting of the PPh_3 modes in the infra-red. One form (α) separated on adding ethanol, isopropanol or ether to a dichloromethane solution, and showed definite splitting of the P-sensitive mode at ca. 1100 $cm.^{-1}$. The other form (β), which was slightly deeper in colour and showed no splitting, was obtained on adding methanol to the dichloromethane solution. The α - and β- forms could be repeatedly interconverted by two successive recrystallisations from the appropriate solvent, and both had

identical visible absorption spectra in solution. The other complexes were also polymorphic, but the conditions under which each form crystallised were not established.

Analyses and isopiestic molecular weights were consistent with the formulation $ReX_3(RCN)(PPh_3)_2$ for R = Me, n-C_3H_7, $Me_2CH.CH_2$, n-C_7H_{15}, Ph and X = Cl, and for R = Me, n-C_3H_7 and X = Br. Oxygen analyses on compounds of this type are unreliable, but there was no systematic discrepancy in the carbon analyses, and indirect evidence showed oxygen to be absent. Infra-red spectra in the region 4000-650 $cm.^{-1}$ showed bands associated with PPh_3 and the alkyl residue only. In particular, the invariably strong bands characteristic of triphenylphosphine oxide and the Re=O grouping (24) were absent. Such bands were also absent from all derivatives prepared under non-oxidising conditions. The compounds are mononuclear and there can be no oxygen bridges, so that if oxygen were present at all, it should be in the form of a ligand $R.CH_xNO$. Aside from negative infra-red evidence for such a ligand, a nitrile was the only organic product isolated on degradation, and in particular no oxime, amide, carbonyl derivative or hydroxamic acid could be detected. When the acetonitrile complex was heated with pyridine, an orange crystalline compound was obtained in 90% yield, which analyses and infra-red results showed to be trichlorobis(pyridine)triphenylphosphinerhenium(III), $ReCl_3py_2(PPh_3)$. In a quantitative experiment the same compound was

obtained from pyridine and the caprylonitrile complex, together with free PPh_3 and one molar equivalent of caprylonitrile as the only other products (see experimental section). No phosphine-oxide or water was produced, indicating the absence of oxygen in the original compound. The complex $ReCl_3(MeCN)(PPh_3)_2$ likewise reacted with a slight excess of $\alpha\alpha'$-dipyridyl to give green $ReCl_3(dipy)(PPh_3)$ and 0.8 ± 0.3 mole of free acetonitrile.

A millimole sample of $ReCl_3(MeCN)(PPh_3)_2$, recrystallised from dichloromethane-ethanol and thoroughly dried at 80° under vacuum, was stable in a vacuum up to 200°. Decomposition began at 210° with the formation of free PPh_3 and an olive-green powdery residue. A colourless mobile liquid collected in a cold trap, and was shown to consist of 1.00 ± 0.05 millimole of acetonitrile, 0.06 millimole of dichloromethane, and 0.02 millimole of ethanol. The green residue was insoluble in all common solvents and showed only PPh_3 bands in the infra-red. It was shown by analysis to be non-stoicheiometric and contain 15% more PPh_3 than is required by the formula $ReCl_3PPh_3$. The compound is possibly the same as the green polymeric $(ReCl_3PPh_3)_n$ described by others (18). Yields of all products were close to those required by the equation:

$$ReCl_3(MeCN)(PPh_3)_2 \xrightarrow{\Delta} ReCl_3PPh_3 + PPh_3 + Me.CN \qquad (4)$$

The small amounts of dichloromethane and ethanol are presumably trapped in the crystal lattice, and may determine the stability of a particular polymorph.

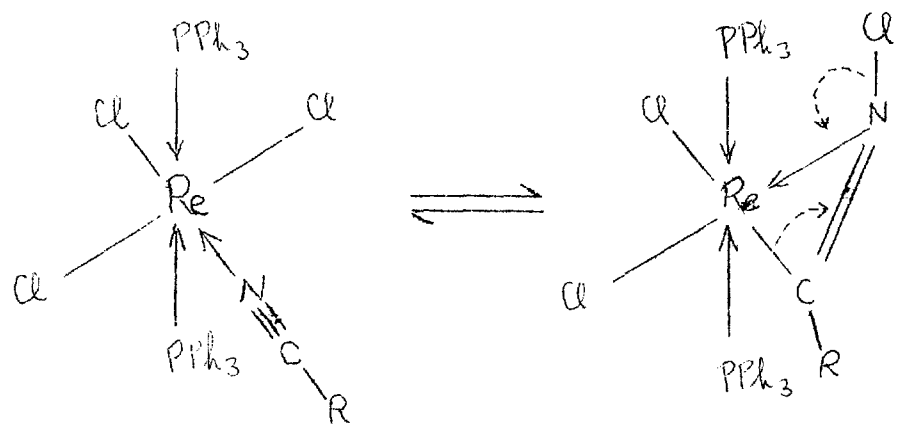
The above results leave no doubt that the compounds described behave as though they were $ReX_3(RCN)(PPh_3)_2$. The absence of a C — N stretching mode in the infra-red spectra of mulls is therefore surprising. The strong C — N stretch of free nitriles is known to <u>increase</u> in intensity on coordination (59). A weak band occurs at 2257 $cm.^{-1}$ in the spectrum of a concentrated (0.4 molar) <u>solution</u> of $ReCl_3(n\text{-}C_7H_{15}CN)(PPh_3)_2$ in dichloromethane. If this be assigned to the C — N stretch, the intensity is 30% less that of the free nitrile, and the frequency is 10 $cm.^{-1}$ higher. The C — N stretch in benzonitrile (2232 $cm.^{-1}$) is much stronger than in aliphatic nitriles, and a very weak band appears at 2240 $cm.^{-1}$ in mulls of the benzonitrile complex. Three possibilities arise:

(i) The nitrile is bonded to the metal via the lone pair on the nitrogen atom (VI) as in most known nitrile complexes. Such bonding invariably leads to a shift of the C — N stretch to higher frequencies (59), and if the weak bands mentioned above were correctly assigned, our observations would be consistent with this. The factors influencing infra-red intensities are complex and not well understood (60), and it may well be that the change of dipole moment associated with the vibration is so delocalised over the π-bonded phosphines, as to lead to the observed decrease in intensity. We note in this connection that the C — N stretch in the nitrile complexes of metal carbonyls tends to be weak (61),

and does not appear at all in mulls of methylmercury cyanide, though strong in the Raman (62). No explanation has been given.

(ii) The nitrile is bonded via the π-electrons of the C—N triple bond. By analogy with other systems a shift to lower frequencies might be expected, and this is observed in the two authentic examples of a π-bonded nitrile (63,64). No predictions can be made concerning the intensity.

(iii) The complex is in tautomeric equilibrium with compound VII, the latter form predominating in the solid state. None of the above observations are in conflict with such a structure, since the C≡N stretch is often too weak to observe, and the N—Cl stretch would be obscured by PPh_3 vibrations. Only an X-ray structure determination could adequately distinguish



VI VII

between these three possibilities, but structure VI appears the simplest and most plausible, and we therefore assign it to the complexes. By analogy with the most stable isomer of $ReOCl_3(PPh_3)_2$ we assume the PPh_3 groups are trans (the ligands being labile).

Oxidation of the complex $ReCl_3(MeCN)(PPh_3)_2$. -

When solutions of the complex in inert solvents were warmed in air, they turned greenish and small amounts of a pastel-green, crystalline solid sometimes separated out. This was identical with the product obtained by working up in air the mother liquors from the reaction of trans-$ReOCl_3(PPh_3)_2$ with nitriles. The compound could best be prepared by passing a current of air through a suspension of $ReCl_3(MeCN)(PPh_3)_2$ in boiling benzene for 20 min., allowing the acetonitrile generated to distil off as the azeotrope. These conditions were found to be critical, and oxidation was inhibited by free nitrile. The infra-red spectrum of the solid showed strong bands which were assigned to the Re=O stretch (978 $cm.^{-1}$) and to coordinated triphenylphosphine oxide (ν - P = O at 1119 $cm.^{-1}$ and P-sensitive vib. at 1064 $cm.^{-1}$) as well as PPh_3 bands (P-sensitive vib. at 1090 $cm.^{-1}$). Analyses were consistent with the formula $ReOCl_3(PPh_3O)(PPh_3)$. Equimolar quantities of the complex and PPh_3 reacted rapidly and quantitatively in solution to give trans-$ReOCl_3(PPh_3)_2$ and triphenylphosphine oxide only, thus proving that the pastel-green compound is indeed a mixed phosphine-phosphine

oxide complex. Under the above conditions trans-$ReOCl_3(PPh_3)_2$ was not oxidised, though it is converted into $ReOCl_3(PPh_3O)(PPh_3)$ when ozone is passed into a cold dichloromethane solution (57).

The PPh_3O group in $ReOCl_3(PPh_3O)(PPh_3)$ is quite labile and is easily replaced by various ligands. The complex reacted rapidly with acetylacetone, $\alpha\alpha'$-dipyridyl, and diethylphenylphosphine to give green $ReOCl_2(acac)(PPh_3)$ (17), brown $ReOCl_3(dipy)$ (57), and blue cis-$ReOCl_3(PEt_2Ph)_2$ (14), respectively. Unlike $ReOCl_3(PPh_3)_2$ or the nitrile complexes, $ReOCl_3(PPh_3O)(PPh_3)$ was hydrolysed at once in wet solvents. It was decomposed by aliphatic amines through a series of colour changes, but gave a stable orange substance with dry ammonia in organic solvents. This was not investigated further.

Reaction of $ReX_3(RCN)(PPh_3)_2$ with halogenated compounds. -

When the compounds $ReCl_3(RCN)(PPh_3)_2$ were heated with carbon tetrachloride, alone or in various solvents (benzene, dichloromethane), the complex $ReCl_4(PPh_3)_2$ was formed rapidly and in high yield (ca. 90%). The bromo-compounds $ReBr_3(RCN)(PPh_3)_2$ and carbon tetrabromide likewise gave $ReBr_4(PPh_3)_2$, but the yield was lower (ca. 40%). Compounds with three chlorine or bromine atoms on the same carbon atom reacted similarly, whereas those with less, as well as fluoro-compounds, were generally inert. Thus hexachloroethane, benzotrichloride, and trichloroacetic acid reacted as readily as carbon tetrachloride; chloroform, bromoform, fluorotrichloromethane, and dichloroacetic acid reacted more

slowly, and benzotrifluoride, hexachlorobenzene, tetrachloroethylene, dichloromethane, phosgene, hexachlorobutadiene, chloramine T, chlorobenzene, α-chloropropionic acid, di-iodomethane, and methyl iodide were inactive.

The organic products of the reaction of $ReCl_3(n\text{-}C_3H_7CN)(PPh_3)_2$ with carbon tetrachloride were shown by gas-liquid chromatography (g.l.c.) to be free n-butyronitrile (yield quantitative), hexachloroethane [60% based on equation (5)] and a little tetrachloroethylene, so that the main course of the reaction is as follows:

$$2ReCl_3(n\text{-}C_3H_7CN)(PPh_3)_2 + 2CCl_4 \longrightarrow 2ReCl_4(PPh_3)_2 + 2n\text{-}C_3H_7CN + C_2Cl_6 \qquad (5)$$

The reaction proceeded in the dark, and the rate was not influenced by ultraviolet radiation, radical initiators or scavengers. Hence the rate-determining step does not involve free radicals. However, the formation of hexachloroethane strongly suggests the generation of trichloromethyl radicals, and this was confirmed by the fact that a mixture of the complex and carbon tetrachloride promoted the polymerisation of styrene, whereas either compound alone did not. The rate of the reaction increased with carbon tetrachloride concentration, but decreased on the addition of nitrile. The simplest mechanism consistent with these observations is the following. Carbon tetrachloride substitutes coordinated nitrile in the complex in a reversible,

rate-determining step. The intermediate then undergoes rapid homolytic dissociation with cleavage of the Cl - CCl_3 bond to give $ReCl_4(PPh_3)_2$ and trichloromethyl radicals, which recombine to form hexachloroethane:

$$ReCl_3(RCN)(PPh_3)_2 + CCl_4 \overset{slow}{\rightleftharpoons} ReCl_3(CCl_4)(PPh_3)_2 + RCN \qquad (6)$$

$$(PPh_3)_2ReCl_3 \leftarrow Cl\text{-}CCl_3 \xrightarrow{fast} (PPh_3)_2ReCl_3 - Cl + CCl_3^{\cdot} \qquad (7)$$

The small amount of tetrachloroethylene probably arises from subsequent reaction of hexachloroethylene with unreacted $ReCl_3$-$(n\text{-}C_3H_7CN)(PPh_3)_2$. The intermediate $ReCl_3(C_2Cl_6)(PPh_3)_2$ would dissociate into $ReCl_4(PPh_3)_2$ and pentachloromethyl radicals, which would then enter into chain reactions such as:

$$C_2Cl_5^{\cdot} \longrightarrow C_2Cl_4 + Cl^{\cdot} \qquad (8)$$

$$C_2Cl_6 + Cl^{\cdot} \longrightarrow C_2Cl_5^{\cdot} + Cl_2 \qquad (9)$$

$$C_2Cl_5^{\cdot} + Cl^{\cdot} \longrightarrow C_2Cl_6 \qquad (10)$$

Rather more than one mole of tetrachloroethylene was in fact obtained when $ReCl_3(RCN)(PPh_3)_2$ (R = Me, $n\text{-}C_3H_7$) was treated with hexachloroethane instead of carbon tetrachloride.

As expected, $ReCl_3(MeCN)(PPh_3)_2$ gave $ReCl_3Br(PPh_3)_2$ with carbon tetrabromide, but $ReBr_3(MeCN)(PPh_3)_2$ gave $ReCl_2Br_2(PPh_3)_2$ with both carbon tetrachloride and benzotrichloride, and not the expected chlorotribromo-complex. This is probably derived from the normal product by further reaction with the free radicals generated.

The visible spectra of the complexes were similar, and

shifted progressively towards the red as the number of bromine atoms increased. The tetrabromo-complex in addition absorbed strongly at 430 mμ (ε2500) and 383 mμ (ε5000), and since these bands were absent from the mixed halide complexes, they were genuine compounds and not mixtures.

The reaction is of interest in connection with the detailed work of Bamford and his school (65), who found that several carbonyls will promote olefin polymerisation only in the presence of the active chloro-compounds we mention above. On kinetic grounds a mechanism essentially similar to the above was postulated, but it was found that the carbonyl had to be activated first by coordination with a second body (e.g. olefin monomer).

Other Reactions of $ReCl_3(Me.CN)(PPh_3)_2$. -

When $ReCl_3(MeCN)(PPh_3)_2$ was heated with benzil in benzene solution a dark purple crystalline solid of stoicheiometry $ReCl_3(Ph.CO.CO.Ph)(PPh_3)$ (50%), together with $ReCl_4(PPh_3)_2$ (35%), was obtained. The purple solid gave intensely purple, non-conducting solutions in organic solvents (λ 548 mμ, ε 17,000 in dichloromethane). The magnetic moment was 1.85 B.M. at 26°, and the infra-red spectrum showed the presence of phenyl and PPh_3 groups, but not of phosphine oxide, Re=O or OH functions. A band of medium intensity at 1590 $cm.^{-1}$ could be due to the C=O stretch, or to a phenyl vibration. The compound gave benzil and trichlorotris(pyridine)rhenium(III), $ReCl_3py_3$, when heated with pyridine

and may hence be formulated as $ReCl_3(Ph.CO.CO.Ph)(PPh_3)$, where benzil acts as a neutral, bidentate ligand. On hydrolysis benzoin and not benzil was obtained, presumably through reduction by the hydrated rhenium(III) oxide. It is interesting that $ReCl_3py_3$ is readily obtained from the benzil complex, whereas $ReCl_3(MeCN)(PPh_3)_2$ gives only $ReCl_3py_2(PPh_3)$ under the same conditions.

A blue compound $ReCl_3(phenquin)(PPh_3)$, similar to the benzil complex, was obtained from $ReCl_3(MeCN)(PPh_3)_2$ and 9:10-phenanthraquinone, and was again accompanied by some $ReCl_4(PPh_3)_2$. Solutions in non-polar solvents were blue and in polar solvents indigo (λ 592 mμ in benzene and 588 mμ in dichloromethane, ε 20,000). Analogous orange complexes were obtained from aliphatic α-diketones, but the products were not analytically pure.

The known compounds $ReCl_2(acac)(PPh_3)_2$ (17) and $Re_2Cl_2(Et.CO_2)_4$ (25) were produced when $ReCl_3(MeCN)(PPh_3)_2$ was heated with acetylacetone and propionic acid, respectively. The nitrile complex did not react with diethyl oxalate, acetonitrile, triphenylphosphine, or triphenylphosphine oxide in boiling benzene.

Near its melting point fused PPh_3 dissolved $ReCl_3(MeCN)(PPh_3)_2$ under vacuum without reaction. When the temperature was raised, the orange solution turned red-brown, and a brown mass was obtained on cooling. This perhaps contained $ReCl_3(PPh_3)_3$, but when it was extracted with ether, the brown substance was

almost immediately converted into green, insoluble $(ReCl_3PPh_3)_n$. Since the complex $ReCl_3(PEt_2Ph)_3$ is quite stable, the instability of $ReCl_3(PPh_3)_3$ must be attributed to steric factors, and a parallel is provided by the formation of five-coordinate $ReNCl_2(PPh_3)_2$ where other phosphines yield $ReNCl_2(PR_3)_3$ under the same conditions (10,11). Related is the fact that $ReOCl_3(PPh_3)_2$, though readily reduced to Re(III) by diethylphenylphosphine, is not reduced by PPh_3 (14). Prolonged heating of $ReOCl_3(PPh_3)_2$ with PPh_3 results in reduction to impure $(ReCl_3PPh_3)_n$, and in the presence of acid, to disproportionation.

Mechanism of formation of $ReCl_3(MeCN)(PPh_3)_2$.

When $ReCl_3(MeCN)(PPh_3)_2$ is prepared in the presence of free PPh_3, the only other major product is triphenylphosphine oxide, and in the amount required by the equation:

$$ReOCl_3(PPh_3)_2 + MeCN + PPh_3 \longrightarrow ReCl_3(MeCN)(PPh_3)_2 + OPPh_3 \quad (11)$$

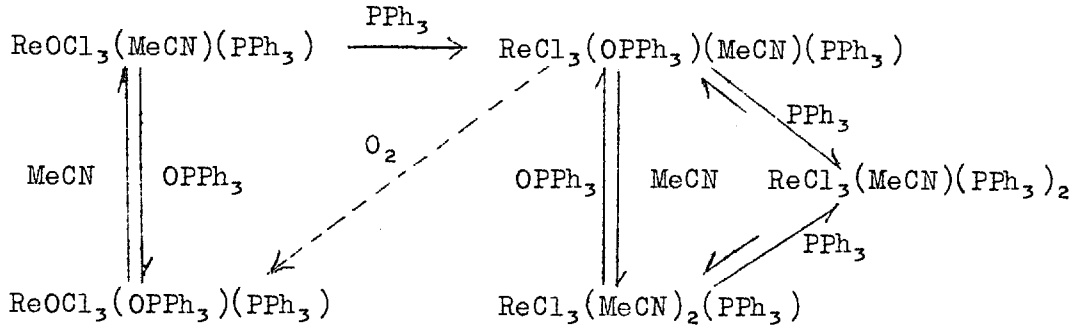
The overall reaction is evidently a reduction of Re(V) to Re(III) by the PPh_3. Since PPh_3 will not reduce $ReOCl_3(PPh_3)_2$ directly, we believe the first step to be reversible substitution of PPh_3 by acetonitrile:

$$ReOCl_3(PPh_3)_2 + MeCN \rightleftharpoons ReOCl_3(MeCN)(PPh_3) + PPh_3 \quad (12)$$

Reduction of the product then becomes sterically possible, and this takes place in one step to give initially $ReCl_3(OPPh_3)(MeCN)(PPh_3)$. The most stable product formed subsequently by ligand substitution in the presence of excess PPh_3 would then be $ReCl_3$-

$(MeCN)(PPh_3)_2$.

When PPh_3 was omitted, the yield of $ReCl_3(MeCN)(PPh_3)_2$ was only 30-40%. The PPh_3 required for reduction is generated by reaction (12). Since only one mole of PPh_3 is now available, and as much is required for the complete reduction of the Re(V) species, there will be insufficient PPh_3 to react with the intermediate $ReCl_3(OPPh_3)(MeCN)(PPh_3)$ unless some $ReOCl_3(MeCN)(PPh_3)$ remains unreduced. Also, since there is little free PPh_3 in the solution, the equilibrium (12) would be shifted to the right and the reactions shown in Scheme 1 would become important.



Scheme 1.

In order to test this mechanism, and bearing in mind reports that nitriles can reduce transition metal halides (59), we heated trans-$ReOCl_3(PPh_3)_2$ (5.00 g.) with acetonitrile, filtered off the $ReCl_3(MeCN)(PPh_3)_2$ (2.29 g.) and evaporated the filtrate to dryness under vacuum, all operations being carried out in the absence of oxygen or moisture, and with freshly purified solvents. The residue was a friable yellow mass weighing 2.98 g., and since

there were no volatile reaction products one mole of $ReOCl_3(PPh_3)_2$ must have reacted with 1.1 mole of acetonitrile. The infra-red spectrum of the solid showed an Re=O stretch of medium intensity at 985 $cm.^{-1}$, and both free and coordinated $OPPh_3$, but no other bands. The solid was extremely soluble in dichloromethane (ca. 1 g./ml.) and therefore did not contain $ReOCl_3(PPh_3)_2$ or $ReCl_3(MeCN)(PPh_3)_2$ as major constituents. A solution of PPh_3 (2 g.) in dichloromethane was added to the solution of the residue and the mixture allowed to stand at 30° for 15 min. under nitrogen. Yellow crystals began to separate and the mixture was then shaken with ethyl acetate/dichloromethane (3:2 v/v). The solid was identified as trans-$ReOCl_3(PPh_3)_2$ and the solution was found to contain $ReCl_3(MeCN)(PPh_3)_2$. These observations are entirely consistent with the mechanism we propose. In another experiment we found that the residue from the reaction dissolved readily in acetone, but after a few minutes crystals of an isomer of $ReOCl_3(OPPh_3)(PPh_3)$ separated out. The original residue was found to contain 0.33 mole of free $OPPh_3$ per mole of starting material and when this was removed by ether extraction, $ReOCl_3(OPPh_3)(PPh_3)$ separated from the acetone solution only after standing in air for several hours. We believe the $ReOCl_3(OPPh_3)(PPh_3)$ was formed by two independent routes, namely by substitution of acetonitrile in the $ReOCl_3(MeCN)(PPh_3)$ (fast), and by aerial oxidation of the Re(III) species. Acetonitrile inhibits both reactions, and no

phosphine oxide complex separated in its presence.

There is no indication that nitriles acted as reducing agents in these reactions.

CHAPTER III.

THE PREPARATION AND REACTIONS OF THE COMPLEXES $ReCl_4(RCN)_2$.

The reactions of metal halides with nitriles has been the subject of a recent review (59). The nitrile complexes obtained from transition metal halides can be divided into two groups according to their solvolytic behaviour: Complexes of metals to the left of Group VIIa are sensitive to moisture and can be handled only under rigorously anhydrous conditions, whereas complexes of metals to the right are relatively stable (59). Of the Group VIIa metals themselves only the complexes of manganese (II) had been investigated when this work was commenced, and they appeared to be similar to those of metals of subsequent groups (68). Trinuclear complexes $Re_3Cl_9(RCN)_3$ (R = Me, Ph) were recently prepared from rhenium trichloride (34), and the α-tetrachloride was reported to give a brown solution in acetonitrile, without further details (69). The β-tetrachloride is insoluble (70).

Rhenium pentachloride dissolves exothermically in anhydrous acetonitrile with evolution of hydrogen chloride to give an intensely red-brown solution. When the solution was warmed, made slightly moist, or allowed to stand overnight even in the strictest absence of moisture, it became much paler in colour and large, greenish yellow crystals of tetrachlorobis(acetonitrile)rhenium(IV), $ReCl_4(MeCN)_2$, separated out. A further crop was obtained by

diluting the mother-liquor with water at 0°, and the overall yield was 65-75%. Similar complexes were obtained from other nitriles, but the reactions were slower and the yields low. The complex $ReCl_4(PhCN)_2$ could be prepared more conveniently from $ReCl_4(MeCN)_2$ by exchange. The reaction of rhenium pentachloride is thus analogous to the pentahalides of molybdenum and tungsten which likewise give tetravalent complexes $MX_4(RCN)_2$ (X = Cl, Br) (71).

Properties and reactions of the complexes $ReCl_4(RCN)_2$.

The complexes were obtained as yellow or greenish-yellow crystals, readily soluble in polar solvents to pale yellow, non-conducting solutions (solubility for R = Me was 100 g./l. in acetone at 20° and 200 g./l. in acetonitrile at 70°). Analyses were consistent with the formulation $ReCl_4(RCN)_2$ for R = Me, n-C_3H_7, and Ph, and the complexes were monomeric in acetone and acetonitrile. The magnetic moment of solid $ReCl_4(MeCN)_2$ (μ_{eff} = 3.40 B.M. at 20°) was in the range observed for other Re(IV) compounds. The infra-red C—N stretching vibration was at 2292 $cm.^{-1}$ vs for R = Me ($\Delta\nu$ = 45 $cm.^{-1}$), 2282 $cm.^{-1}$ vs for R = n-C_3H_7 ($\Delta\nu$ = 32 $cm.^{-1}$), and 2260 vs, 2251 vs for R = Ph ($\Delta\nu$ = 28 $cm.^{-1}$, 19 $cm.^{-1}$) and showed the usual increase in frequency ($\Delta\nu$) and intensity compared to the free nitrile, characteristic of σ-bonded nitrile complexes (59). When recrystallised from dichloromethane, $ReCl_4(MeCN)_2$ retained a small amount of solvent (with infra-red absorption at 1260 $cm.^{-1}$ and

732 $cm.^{-1}$ vs) even at 60° under vacuum, but this was expelled rapidly above 70°.

When $ReCl_4(MeCN)_2$ was heated to 210-240° under vacuum, acetonitrile was evolved and a black liquid remained, which solidified on cooling to a dark brown crystalline mass. A small quantity of a red-brown crystalline sublimate ($ReCl_6$?) was also obtained, which fumed in moist air. The infra-red spectrum of the residue showed a weak C≡N stretch, and rhenium and chlorine analyses corresponded to the formula $ReCl_4(0.5MeCN)$. It is clear that rhenium tetrachloride begins to disproportionate (69,72) at temperatures lower than those required for the complete elimination of acetonitrile. Since the product was completely soluble in acetonitrile, it was the α-form which was produced (69, 70).

In their hydrolytic behaviour, the complexes occupied an intermediate position between the two groups of transition metal nitrile complexes. Thus $ReCl_4(MeCN)_2$ crystallised out unchanged when cold water was added to an acetone solution, whereas a suspension of $ReCl_4(PhCN)_2$ in acetone reacted with water at once and the rhenium passed into solution as a bright orange anionic complex. The orange species could be precipitated with large cations but the product was heavily contaminated with perrhenate. The complex $ReCl_4(MeCN)_2$ was rapidly hydrolysed to $ReO_2.aq$ by hot water or alkali, and slowly dissolved in boiling concentrated

hydrochloric acid as $ReCl_6^{2-}$.

Carmine red $ReCl_4(PPh_3)_2$, scarlet $ReCl_4(AsPh_3)_2$ and royal blue $ReCl_4(SbPh_3)_2$ were obtained from $ReCl_4(MeCN)_2$ by ligand substitution. Triphenylphosphine reacted readily even in acetonitrile solution, but triphenylarsine and especially triphenylstibine reacted only on heating under vacuum when the acetonitrile liberated could escape, and reaction conditions were critical. Prolonged heating of $ReCl_4(MeCN)_2$ with acetonitrile gave, inter alia, the complex $ReCl_3(MeCN)(PPh_3)_2$. As might be expected, the infra-red spectra of the three compounds differed significantly only in the position of the first A sensitive vibration of the APh_3 group (48) which was at 1087 $cm.^{-1}$s for the phosphine, 1074 $cm.^{-1}$ for the arsine and 1064 $cm.^{-1}$ for the stibine complex.

Reduction of $ReCl_4(MeCN)_2$.

When ethanolic trimethylamine was added to an acetone solution of $ReCl_4(MeCN)_2$ crystals of an orange salt separated out. The salt was readily soluble in water (ca. 50 g./l. at 20°) and the conductivity of the solution (Λ_0 = 90 mhos $cm.^2 mole^{-1}$) corresponded to a uni-univalent electrolyte. An orange ceasium salt was precipitated by an excess of caesium chloride from aqueous solution, and the cation was identified as trimethylammonium (Me_3NH^+) by isolating the tetraphenylborate. Aqueous solutions were rapidly oxidised to $ReCl_4(MeCN)_2$ by a number of mild oxidising agents, including cold nitric acid, iodine, ceric, ferric and

cupric salts, but not by molecular oxygen. Analyses corresponded approximately to the formula $[ReCl_4(MeCN)_2]^-$ for the anion, and a magnetic moment of 1.70 B.M. at 22° for the Me_3NH^+ salt was consistent with trivalent rhenium.

If the anion were indeed $[ReCl_4(MeCN)_2]^-$ then it should be formed by simple reduction of $ReCl_4(MeCN)_2$. The complex was shaken with ascorbic acid in aqueous acetonitrile buffered to pH 6 for a few minutes and caesium chloride was added to the resulting orange solution. Orange crystals, chemically identical with the caesium salt described above were obtained, but analyses were unsatisfactory. A solution of $ReCl_4(MeCN)_2$ in anhydrous acetonitrile was then reduced with cadmium amalgam and precipitated with caesium perchlorate in acetonitrile to give analytically pure $CsReCl_4(MeCN)_2$. If addition of caesium perchlorate was omitted, the reduced solution slowly deposited crystals of a hygroscopic cadmium salt. This initially contained acetonitrile in excess of that required by the formula $Cd[ReCl_4(MeCN)_2]_2$ (ν-CN at 2270 $cm.^{-1}$), but the excess was lost on prolonged storage under vacuum with disappearance of the infra-red CN absorption. Both the caesium and the cadmium salt could be titrated with ferric ions to a sharp Variamine Blue end-point (75). One electron (1.00 ± 0.03) per $[ReCl_4(MeCN)_2]^-$ ion was transferred in each case, and a precipitate of $ReCl_4(MeCN)_2$ was found (recovered in 85% yield).

The absence of a C≡N stretching absorption in the

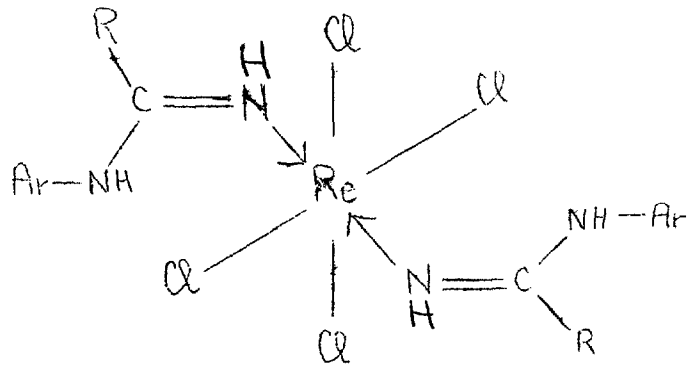
infra-red from even the thickest mulls is surprising and may be compared to the behaviour of the complexes $ReX_3(RCN)(PPh_3)_2$. Imine or di-imine structures for the $[ReCl_4(MeCN)_2]^-$ ion would require at least two equivalents of ferric salt in the redox reaction and must therefore be excluded. It thus seems that the quenching of the intense CN absorption in $ReCl_4(MeCN)_2$ results solely from the acquisition of a negative charge by the rhenium atom. It is far from obvious how this leads to a negligible change in dipole moment during the C≡N vibration.

Nucleophilic additions to the coordinated nitrile group.

The complexes $ReCl_4(RCN)_2$ reacted rapidly in the cold with primary aromatic amines ($ArNH_2$) to give orange crystalline compounds of stoicheiometry $ReCl_4(RCN)_2(ArNH_2)_2$. These were readily soluble in polar organic solvents to give non-conducting solutions. The magnetic moment of the p-toluidine complex (μ_{eff} = 3.54 B.M. at 22° for the solid) was in the usual range for octahedral rhenium(IV) compounds. The nitrile stretch disappeared from the infra-red and was replaced by intense C=N and >NH vibrations. In the light of these facts the compounds may be formulated as octahedral complexes of N-substituted amidines, and the infra-red spectra may be completely interpreted on this basis. The assignments are based on work on the free amidines (76) and are given in the experimental section. The amidine structure was confirmed in the complex from p-toluidine and $ReCl_4(MeCN)_2$ by

isolating N-p-tolyacetamidine on solvolysis in methanolic hydrogen chloride (see experimental section).

Analyses and physical measurements were consistent with the formulation $ReCl_4[RC(:NH).NH.Ar]_2$ for Ar = p-C_6H_4Me, m-C_6H_4F, and p-$C_6H_4(CO_2Et)$ and R = Me; and for Ar = p-$C_6H_4(OMe)$ and R = Ph. It is not possible to tell whether bonding is through the imine or the secondary amine nitrogen from the infra-red spectrum alone, but the imine group is by far the most basic (77,78) and structure VIII is therefore assigned to the compounds. The complexes were exceptionally stable to ligand substitution and dissolved in fused triphenylphosphine without reaction.



VIII

Electron drainage by the metal renders the nitrile carbon in $ReCl_4(RCN)_2$ more positive than in the free nitrile, and the amidine is evidently formed by nucleophilic attack of the activated carbon by the amine. The reaction is analogous to the formation of the well-established amidine complexes of platinum(II), $\{Pt[RC(:NH).NH.R']_2(R'NH_2)_2\}X_2$ (79,80), from $Pt(RCN)_2X_2$ and ammonia or amines (79,81). A method for the synthesis of amidines from nitriles and amines in the presence of Friedel Crafts catalysts ($AlCl_3$, $ZnCl_2$, $FeCl_3$, $SnCl_4$) is presumed to involve intermediate nitrile complexes (82).

Primary aliphatic amines gave a transient orange colouration with solutions of $ReCl_4(MeCN)_2$ but the colour rapidly faded and no amidine complexes were isolated. An attempt to prepare an amidine complex from $ReCl_4(MeCN)_2$ and N-p-tolylacetamidine was likewise unsuccessful. Aliphatic amines and amidines (78) are strong bases and presumably attack neutral ligands and chlorine atoms indiscriminately to give mixtures of products.

When $ReCl_4(MeCN)_2$ was briefly heated with methanol a complex reaction took place, and pale green crystals slowly separated on cooling. Analyses corresponded to the addition of two molecules of methanol and the infra-red spectrum included strong bands at 3268 $cm.^{-1}$, 1596 $cm.^{-1}$, 1248 $cm.^{-1}$ and 1059 $cm.^{-1}$ corresponding to the $>N-H$, $C=N$, asymmetric $\gtrsim C-O-Me$, and symmetric $\gtrsim C-O-Me$ stretching vibrations respectively, but there was

no nitrile absorption. A similar green complex was obtained by evaporating an acetonitrile solution of $ReCl_4(MeCN)_2$ with ethanol at room temperature. Both complexes may be formulated as derivatives of imidate esters, $ReCl_4[MeC(:NH).OR']_2$ (R' = Me, Et) formed by nucleophilic addition of alcohol to the nitrile group, in the same way as with the amidine complexes. The complexes were soluble in a number of organic solvents but severe losses occurred on attempted recrystallisation.

Mechanism of the reduction of rhenium pentachloride by acetonitrile.

Acetonitrile has been reported to reduce a number of metal halides, including cupric bromide with evolution of bromine (84), and the higher chlorides and bromides of vanadium (85), molybdenum and tungsten (71) with evolution of hydrogen halide, to form lower-valent complexes. No organic oxidation products were ever isolated from these systems, but it was suggested that the reaction might involve free radicals, such as $^{\cdot}CH_2CN$.

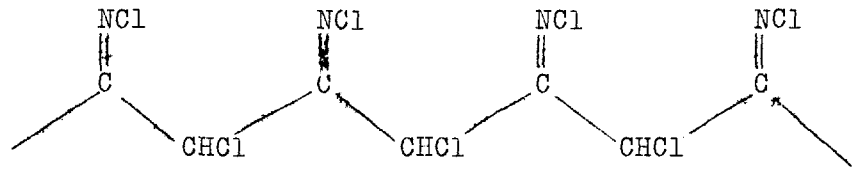
Rhenium pentachloride (7.3 g., 20 mM) was heated with acetonitrile to reflux for 30 min. under strictly anhydrous conditions with a stream of pure nitrogen passing through the solution. Hydrogen chloride (0.25 g., 6.8 mM) was evolved and was collected in potash, and the cold reaction mixture gave $ReCl_4(MeCN)_2$ (6.6 g., 80%) when diluted with ice. The solid was washed with a little methanol and the filtrate and washings were extracted at once with petroleum ether (b.p. 30-40°), into which neither

methanol nor acetonitrile are extracted from aqueous solution. The dried extract was concentrated under vacuum to give a pungent, light-yellow oil (0.36 g.), which contained 5.3% of nitrogen and 58% of chlorine. A fresh solution of the oil in aqueous ethanol was almost neutral and contained no ionic chlorine (no precipitate with silver nitrate). On warming the solution, it became strongly acidic and hydrochloric acid was liberated. It is clear that the oxidation product is an organic chlorocompound. Of the one chlorine atom lost by rhenium pentachloride, at least 34% formed hydrogen chloride and at least 30% entered the chlorocompound.

It is known that acetonitrile forms labile compounds with hydrogen chloride, hydrolysis of which gives acetamide or regenerates the nitrile (88). Acetonitrile containing hydrogen chloride was heated in a current of nitrogen and then extracted with petrol under the same conditions as used for the reaction mixture. No chlorocompound was obtained. When acetonitrile containing hydrogen chloride and 10 mg./ml. of chloroacetonitrile was similarly treated, a mixture of chloroacetamide and chloroacetonitrile was recovered.

The infra-red spectrum of the oil showed the absence of nitrile and N—H groups, and specifically of chloroacetamide and chloroacetonitrile. The only bands between 4000 and 1500 $cm.^{-1}$ were at 2940 vs (multiplet, γ-C—H), 1658 vs (γ-C=O), and 1538 s (γ-C=N or γ-C=O of $\alpha\beta$-unsaturated ketone?). The strongest bands below that region were at 1260 s, 1053 vs, and a

multiplicity of broad bands in the C—Cl stretching region (750-850 $cm.^{-1}$). These facts are best explained by assuming that the chlorocompound is a polymer formed by a radical mechanism, of which an idealised structure would be IX, but in which about



IX

half of the chlorimino groups are hydrolysed to carbonyl groups, and with the chlorine atoms distributed randomly. A solution of rhenium pentachloride in acetonitrile causes styrene to polymerise instantly, whereas a solution of the complex $ReCl_4(MeCN)_2$ in acetonitrile containing hydrogen chloride does not.

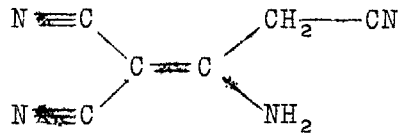
The reaction of trans-$ReOCl_3(PPh_3)_2$ with malononitrile.

The reaction of trans-$ReOCl_3(PPh_3)_2$ with malononitrile was investigated in an attempt to prepare a metal-carbene derivative by a Knoevenagel type condensation of the Re=O group. When the reactants were heated in benzene a complex reaction took place, hydrogen chloride was evolved, and a mixture of at least four substances resulted. These were initially detected by paper chromatography and were: (i) a black, presumably polymeric substance, insoluble in all solvents, (ii) an intensely brown substance, readily soluble in highly polar organic solvents, (iii) a soluble

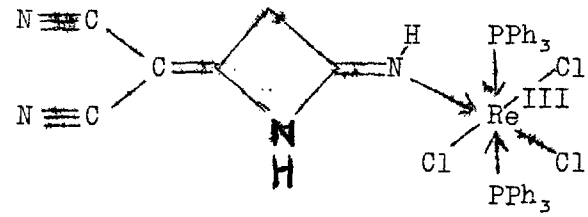
blue substance, adsorbed tenaciously by silica, and (iv) a crystalline red compound formed in 10-12% yield. Only the last product was obtained pure, and could be isolated almost quantitatively from the dark reaction mixture by the method described in the experimental section.

The red product analysed to $ReCl_3(C_6H_4N_4)(PPh_3)_2$ and a cryoscopic molecular weight measurement in sulpholan showed it to be monomeric. Solutions were non-conducting and the magnetic moment (μ_{eff} = 1.76 B.M. at 17°) suggested rhenium(III). The formula includes twice the elements of malononitrile, and since malononitrile is known to dimerise in the presence of acid to 2-amino-1,3,3-tricyano-2-propene (MND) (89), the reaction was carried out with MND in place of malononitrile. The yield increased to 30%, showing that MND(X) was indeed the reactive species. A reduction of the R = O function by triphenylphosphine (PPh_3) via substitution, in a manner analogous to the formation of the complexes $ReX_3(RCN)(PPh_3)_2$ (see Chapter II), was suspected and the yield of the red product increased further to 53% when additional PPh_3 was heated with the reactants. However, the compound is <u>not</u> $ReCl_3(MND)(PPh_3)_2$ with MND coordinated via a nitrile group, as it could not be obtained from, or converted into $ReCl_3(MeCN)(PPh_3)_2$ by substitution, nor did it react with carbon tetrachloride.

The infra-red spectrum showed only one sharp band in



X



XI

the C≡N stretching region. The very low frequency (2189 $cm.^{-1}$vs) is characteristic (90) of the enaminonitrile group, >N—C=C—C≡N, which is therefore retained in the complex. The absence of a band associated with the non-conjugated nitrile group shows that this group is coordinated or otherwise modified. In free MND occur three strong bands, two associated with the - NH_2 stretch and one with the - NH_2 bend (89,90). There is only one NH stretching vibration (3311 $cm.^{-1}$mw) in the complex and no NH bend was observed. This is consistent with the presence of a secondary amino group, of which the N—H bend is known to be extremely weak (91). These structural features are best encompassed by structure XI for the complex, which we suggest is trichloro[4-(dicyanomethylene)-azetid-2-imine]bis(triphenylphosphine)rhenium(III). The complex would be formed by intramolecular nucleophilic addition of the enamine amino group to the non-conjugated nitrile group, activated by initial coordination. The reaction is similar to the formation of amidines from $ReCl_4(RCN)_2$ and primary aromatic amines. The absence of a strong γ-C≡N absorption in the complex (XI) is note-

worthy, but an exact parallel may be drawn between the strong ν-C$\equiv$N absorption in $ReCl_4(RCN)_2$ but extremely weak absorption in $ReCl_3(RCN)(PPh_3)_2$, and the strong ν-C$=$N absorption in $ReCl_4$-(amidine)$_2$ but (presumably) extremely weak absorption in $ReCl_3$-(amidine)$(PPh_3)_2$.

When the red complex (XI) was heated with pyridine, free MND was obtained. Presumably the cyclic amidine is unstable in the free state and decyclises in basic solution.

EXPERIMENTAL

Microanalyses and molecular weights were by the Microanalytical Laboratories, Imperial College, and A. Bernhardt, Mikroanalytisches Laboratorium, Mülheim. Chlorine and bromine were determined as the silver halide, precipitated from dilute solutions ca. 0.5 N with respect to nitric acid, under which conditions we have shown rhenium does not interfere. Rhenium was determined gravimetrically as tetraphenylarsonium perrhenate. Samples which resisted hydrolysis by aqueous alkali were brought into solution for analysis by heating with potassium t-butoxide in t-butanol/tetrahydrofuran, evaporating almost to dryness, and extracting with hot, very dilute aqueous hydrogen peroxide. Molecular weights were determined with a Mechrolab Osmometer operating at 37°. Infra-red spectra were recorded in nujol or hexachlorobutadiene mulls unless otherwise stated, on a Grubb-Parsons Spectromaster, and visible spectra on a Perkin Elmer 350 Spectrophotometer. Infra-red frequencies are in wave numbers. Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian Associates Model B instrument at 56.45 Mc/sec. Chemical shifts are in p.p.m. relative to tetramethylsilane. Magnetic susceptibilities of solids were measured by the Gouy method and of solutions by the Evans n.m.r. method (83) at 20° in dichloromethane. Magnetic moments are corrected for the diamagnetism of

the ligands (52) unless otherwise stated. Commercial reagents were suitably purified when liable to contain moisture or oxidising impurities. Solvents were dried by standard methods (74) when necessary. All heating operations were under dry, oxygen-free nitrogen, unless otherwise stated. All samples were dried under vacuum over phosphorus pentoxide for at least 12 hr. unless otherwise stated.

Analytical data for the new carboxylato complexes described in this work are given in Table 2, for the other new rhenium(III) complexes in Table 3, and for the new rhenium(IV) complexes in Table 4. Other analytical data are given in the text of the experimental section.

Interaction of trans-Oxotrichlorobis(triphenylphosphine)-rhenium(V) and Carboxylic Acids under Pure Nitrogen. - trans-Oxotrichlorobis(triphenylphosphine)rhenium(V) (2.0 g.), prepared from rhenium metal by the standard method (51), was refluxed with carboxylic acid (10 g.) and toluene (20-40 ml.) for 6 hr. in a slow current of nitrogen (purified by passing successively through alkaline pyrogallol and concentrated sulphuric acid, then over solid potassium hydroxide and anhydrous calcium chloride). The nitrogen was allowed to escape through concentrated sulphuric acid, aqueous potassium hydroxide, and alkaline pyrogallol. The reaction products were allowed to cool under nitrogen for ca. 2 hr., but thereafter handled in air. Small, red crystals of tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4(PPh_3)_2$, and large, purple crystals of μ-chloro-di-μ-carboxylato-bis-(chlorotriphenylphosphinerhenium), $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$, separated out, and a further crop of the latter was obtained by concentrating the purple mother liquor. Triphenylphosphine oxide was isolated from the mother liquor and hydrogen chloride collected in the potash wash bottles. Small amounts of orange tetra-μ-carboxylato-bis[chlororhenium(III)], $Re_2Cl_2(R.CO_2)_4$, were invariably formed, but not always isolated.

Purification of the compounds $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ clearly depends on the nature of R, but the following procedure was found adequate in most cases. Extraction of the solid

mixture with small amounts of dichloromethane left most of the $ReCl_4(PPh_3)_2$ undissolved, and crude $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ separated from the extract on addition of ether (petrol for R higher than C_6). The compound was then extracted with warm 1-chlorobutane [in which $ReCl_4(PPh_3)_2$ is almost insoluble], recrystallised by evaporation, further recrystallised from hot benzene (unsuitable for R higher than C_9) and dichloromethane ether, then dried under vacuum below 40°. All solvents likely to contain peroxides must be freshly redistilled over ferrous sulphate, and alcohols, ketones, and carbon tetrachloride should not be used for a final recrystallisation as they slowly react with these compounds. Only significant departures from the above procedure will be indicated below.

(a) Acetic Acid. - As above, except that 40 ml. of glacial acetic acid were used and the toluene omitted, to give purple hexagonal prisms of μ-chloro-di-μ-acetato-bis(chlorotriphenylphosphinerhenium), (1.2 g., 88%). This compound proved to be the most difficult member of the series to purify, and analytically pure material could not be obtained. It was identified as a member of the series by its physical properties. The compound was insoluble in petrol, ether, ethanol, toluene, etc., sparingly soluble in benzene (ca. 1.3 g./l.), but readily soluble in chloroform (ca. 50 g./l.) and dichloromethane to give vivid purple solutions. A sample of the compound (0.25 g.)

in chlorobenzene (10 ml.) was refluxed with acetic acid (10 ml.) under nitrogen for 3 days to give tetra-μ-acetato-bis[chloro-rhenium(III)], (0.1 g., 66%).

(b) Caproic acid. The above method gave $ReCl_4(PPh_3)_2$ (0.7 g., 34%) and purple needles of μ-chloro-di-μ-caproato-bis-(chlorotriphenylphosphinerhenium) (0.5 g., 33%). The compound was sparingly soluble in ether, readily soluble in hot benzene, and very soluble in dichloromethane and tetrahydrofuran. The magnetic moment in solution was 1.43 B.M.

(c) Caprylic acid. The above method gave $ReCl_4(PPh_3)_2$ (0.7 g., 34%) and purple needles of μ-chloro-di-μ-caprylato-bis-(chlorotriphenylphosphinerhenium) (0.5 g., 32%), readily soluble in toluene and acetone, and very soluble in benzene and dichloro-methane. The corrected (52) paramagnetic susceptibility of the solid was 1.60×10^{-3} CG $mole^{-1}$ at 27°, corresponding to a magnetic moment of 1.96 B.M., and in solution, the magnetic moment was 1.33 B.M. The n.m.r. spectrum in dichloromethane showed two broad resonances of roughly equal intensity at τ 2.58 (phenyl protons) and τ 9.17 (methylene protons). The infra-red spectrum in the region 1600-1300 $cm.^{-1}$ showed bands at 1479vs (ν-CC of Ph), 1468s, 1460(sh), 1458(sh), 1437vs (ν-CC of Ph), 1409vs (ν_s-CO_2), 1387w, and 1366vw.

(d) Lauric acid. As above, except that 5 g. of trans-$ReOCl_3(PPh_3)_2$, 10 g. of lauric acid, and 50 ml. of toluene were

used. After completion of the reaction, the mixture was evaporated to dryness in vacuo and the residue extracted with warm ethylene glycol to remove excess lauric acid. A further extraction with hot petrol (b.p. 60-80°) left crude $ReCl_4(PPh_3)_2$ (2.2 g., 43%) undissolved, and crude μ-chloro-di-μ-laurato-bis(chlorotriphenylphosphinerhenium) (1.3 g., 31%) crystallised out on concentrating the petrol extract. The compound was purified by recrystallisation from warm methanol, then twice from hot petrol (b.p. 60-80°) and dried in vacuo to give purple needles. On alkaline hydrolysis, followed by acidification, the compound yielded two moles of lauric acid per mole [Found: lauric acid, 29.3%. $Re_2Cl_3(C_{11}H_{23}CO_2)_2(PPh_3)_2$ requires lauric acid 28.6%] The compound was sparingly soluble in alkanes at 0°, but at 40° was readily soluble in most classes of organic solvents, except polyhydric alcohols, to give vivid purple solutions (in dimethyl phthalate: λ 715 mμ, ε 1250; λ 560 mμ, ε 1060).

(e) Phenylacetic acid. The above method gave $ReCl_4(PPh_3)_2$ (0.5 g., 25%) and μ-chloro-di-μ-phenylacetato-bis(chlorotriphenylphosphinerhenium) (0.4 g., 26%), which was recrystallised from methanol and benzene to give purple prisms. The compound was sparingly soluble in ether, methanol, and carbon tetrachloride but was readily soluble in hot benzene and dichloromethane. The magnetic moment in solution was 1.29 B.M. Small amounts of tetra-μ-phenylacetato-bis[chlororhenium(III)] were also isolated, and

were recrystallised from hot acetone to give orange needles.

(f) Cyclohexanecarboxylic acid. The above method gave $ReCl_4(PPh_3)_2$ (0.7 g., 34%) and purple prisms of μ-chloro-di-μ-cyclohexanecarboxylato-bis(chlorotriphenylphosphinerhenium) (0.5 g., 33%). The compound was insoluble in ether and cold carbon tetrachloride, but very soluble in benzene and dichloromethane.

Interaction of trans-Oxotrichlorobis(triphenylphosphine)-rhenium(V) and Carboxylic Acids in Air. - trans-Oxotrichlorobis-(triphenylphosphine)rhenium(V) (2.0 g.) was refluxed with carboxylic acid (10 g.) and toluene (20-40 ml.) for 6 hr. in air. Crystals of red $ReCl_4(PPh_3)_2$, dark purple $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$, and dark green μ-oxo-μ-chloro-μ-carboxylato-bis[dichlorotriphenyl-phosphinerhenium(IV)], $Re_2OCl_5(R.CO_2)(PPh_3)_2$, separated on cooling or on concentrating the mother liquor. The last two compounds were separated from $ReCl_4(PPh_3)_2$ as before, and from each other by fractional crystallisation from one (or more) of the following solvents: benzene, methyl ethyl ketone, 1-chlorobutane, carbon tetrachloride, and dichloromethane/ether. Less soluble $Re_2OCl_5(R.CO_2)(PPh_3)_2$ was easy to obtain pure, but the purple compound $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ could generally be obtained only with considerable loss by extracting it from the tail fractions with carbon tetrachloride/petrol, then recrystallising several times from one (or more) of the above solvents.

(a) Acetic acid. As above, except that 40 ml. of

glacial acetic acid were used, the toluene was omitted, and refluxing prolonged to 12 hr., to give red $ReCl_4(PPh_3)_2$ (0.7 g., 33%) and green μ-oxo-μ-chloro-μ-acetato-bis[dichlorotriphenylphosphinerhenium(IV)] (0.4 g., 29%), but only small amounts of purple $Re_2Cl_3(CH_3.CO_2)_2(PPh_3)_2$ and traces of orange $Re_2Cl_2(CH_3.CO_2)_4$. When refluxing was further prolonged to 48 hr. only the compounds $Re_2OCl_5(CH_3.CO_2)(PPh_3)_2$ (0.7 g., 50%), and $Re_2Cl_2(CH_3.CO_2)_4$ (0.2 g., 24%), could be isolated, and were accompanied by dark brown, soluble material.

The compound $Re_2OCl_5(CH_3.CO_2)(PPh_3)_2$ separates from dichloromethane in large, splendid black hexagonal prisms (green when powdered), m.p. 247.5° (decomp.). The solid is diamagnetic [χ_M = -0.48 x 10^{-3} CG mole^{-1} at 20°, in agreement with the value calculated from Pascal's constants (52)] and gives non-conducting solutions in nitrobenzene. It is insoluble in alkanes, alcohols, ethers, and carbon tetrachloride, sparingly soluble in benzene (ca. 1.3 g./l., almost independent of temp.) and acetic acid, moderately soluble in nitrobenzene, acetone, and chloroform (ca. 10 g./l., almost independent of temp.), readily soluble in dichloromethane and tetrahydrofuran, and freely soluble in thionyl chloride without decomposition. All solutions are vivid blue [in dichloromethane: λ 614 mμ, ε 2300; λ 568 mμ, ε 2300; λ 420 mμ (weak); λ 372 mμ, ε 2400]. The n.m.r. spectrum in "deuterochloroform" or thionyl chloride showed singlets at τ 2.64 (phenyl

protons) and τ 9.16 (methyl protons), intensity ratio ca. 10:1. The infra-red spectrum in the region 3000-600 cm.$^{-1}$ showed bands at 1479vs (ν-CC of Ph), 1445vs (ν-CO_2 ?), 1439vs (sh), and 1432vs (ν-CC of Ph ?), all of which persisted in thionyl chloride solution and were shifted by no more than 4 cm.$^{-1}$. All other bands in this region could be definitely assigned to triphenylphosphine (PPh_3) modes. A sample of the compound (0.4 g.) was refluxed in acetic acid (10 ml.) for 4 days under nitrogen; at least 90% was recovered. A millimolar solution in dichloromethane showed no change in the visible spectrum after standing in air for 2 months.

(b) Propionic acid. As above, except that 40 ml. of propionic acid were used, the toluene omitted, and the mixture refluxed for 20 min. to give $ReCl_4(PPh_3)_2$ (0.7 g., 33%) and dark green prisms of μ-oxo-μ-chloro-μ-propionato-bis[dichlorotriphenylphosphinerhenium(IV)] (0.5 g., 35%), together with some purple compound (not isolated). The infrared spectrum of the green compound showed bands at 1480vs (ν-CC of Ph), 1462s (ν_2-CO_2 ?), 1458(sh), 1451(sh), 1437(sh), 1434vs (ν-CC of Ph), ca. 1420(sh) (ν_1-CO_2 or δ-CH_2), 1376m (δ_1-CH_3), 1353vw (PPh_3 mode), 1299m (skeletal vib. of Et), and thereafter only PPh_3 modes down to 600 cm.$^{-1}$.

(c) Pivalic acid. The above method gave $ReCl_4(PPh_3)_2$ (0.9 g., 44%) and purple crystals of μ-chloro-di-μ-pivalato-bis-

(chlorotriphenylphosphinerhenium) (0.5 g., 35%) only. The compound gave vivid purple solutions in organic solvents (in dimethyl phthalate: λ 715 mμ, ε 1200; λ 560 mμ, ε 1000) and was non-conducting in nitrobenzene. The n.m.r. spectrum in dichloromethane showed broad singlets at τ 2.56 (phenyl protons) and τ 9.77 (methyl protons), intensity ratio ca. 3:2. The infrared spectrum in the region 1600-1200 $cm.^{-1}$ showed bands at 1481vs (ν-CC of Ph), 1473sh (ν_2-CO_2 ?), 1456sh, 1453m, 1433vs (ν-CC of Ph), 1412vs (ν_1-CO_2 or δ_2-CH_3), 1376s and 1361s (δ_1-CH_3), and 1218s (skeletal vib. of t-Bu). The bands in the region 1600-1400 $cm.^{-1}$ persisted in bromoform solution. A millimolar solution in dimethyl phthalate showed no change in the visible absorption spectrum after standing for 24 hr. in air, but extensive decomposition was apparent after 7 days. A similar solution, sealed under nitrogen, underwent no apparent change in 2 months.

(d) Caprylic acid. The above method gave $ReCl_4(PPh_3)_2$ (0.7 g., 33%), $Re_2Cl_3(n\text{-}C_7H_{15}.CO_2)_2(PPh_3)_2$ (0.2 g., 13%), and dark green needles of μ-oxo-μ-chloro-μ-caprylato-bis[dichlorotriphenylphosphinerhenium(IV)] (0.4 g., 27%). The compound was sparingly soluble in acetone and nitrobenzene, readily soluble in chloroform and dichloromethane, and freely soluble in thionyl chloride, giving vivid blue solutions. It was non-conducting in nitrobenzene. The n.m.r. spectrum in thionyl chloride showed a singlet at τ 2.64 (phenyl protons) and a poorly resolved multiplet

at τ 9.04 (methyle protons), intensity ratio ca. 1.7:1. The infra-red spectrum in the region 3500-600 cm.$^{-1}$ showed bands at 3063w (ν-CH of Ph), 2955w and 2946(sh) (ν_2-CH_3), 2926m (ν_2-CH_2), 2863w (ν_1-CH_3), 2855m (ν_1-CH_2), 1583vw and 1566vw (PPh_3 modes), 1490m (disappears in solution), 1482s (ν-CC of Ph), 1464w, 1458(sh), 1452m, 1439vs, 1435vs (ν-CC of Ph), 1420m (1413m in solution; ν_1-CO_2 or δ-CH_2), and thereafter only PPh_3 modes, except for the CH_2 rocking mode of the -$(CH_2)_n$-chain at 726m.

(e) Capric acid. The above method gave $ReCl_4(PPh_3)_2$ (0.5 g., 25%), some purple compound (not isolated), and dark green needles of μ-oxo-μ-chloro-μ-caprato-bis[dichlorotriphenylphosphinerhenium(IV)] (0.45 g., 30%). On alkaline hydrolysis, followed by acidification at 0°C., the compound yielded one mole of capric acid per mole [Found: capric acid, 13.6%. $Re_2OCl_5(C_9H_{19}\cdot CO_2)(PPh_3)_2$ requires capric acid, 13.7%]. The compound was readily soluble in benzene, chloroform, and acetone giving blue solutions.

Interaction of trans-Oxotrichlorobis(triphenylphosphine)-rhenium(V) and Carboxylic Acids under Nitrogen containing Small Amounts of Oxygen. - The reactions and separations were carried out exactly as described in the preceding section, except that the reaction vessel was flushed with nitrogen and then stoppered before heating was commenced. No precautions were taken to exclude small amounts of oxygen, and compounds of the type

$Re_2OCl_5(R.CO_2)(PPh_3)_2$ were invariably formed in addition to $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ and $ReCl_4(PPh_3)_2$, whenever such compounds could be obtained in air. Yields were naturally rather variable but the reactions proceeded more cleanly than in air. Compounds of the type $Re_2OCl_5(R.CO_2)_2(PPh_3)_2$ were obtained with benzoic and anisic acids, of the type $Re_2Cl_3(R.CO_2)_2(PPh_3)_2$ with pivalic acid, and of both types with acetic, α-methylbutyric, caprylic, capric, lauric, and palmitic acids. Only compounds not already described are mentioned below.

(a) α-Methylbutyric acid. The above method gave $ReCl_4(PPh_3)_2$ (0.6 g., 29%), purple crystals of μ-chloro-di-μ-(α-methylbutyrato)bis(chlorotriphenylphosphinerhenium) (0.6 g., 41%) and green crystals of μ-oxo-μ-chloro-μ-(α-methylbutyrato)-bis[dichlorotriphenylphosphinerhenium(IV)] (0.15 g., 10%).

(b) Lauric acid. The above method gave $ReCl_4(PPh_3)_2$ (0.9 g., 44%), some $Re_2Cl_3(C_{11}H_{23}.CO_2)_2(PPh_3)_2$ (not isolated), and μ-oxo-μ-chloro-μ-laurato-bis[dichlorotriphenylphosphinerhenium(IV)] (0.4 g., 25%). The filtered reaction mixture was evaporated almost to dryness and extracted with petrol (b.p. 30-40°), leaving the compound undissolved as a green tar. This was recrystallised several times from benzene/ether and from dichloromethane/ether to give dark green needles or prisms. These were sparingly soluble in alkanes, alcohols, and ethers, but readily soluble in most other classes of organic solvents to give vivid blue solutions

[in dichloromethane: λ 615 mμ, ε 2400; λ 570 mμ, ε 2300; λ 420 mμ (weak); λ 372 mμ, ε 2500].

(c) Palmitic acid. The above method gave $ReCl_4(PPh_3)_2$ (0.8 g., 39%), some purple compound (not isolated), and μ-oxo-μ-chloro-μ-palmito-bis[dichlorotriphenylphosphinerhenium(IV)] (estimated yield ca. 25%), obtained in the same way as the corresponding laurate, but with greater loss, as dark green needles. The compound was insoluble in water and polyhydric alcohols, sparingly soluble in alkanes, but readily soluble in most other classes of organic solvents giving vivid blue solutions [in dichloromethane: λ 615 mμ, ε 2200 mμ; λ 570 mμ, ε 2200 mμ; λ 420 mμ (weak); λ 372 mμ, ε 2500].

(d) Benzoic acid. As above, except that the reaction mixture was evaporated to dryness and extracted with ether to remove benzoic acid, then with benzene to remove $ReCl_4(PPh_3)_2$, and the residue recrystallised from dichloromethane/benzene to give dark green needles of μ-oxo-μ-chloro-μ-benzoato-bis[dichlorotriphenylphosphinerhenium(IV)] (0.4 g., 27%). These were moderately soluble in dichloromethane, less so in chloroform, and very sparingly in most other solvents. The solutions were blue [in dichloromethane λ 615 mμ, ε 2800; λ 570 mμ, ε 2700; λ 420 mμ (weak); λ 372 mμ, ε 2900].

(e) Anisic acid. As above, except that the solid reaction product was washed thoroughly with hot ethanol and ether,

extracted with benzene to remove $ReCl_4(PPh_3)_2$ (0.6 g., 30%), and the residue recrystallised from dichloromethane/benzene and dichloromethane/ether to give green microcrystals of μ-oxo-μ-chloro-μ-anisato-bis[dichlorotriphenylphosphinerhenium(IV)] (0.7 g., 46%). The compound was very sparingly soluble in most solvents except dichloromethane, in which it gave greenish-blue solutions.

Tetrachlorobis(triphenylphosphine)rhenium(IV). - The crude product obtained above was recrystallised from benzene and cold dichloromethane/acetonitrile and dried in vacuo to give small, carmine-red rhombic prisms (yield ca. 30-40%). Alternatively, trans-$ReOCl_3(PPh_3)_2$ (5.0 g.) and triphenylphosphine (5.0 g.) were heated for 2 hr. in boiling propionic acid (50 ml.) under hydrogen chloride, to give the compound in prisms (4.9 g., 96%) [Found: C, 50.5; H, 3.7; Cl, 16.5; O, absent; Re, 21.7%; M, 839 (chloroform). Calc. for $C_{36}H_{30}Cl_4P_2Re$: C, 50.7; H, 3.6; Cl, 16.6; Re, 21.8%; M, 853]. The compound was sparingly soluble in most organic solvents but was moderately soluble in benzene (ca. 2.3 g./l., independent of temperature), chloroform (ca. 7.4 g./l., independent of temperature), and dichloromethane, and very soluble in thionyl chloride, to give bright-red solutions. The magnetic susceptibility of the solid was 4.78×10^{3} CG $mole^{-1}$ at 23° which, when corrected for the diamagnetism of the ligands (52) corresponds to an effective magnetic moment of 3.54 B.M., in agreement with the value of Freni and Valenti (23). The infra-red spectrum in the

region 2000-500 cm.$^{-1}$ showed only triphenylphosphine bands (48): 1583vw (ν-CC), 1566vw, 1478vs (ν-CC), 1431vs (ν-CC), 1330vw, 1312w, 1188w (β-CH), 1155w (β-CH), 1087s (first P-sensitive vib.), 1073(sh) (β-CH), 1026w (β-CH), 996m (breathing mode), 971(sh) (γ-CH), 844w (γ-CH), 746vs and 742vs (γ-CH), 726w and 703m (second P-sensitive vib.), 692vs (γ-CH), 521vs, 505(sh), 503(sh), 501s, and 493m (third P-sensitive vib., split into quintet).

Tetrachloro(pyridine)(triphenylphosphine)rhenium(IV). - Powdered $ReCl_4(PPh_3)_2$ (0.5 g.) was heated with pyridine (5 ml.) for 10 min. and the solution evaporated to dryness under reduced pressure. The tarry residue was triturated with petrol (b.p. 30-40°) until it crystallised, and recrystallised from dichloro/ether to give the compound $ReCl_4(Py)PPh_3$ in orange needles (0.35 g., 89%) [Found: C, 41.0; H, 3.0; N, 2.1%; M, 608 (chloroform). $C_{23}H_{20}Cl_4NPRe$ requires C, 41.3; H, 3.0; N, 2.1%; M, 670]. The infra-red spectrum in the region 2000-500 cm.$^{-1}$ showed all the triphenylphosphine bands given above for $ReCl_4(PPh_3)_2$ (which did not shift by more than 5 cm.$^{-1}$) and, in addition, the following bands assigned to coordinated pyridine (53): 1607m, 1448s, 1376ms, 1357w, 1217m, 1156w, 1065ms, 1043m, 1011m, 957w, 761s, 690s, and 643m. No other bands [of pyridinum (53) in particular] were observed.

Tetrachlorobis(pentane-2,4-dionato)-di-μ-(pentane-2,4-dionato)dirhenium(IV). - Powdered $ReCl_4(PPh_3)_2$ (1.0 g.) was heated

with acetylacetone (15 ml.) for 1 hr. and the solid separating on cooling was recrystallised from dichloromethane to give orange prisms (0.2 g., 37%) [Found: C, 26.7; H, 3.1; O, 14.3%; M, 887 (chloroform). Calc. for $C_{20}H_{28}Cl_4O_8Re_2$: C, 26.4; H, 3.1; O, 14.1%; M, 911]. The infrared spectrum was identical with that of a sample prepared by Grove's method (17).

Interaction of Tetrachlorobis(triphenylphosphine)rhenium(IV) and Carboxylic Acids under Pure Nitrogen. - Finely powdered $ReCl_4(PPh_3)_2$ (0.2 g.) was refluxed with carboxylic acid (10 ml.) and toluene (30 ml.) for 18 hr. under purified nitrogen (see above). Purple complexes of the type $Re_2Cl_3(R.CO_2)(PPh_3)_2$ were obtained with acetic (R = Me, yield 87%), isovaleric (R = $Me_2CH.CH_2$, yield 16%), and cyclohexanecarboxylic (R = C_6H_{11}, yield 26%) acids. Triphenylphosphine oxide, hydrogen chloride and small amounts of the complexes $Re_2Cl_2(R.CO_2)_4$ were also obtained in each case.

Interaction of Tetrachlorobis(triphenylphosphine)rhenium(IV) and Carboxylic Acids in Air. - (a) Isovaleric acid. Powdered $ReCl_4(PPh_3)_2$ (2.0 g.) was refluxed with isovaleric acid (10 g.) and toluene (20 ml.) for 18 hr. in air. The products were separated as usual, giving purple prisms of μ-chloro-di-μ-isovalerato-bis-(chlorotriphenylphosphinerhenium) (0.3 g., 20%) and green prisms of μ-oxo-μ-chloro-μ-isovalerato-bis[dichlorotriphenylphosphine-rhenium(IV)] (0.2 g., 15%). The infra-red spectrum of the purple complex in the region 1600-1200 $cm.^{-1}$ showed bands at 1485s (ν-CC of Ph), 1466vs (ν_2-CO_2?), 1462(sh), 1439vs, 1436vs (ν-CC of

Ph?), 1418vs, 1397vs (ν_1-CO_2 or δ-CH_2), 1386m and 1370m (δ_1-CH_3), and 1270m (skeletal mode of alkyl residue). The green complex showed bands at 1484s (ν-CC of Ph), 1462m, 1448(sh), 1437vs (ν-CC of Ph), 1417m, 1389w and 1372w (δ_1-CH_3), 1333vw (PPh_3 mode), 1316vw (PPh_3 mode) and 1268w (skeletal mode of alkyl residue).

(b) Phenylacetic acid. Powdered $ReCl_4(PPh_3)_2$ (1.0 g.) was refluxed with phenylacetic acid (5.0 g.) and toluene (30 ml.) for 12 hr. in air, to give $Re_2Cl_3(Ph.CH_2.CO_2)_2(PPh_3)_2$ (0.1 g., 13%) and green microcrystals of μ-oxo-μ-chloro-μ-phenylacetato-bis[dichlorotriphenylphosphinerhenium(IV)] (0.2 g., 27%), sparingly soluble in methanol, ether, and benzene, but readily soluble in dichloromethane.

Disproportionation of trans-Oxotrichlorobis(triphenylphosphine)rhenium(V). - trans-$ReOCl_3(PPh_3)_2$ (2.0 g.) was refluxed with glacial acetic acid (75 ml.) in an atmosphere of hydrogen chloride for 18 hr., and the product recrystallised from dichloromethane/acetonitrile to give red prisms of $ReCl_4(PPh_3)_2$ (1.3 g., 64%). When xylene was used instead of acetic acid under the same conditions, 0.9 g. (44%) of $ReCl_4(PPh_3)_2$ was obtained in 9 hr.

Interaction of the complex $Re_2OCl_5(Me.CO_2)(PPh_3)_2$ with Sodium Methoxide. - A solution of the complex $Re_2OCl_5(Me.CO_2)$-$(PPh_3)_2$ (0.5 g.) in dichloromethane (50 ml.) was shaken with sodium methoxide (0.2 g.) in methanol (5 ml.) for 5 min., then evaporated to dryness in vacuo. The residue was extracted with

benzene, and the purple extract filtered from sodium salts and concentrated to a small volume. Purple crystals of the compound $Re_2OCl_4(OMe)(Me.CO_2)(PPh_3)_2$ separated on addition of ether [Found: C, 40.0; H, 3.3; Cl, 12.2%; M, 1125 (chloroform). $C_{39}H_{36}Cl_4O_4P_2Re_2$ requires C, 40.9; H, 3.2; Cl, 12.4%; M, 1145].

Interaction of trans-Oxotrichlorobis(triphenylphosphine)-rhenium(V) with Acid Anhydrides under Pure Nitrogen. - (a) Acetic anhydride.

(i) Trans-$ReOCl_3(PPh_3)_2$ (5 g.) was refluxed with acetic anhydride for 6 hr. to give tetra-μ-acetato-bis[chlororhenium(III)] (0.4 g., 20%) and μ-chloro-di-μ-acetato-bis(chlorotriphenylphosphine-rhenium) (0.5 g., 14%). The filtrate from the above compounds was diluted with aqueous acetic acid to give a yellow precipitate, which was recrystallised from dichloromethane–ether to give canary yellow crystals [Found: C, 49.0, 49.8; H, 3.8, 3.8; Cl, 19.5, 19.8; Re, 20.83%. $C_{36}H_{30}Cl_5P_2Re$ requires C, 48.7; H, 3.4; Cl, 20.0; Re, 21.0%. $C_{38}H_{33}Cl_5OP_2Re$ requires C, 49.0; H, 3.6; Cl, 19.0; Re, 20.0%]. The magnetic susceptibility of the solid was 5.92×10^{-6} c.g.s. $g.^{-1}$ at 20°. The infra-red spectrum showed bands at 1583ms, 1571vw, 1479vs, 1437vs, 1433vs, 1334m, 1316m, 1188ms, 1149s, 1111vs, 1093s, 1073sh, 1026v, 996s, 979w, 787w, 774w, 744vs, 725vs, 690vs, 686vs.

(ii) Trans-$ReOCl_3(PPh_3)_2$ (2.0 g.) was refluxed with acetic anhydride for 12 hr. and the residue washed with dichloro-

methane to give orange microcrystals of tetra-μ-acetato-bis[chloro-rhenium(III)] (0.5 g., 61%) [Found: C, 14.4; H, 2.0; O, 18.8%. Calc. for $C_8H_{12}Cl_2O_8Re_2$: C, 14.4; H, 1.8; O, 18.8%]. The physical properties and infra-red spectrum of the compound were identical with those reported by Taha and Wilkinson (25).

(b) Propionic anhydride. (i) Trans-$ReOCl_3(PPh_3)_2$ (5.0 g.) was refluxed with propionic anhydride (30 ml.) and toluene (30 ml.) for 18 hr. Orange needles of tetra-μ-propionato-bis[chloro-rhenium(III)] (0.5 g., 22%) separated on cooling, and purple prisms of μ-chloro-di-μ-propionato-bis(chlorotriphenylphosphine-rhenium) (0.6 g., 17%) were obtained on concentrating the mother liquor under reduced pressure. The purple complex was sparingly soluble in alkanes, alcohols, and ether, moderately soluble in benzene, and readily soluble in dichloromethane giving purple solutions. The magnetic moment in solution was 1.34 B.M. The infra-red spectrum in the region 1600-1200 $cm.^{-1}$ showed bands at 1484vs (ν-CC of Ph), 1471s (ν_2-CO_2?), 1462s, 1450w, 1435vs (ν-CC of Ph), 1421vs (ν_1-CO_2?), 1376m (δ_1-CH_3), 1333vw (PPh_3 mode), 1312w (PPh_3 mode), and 1292s (skeletal vib. of Et).

(ii) trans-$ReOCl_3(PPh_3)_2$ (2.0 g.) was refluxed with propionic anhydride (40 ml.) for 6 hr. and the residue recrystallised from benzene/dichloromethane to give orange needles of tetra-μ-propionato-bis[chlororhenium(III)] (0.5 g., 56%) [Found: C, 20.0; H, 2.9%. Calc. for $C_{12}H_{20}Cl_2O_8Re_2$: C, 19.5; H, 27%], readily

soluble in dichloromethane, but sparingly soluble in benzene and ether.

(c) Butyric anhydride. (i) trans-$ReOCl_3(PPh_3)_2$ (4.0 g.) was refluxed with butyric anhydride (25 ml.) and toluene (25 ml.) for 6 hr. to give red $ReCl_4(PPh_3)_2$ (1.3 g., 32%), purple μ-chloro-di-μ-butyrato-bis(chlorotriphenylphosphinerhenium) (0.6 g., 21%) and orange tetra-μ-butyrato-bis[chlororhenium(III)] (0.3 g., 16%). The magnetic moment of the purple complex was 1.37 B.M.

(ii) trans-$ReOCl_3(PPh_3)_2$ (2.0 g.) was refluxed with butyric anhydride (25 ml.) and toluene (25 ml.) for 24 hr. to give orange crystals of tetra-μ-butyrato-bis[chlororhenium(III)] (0.66 g., 70%), which were recrystallised from hot benzene [Found: C, 24.4; H, 3.85%; M, 752 (chloroform). Calc for $C_{16}H_{28}Cl_2O_8Re_2$: C, 24.3; H, 3.5%; M, 792]. No purple compound could be isolated from the mother liquor.

Interaction of trans-Oxotribromobis(triphenylphosphine)-rhenium(V) and Carboxylic Acids under Nitrogen containing Small Amounts of Oxygen. - The reactions were carried out exactly as with trans-$ReOCl_3(PPh_3)_2$ and the products similarly separated. In no case could $Re_2Br_3(R.CO_2)_2(PPh_3)_2$ be detected,but an unidentified yellow substance was usually produced.

(a) Acetic acid. The above method gave red microcrystals of tetrabromobis(triphenylphosphine)rhenium(IV) (0.4 g., 19%) [Found: C, 41.5; H, 3.0%; O, absent; M, 1041 (chloroform). Calc.

for $C_{36}H_{30}Br_4P_2Re$: C, 42.0; H, 2.9%; M, 1031], and dark brownish-green prisms of μ-oxo-μ-bromo-μ-acetato-bis[dibromotriphenylphosphinerhenium(IV)] (0.6 g., 42%). The compound was sparingly soluble in ether and benzene, but readily soluble in chloroform and dichloromethane to give bright green solutions.

(b) Caproic acid. The above method gave $ReBr_4(PPh_3)_2$ and dark brownish-green prisms of μ-oxo-μ-bromo-μ-caproato-bis[dibromotriphenylphosphinerhenium(IV)] (0.4 g., 27%), sparingly soluble in ether and alkanes, but readily soluble in benzene and dichloromethane to give bright green solutions.

Interaction of trans-Oxotribromobis(triphenylphosphine)-rhenium(V) and Acid Anhydrides under Pure Nitrogen. - (a) Acetic anhydride. trans-$ReOBr_3(PPh_3)_2$ (2.0 g.) was refluxed with acetic anhydride (40 ml.) for 18 hr. and the solid product washed with benzene and dichloromethane to give orange microcrystals of tetra-μ-acetato-bis[bromorhenium(III)] (0.35 g., 44%), sparingly soluble in dichloromethane and practically insoluble in all other solvents

(b) Propionic anhydride. trans-$ReOBr_3(PPh_3)_2$ (2.0 g.) was refluxed with propionic anhydride (30 ml.) and toluene (30 ml.) for 18 hr. to give orange needles of tetra-μ-propionato-bis[bromorhenium(III)] (0.35 g., 41%), which were recrystallised from benzene/dichloromethane. The compound was readily soluble in dichloromethane, but sparingly soluble in benzene.

(c) Butyric anhydride. trans-$ReOBr_3(PPh_3)_2$ (2.0 g.) was refluxed with n-butyric anhydride (30 ml.) and toluene (20 ml.) for 18 hr. to give orange needles of tetra-μ-butyrato-bis[bromorhenium(III)], which were recrystallised from benzene/dichloromethane and ether/dichloromethane to give orange microcrystals (0.6 g., 66%). The compound was insoluble in ether, moderately soluble in hot benzene, and freely soluble in dichloromethane giving orange solutions.

Trichloro(acetonitrile)bis(triphenylphosphine)rhenium(III). -

Method A. Trans-$ReOCl_3(PPh_3)_2$ (5.0 g.), acetonitrile (20 ml.), and toluene (60 ml.) were heated for 2 hr. under reflux. Orange-yellow crystals of the compound (1.6 g., 31%) separated on cooling, and were recrystallised from dichloromethane-ethanol, and for analyses also from dichloromethane-ether.

Method B. Trans-$ReOCl_3(PPh_3)_2$ (5.0 g.), triphenylphosphine (5.0 g.), acetonitrile (35 ml.), and toluene (40 ml.) were heated for 2 hr. under reflux. Ethanol (100 ml.) was added to the cold solution to give crystals of the compound (4.6 g., 90%). The pure compound separated as orange-yellow leaflets or needles (4.3 g.) on adding ethanol to a saturated dichloromethane solution. The filtrate from the reaction was evaporated to dryness under vacuum, and the dirty-white residue separated by solvent extraction using aqueous methanol, ether, and petrol into triphenylphosphine (3.2 g.) and triphenylphosphine oxide (1.5 g.). The amounts

calculated from equation (8) are 3.4 g. and 1.7 g. respectively.

The magnetic susceptibility (Gouy method) of solid $ReCl_3(MeCN)(PPh_3)_2$ corrected for diamagnetism of ligands is $\chi_m(corr) = 1.10 \times 10^{-3}$ c.g.s.u. at 23°C. Its infra-red spectrum showed PPh_3 bands only.

Trichloro(isovaleronitrile)bis(triphenylphosphine)rhenium-(III). - Isovaleronitrile was prepared by a standard method (66). Trans-$ReOCl_3(PPh_3)_2$, isovaleronitrile (7 ml.) and toluene (30 ml.) were heated under reflux for $2\frac{1}{2}$ hr. to give yellow crystals of the compound (1.6 g., 49%), which was recrystallised from benzene and dichloromethane-methanol. The product was insoluble in ether and ethanol, moderately soluble in benzene and tetrahydrofuran, and readily soluble in dichloromethane. In addition to PPh_3 modes, the infra-red spectrum showed bands at 2963mw, 2874vw, 1463m, 1458sh, 1417w, 1391v, 1371w, and 1157m, associated with the Bu^i group.

Trichloro(caprylonitrile)bis(triphenylphosphine)-rhenium(III). - Trans-$ReOCl_3(PPh_3)_2$ (5 g.), caprylonitrile (10 ml.), and toluene (50 ml.) were heated under reflux for 2 hr., and ethanol was added to the cool product to give yellow crystals of the compound (1.0 g., 18%). These were recrystallised from dichloromethane-ethyl acetate and dichloromethane-ether. The compound was insoluble in alcohols and petrol, sparingly soluble in ether and acetic acid, readily soluble in acetone and benzene,

and freely soluble in dichloromethane. The infra-red spectrum of mulls showed PPh_3 modes, as well as bands at 2963w (ν_2-CH_3), 2924s (ν_2-CH_2), 2857m (ν_1-CH_2), 1464w (δ-CH_2), 1451vw (δ_2-CH_3), 1404w, 1379vw (δ_1-CH_3), and 722mw [$(CH_2)_n$ rock]. A 23% solution (w/w) in dichloromethane showed very intense PPh_3 bands in the region 4000-1400 $cm.^{-1}$, as well as bands at 2924vs (ν_2-CH_2), 2857vs (ν_1-CH_2), 2257w (ν-CN?), 2179vw (PPh_3?) and 1603sh.

Trichloro(benzonitrile)bis(triphenylphosphine)rhenium(III). - $ReCl_3(MeCN)(PPh_3)_2$ (0.2 g.) and benzonitrile (5 ml.) were heated in benzene under reflux for 15 min. and ethanol added to give orange-yellow prisms of the compound (0.1 g., 50%). The infra-red spectrum showed bands associated with phenyl groups of two kinds (PPh_3 and PhCN) and a very weak band at 2241 $cm.^{-1}$ (ν-CN).

Other Trihalogeno(alkanonitrile)bis(triphenylphosphine)-rhenium(III) Complexes. - The complexes $ReX_3(RCN)(PPh_3)_2$ (R = n-C_3H_7 and X = Cl; R = Me, n-C_3H_7 and X = Br) were all prepared in 90% yield in a way similar to method B for $ReCl_3(MeCN)(PPh_3)_2$. The complex $ReBr_3(MeCN)(PPh_3)_2$ was obtained as orange-red needles, insoluble in ether, ethanol and acetone, sparingly soluble in benzene, and moderately in dichloromethane. The magnetic susceptibility of the solid was $\chi_M(corr.) = 1.07 \times 10^{-3}$ c.g.s.u. at 23°, and its infra-red spectrum showed only PPh_3 bands. $ReBr_3(n\text{-}C_3H_7CN)(PPh_3)_2$ was obtained in an orange (dichloromethane/benzene) and a brown (dichloromethane/ethanol) polymorph.

Pyrolysis of Trichloro(acetonitrile)bis(triphenylphosphine)-rhenium(III). - A purified sample of $ReCl_3(MeCN)(PPh_3)_2$ (860 mg) was further dried at 80° under vacuum for 1 hour, then placed in a bulb connected to a trap, and the apparatus evacuated and sealed. The trap was cooled in liquid nitrogen and the bulb maintained at 200° for 30 min. There was no reaction. The temperature was then raised to 215-225° and after a further 30 min. decomposition was complete. A colourless liquid (47 mg., $n_{1,5}^{D}$ 1.3520) was obtained in the trap, and was shown by infra-red spectroscopy and g.l.c. on Carbowax at 100° to consist of acetonitrile (41 mg.), dichloromethane (5 mg.), and ethanol (1 mg.). Such a mixture was identical in all respects ($n_{1,5}^{D}$ 1.3512) with the liquid obtained.

The residue in the bulb was extracted with ether and the extract evaporated to dryness to give colourless crystals (240 mg., m.p., 79°) of triphenylphosphine. The olive-green residue was washed thoroughly with dichloromethane and methanol to give trichloro(triphenylphosphine)rhenium(III) (585 mg.) [Found: C, 41.8; H, 3.1%; N, absent. Calc. for $C_{18}H_{15}Cl_3PRe$: C, 39.0; H, 2.7%].

Reaction of Trichloro(alkanonitrile)bis(triphenylphosphine)-rhenium(III) with Pyridine. - $ReCl_3(MeCN)(PPh_3)_2$ (0.20 g.) was heated with dry pyridine (2 ml.) to the boiling point for a few seconds. The red solution quickly turned orange, and was poured into ether (50 ml.) to give orange-brown crystals of trichloro-

bis(pyridine)triphenylphosphinerhenium(III) (0.15 g., 90%), which were recrystallised from ethyl acetate and dichloromethane ether. The compound was insoluble in ether and sparingly soluble in ethanol, but dissolved readily in benzene and dichloromethane. Solutions in nitrobenzene were non-conducting. The infra-red spectrum could be interpreted in terms of pyridine and PPh_3 modes only. A very broad band at 3800 $cm.^{-1}$ (width at half height 700 $cm.^{-1}$) is attributed to an electronic transition.

A closed tube containing $ReCl_3(n\text{-}C_7H_{15}CN)(PPh_3)_2$ (123 mg.) and dry pyridine (511 mg., redistilled twice over potassium hydroxide), and a control containing pyridine only, were heated to 80-100° for 1 min. in a dimethyl phthalate bath, cooled and introduced immediately into 0.5 mm. solution cells. The infra-red spectrum was examined with and without the control pyridine as compensator. In addition to intense PPh_3 and (coordinated) pyridine bands and the broad electronic band at 3800 $cm.^{-1}$, bands at 2920vs (ν_2-CH_2), 2857vs (ν_1-CH_2), and 2247s (ν-CN of free nitrile) were observed. The position and intensity of the ν_1-CH_2 and ν-CN bands was the same as in a solution of caprylonitrile (19 mg.) in control pyridine (550 mg.). Hence 1.02 $\pm$ 0.07 mole of free caprylonitrile was obtained per mole of complex, the limits of error being estimated using the observed densities (flotation) of 1.60 and 1.73 for the nitrile and pyridine complexes respectively, and assuming probable deviations from

ideality. If the complex contained one mole of oxygen, all of which ended up as water, then the pyridine solution should contain 2.3 mg. of water. None was observed in the infra-red spectrum, and standards showed that much less would be easily detected. The other reaction products were PPh_3 and $ReCl_3py_2(PPh_3)$.

Reaction of Trichloro(acetonitrile)bis(triphenylphosphine)-rhenium(III) with αα'-Dipyridyl.- $ReCl_3(MeCN)(PPh_3)_2$ (430 mg., 0.5 millimole) in dichloromethane (15 ml.) was added to a solution of αα'-dipyridyl (93 mg., 0.6 millimole) in benzene (30 ml.) and the solution heated for 10 min. Dark green crystals separated on cooling, and were recrystallised from dichloromethane-benzene and dichloromethane-ether to give green trichloro(αα'-dipyridyl)-triphenylphosphinerhenium(III) (250 mg., 70%). The compound was insoluble in ether and benzene, slightly soluble in acetone, and readily in dichloromethane to grass-green solutions. The infra-red spectrum showed bands associated with PPh_3 and dipyridyl only.

The filtrate from the dipyridyl complex was distilled to dryness and the distillate examined by g.l.c. on Carbowax at 95°. The only volatile product was acetonitrile (0.8 ± 0.3 mole/mole of nitrile complex).

Trichloro(benzil)triphenylphosphinerhenium(III). - $ReCl_3(MeCN)(PPh_3)_2$ (1.0 g.) and benzil (1.0 g.) were heated in benzene (50 ml.) for 30 min. under reflux. Dark purple crystals separated on cooling, and were recrystallised three times from

dichloromethane-benzene, and from dichloromethane-ether to give the compound (0.43 g., 50%) in black prisms with a metallic bronze lustre, but purple when finely ground [χ_M(corr.) = 1.43 x 10^{-3} c.g.s.u. at 26°]. The compound was almost insoluble in ether, ethanol, and cold benzene, moderately soluble in hot benzene and acetone, and readily in dichloromethane. To a solution of the complex (150 mg.) in boiling methyl cellosolve (3 ml.) were added, drop by drop, 30 ml. of water. The solution was filtered from black rhenium oxides, diluted to 50 ml. and allowed to stand at 0° to give colourless needles (20 mg., m.p., 132°), whose infra-red spectrum was identical with that of benzoin (m.p., 137°). From the known solubility of benzoin, the yield was estimated as at least 75%.

The filtrate from $ReCl_3(Ph.CO.CO.Ph)(PPh_3)$ was combined with the mother-liquor from the first recrystallisation and poured into ether to give carmine-red crystals (0.35 g., 35%), which were recrystallised from dichloromethane-acetone. The physical and chemical properties were identical with those of $ReCl_4(PPh_3)_2$ [Found: Cl, 16.6%. Calc. for $C_{36}H_{30}Cl_4P_2Re$: Cl, 16.6%].

$ReCl_3(Ph.CO.CO\ Ph)(PPh_3)$ (0.4 g.) was heated with pyridine (5 ml.) for 5 min., diluted with benzene (5 ml.) and poured into ether (50 ml.). The solid separating (200 mg., 72%) was recrystallised from dichloromethane-benzene and hot ethanol to give red-brown leaflets of trichlorotris(pyridine)rhenium(III).

The compound was insoluble or sparingly soluble in ether, benzene, and cold ethanol, but readily soluble in hot ethanol, acetone, and dichloromethane. The infra-red spectrum showed pyridine bands at 1605m, 1481vs, 1444vs, 1357w, 1232w, 1214m, 1155w, 1146m, 1063sh, 1067s, 1003ms, 820w, 779s, 768sh, 761vs, 758sh, 696sh, 690vs, and 680vs, but no PPh_3 bands. The filtrate from $ReCl_3py_3$ was evaporated to dryness and extracted with hot aqueous ethanol. The extract was cooled to -5° to give yellowish solid (50 mg.) whose infra-red spectrum was identical with that of benzil. When extracted with ether and the evaporated extract was recrystallised from methanol, needles of pure benzil (m.p. 95°) were obtained.

Trichloro(9:10-phenanthraquinone)triphenylphosphine-rhenium(III). - 9:10-Phenanthraquinone was prepared by a standard method (67). $ReCl_3(MeCN)(PPh_3)_2$ (0.43 g., 0.50 millimole) and 9:10-phenanthraquinone (0.11 g., 0.53 millimole) were heated in benzene (15 ml.) for 15 min. and poured into ether. The precipitate was recrystallised twice from benzene-dichloromethane to give blue-black microcrystals of the compound (0.25 g., 65%). These were sparingly soluble in ether, ethyl acetate, and cold benzene, moderately in acetone and hot benzene, and readily in chlorobenzene and dichloromethane.

Dichloro(pentane-2,4-dionato)bis(triphenylphosphine)-rhenium(III). - $ReCl_3(MeCN)(PPh_3)_2$ (0.43 g.) and pentane-2:4-dione (3 ml.) were boiled in toluene for 30 min. under reflux.

Orange-red crystals of $ReCl_2(acac)(PPh_3)_2$ (270 mg., 63%) crystallised out on cooling, and were recrystallised from dichloromethane-benzene and dichloromethane-ether [Found: C, 56.2; H, 4.6%; M (chloroform), 800. $C_{41}H_{37}Cl_2O_2P_2Re$ requires C, 55.9; H, 4.2%; M, 881]. The infra-red spectrum was identical with that of an authentic sample prepared from trans-$ReOCl_3(PPh_3)_2$ (17).

Oxotrichloro(triphenylphosphine oxide)triphenylphosphine-rhenium(V). - Method A. The filtrate from $ReCl_3(MeCN)(PPh_3)_2$ prepared by method A was evaporated almost to dryness under vacuum, dissolved in dichloromethane (10 ml.) and poured into acetone (100 ml.). The solution was boiled in an open flask for a few minutes and allowed to stand, when green microcrystals of the compound (1.6 g., 30%) separated out.

Method B. A suspension of $ReCl_3(MeCN)(PPh_3)_2$ (1.0 g.) in benzene (100 ml.) was heated in a slow current of air, and the benzene allowed to distil off. About 30 ml. of benzene remained after 20 min. and the solution deposited crystals when cooled and allowed to stand overnight. These were recrystallised from dichloromethane-benzene and dichloromethane-acetone to give pastel-green (pistachio) prisms of the compound (0.6 g., 60%) [Found: C, 50.8; H, 3.7; N, absent; O, 3.5%. $C_{36}H_{30}Cl_3O_2P_2Re$ requires C, 50.9; H, 3.6; O, 3.8%].

The compound was sparingly soluble in ether, acetone, and benzene, but moderately soluble in dichloromethane to a pale

green solution. This reacted instantly with pyridine, $\alpha\alpha'$-dipyridyl, and 1:10-phenanthroline. From dipyridyl black crystals were obtained, whose infra-red spectrum showed the Re = O and dipyridyl modes but no PPh_3, and was identical with that of an authentic sample (57) of $ReOCl_3(dipy)$.

$ReOCl_3(OPPh_3)(PPh_3)$ (425 mg., 0.50 millimole) in dichloromethane was mixed with a solution of PPh_3 (132 mg., 0.505 millimole). A transient bright green coloration appeared momentarily, then changed to yellow, and crystals began to separate. The solution was concentrated and poured into ether to give yellow crystals of trans-$ReOCl_3(PPh_3)_2$ (400 mg., 0.48 millimole) containing a little cis-isomer, but otherwise pure. The mother liquor was evaporated to dryness to give colourless crystals of pure triphenylphosphine oxide (m.p. 155.5°).

$ReOCl_3(OPPh_3)(PPh_3)$ in dichloromethane was shaken with an excess of diethylphenylphosphine in the cold for 1 min., and the blue-green solution poured into ethanol and concentrated to a small volume in vacuo. Sky-blue crystals of cis-oxotrichlorobis(diethylphenylphosphine)rhenium(V) were obtained, and were recrystallised from benzene-petrol [Found: C, 37.6; H, 4.7%. Calc. for $C_{20}H_{30}Cl_3OP_2Re$: C, 37.5; H, 4.7%].

$ReOCl_3(OPPh_3)(PPh_3)$ (0.5 g.) was heated with pentane-2:4-dione (3 ml.) to the boiling point for a moment, and the clear green solution was poured into petroleum ether (b.p. 60°-80°).

The tarry residue was extracted quickly with cold methanol and the undissolved material recrystallised from dichloromethane-petroleum ether to give grass-green leaflets of oxodichloro-(pentane-2:4-dionato)triphenylphosphinerhenium(V) (0.3 g., 80%) [Found: C, 43.1; H, 3.7%. Calc. for $C_{23}H_{22}Cl_2O_3PRe$: C, 43.5; H, 3.5%]. The infra-red spectrum was identical with that of a standard sample of $ReOCl_2(acac)(PPh_3)$ (17).

Reaction of Trihalogeno(alkanonitrile)bis(triphenylphosphine)rhenium(III) with Halogenated Compounds. -

(a) Reaction of trichloro(acetonitrile)bis(triphenylphosphine)rhenium(III) with carbon tetrachloride. The compound $ReCl_3(MeCN)(PPh_3)_2$ (0.50 g.) in dichloromethane (40 ml.) was heated with freshly redistilled carbon tetrachloride (40 ml.) under reflux for 30 min. After 5 min. the solution was bright red and, at the end of the heating period, it was concentrated under reduced pressure to give carmine-red crystals (0.45 g., 90%) whose solubility, visible, and infra-red spectrum were identical with those of a sample of tetrachlorobis(triphenylphosphine)rhenium(IV), $ReCl_4(PPh_3)_2$, prepared by standard methods. The compound was recrystallised from dichloromethane [Found: C, 50.0; H, 3.3; N, nil; Cl, 16.7%. Calc. for $C_{36}H_{30}Cl_4P_2Re$: C, 50.7; H, 3.6; N, nil; Cl, 16.6%]. Alternatively, a suspension of $ReCl_3(MeCN)(PPh_3)_2$ (0.5 g.) in dichloromethane (5 ml.) and carbon tetrachloride (15 ml.) was boiled for 20 min. in air to give $ReCl_4(PPh_3)_2$ as

crystals (0.46 g., 92%).

Reactions with the complexes of higher nitriles and with other chloro-compounds were carried out similarly. The product was $ReCl_4(PPh_3)_2$ in each case.

In the cold the reaction still proceeded to completion, but took several hours, so that the rate could conveniently be estimated by observing the colour change from yellow to red. A solution of $ReCl_3(MeCN)(PPh_3)_2$ in dichloromethane, and carbon tetrachloride, were stored in the dark for 24 hours, then mixed. Different aliquots of the mixture at room temperature were (i) stored in the dark, (ii) kept in diffuse daylight, (iii) irradiated with ultra-violet light in a quartz vessel, (iv) kept over several grams of potassium perrhenate, (v) kept over ignited thoria, and to other aliquots was added (vi) t-butyl peroxide, (vii) freshly ignited t-butyl perbenzoate, (viii) triphenylmethane, (ix) hydroquinone, (x) acetic acid, and (xi) sulpholan. The rate of the reaction was the same in each case. To different aliquots of solution containing an excess of carbon tetrachloride were added increasing amounts of acetonitrile. The reaction was retarded markedly by even a little acetonitrile, and was arrested altogether by excess. When, however, the acetonitrile was expelled by boiling, reaction followed rapidly. Acetonitrile, added to the mixture after reaction had commenced, arrested but did not reverse the reaction. To different aliquots of the dichloromethane solution

were added 1,2,5 and 10 drops of carbon tetrachloride. The rate increased with carbon tetrachloride concentration, and reaction was eventually complete in all cases.

To different 2 ml. aliquots of styrene were added (i) 10 drops of carbon tetrachloride, (ii) 50 mg. of $ReCl_3(MeCN)(PPh_3)_2$, (iii) 10 drops of carbon tetrachloride and 50 mg. of $ReCl_3(MeCN)(PPh_3)_2$ and (iv) 10 drops of carbon tetrachloride, 50 mg. of $ReCl_3(MeCN)(PPh_3)_2$, and 5 drops of acetonitrile to inhibit reaction. The aliquots were kept at 90° for 20 min., then diluted with ethanol. Only in case (iii) was there extensive separation of polystyrene.

(b) Reaction of trichloro(n-butyronitrile)bis(triphenylphosphine)rhenium(III) with chlorocarbons. The compound $ReCl_3(n\text{-}C_3H_7CN)(PPh_3)_2$ (43 mg.) in dichloromethane (1.5 ml.) was heated with carbon tetrachloride (0.5 ml.) at 60° for 15 min. The volume was adjusted to 2 ml. and when most of the $ReCl_4(PPh_3)_2$ crystallised out the g.l.c. of the solution was examined on a squalene column at 160°. By comparing areas of peaks with standards it was estimated that the solution contained n-butyronitrile (3.3 mg.), hexachloroethane (3.5 mg.) and tetrachloroethylene (0.5 mg.).

When hexachloroethane was used instead of carbon tetrachloride under similar conditions, $ReCl_3(n\text{-}C_3H_7CN)(PPh_3)_2$ (22 mg.) gave n-butyronitrile (1.7 mg.) and tetrachloroethylene (4.9 mg.).

The complex $ReCl_3(MeCN)(PPh_3)_2$ (59 mg.) also gave tetrachloroethylene (12.3 mg.).

(c) Reaction of tribromo(n-butyronitrile)bis(triphenylphosphine)rhenium(III) with carbon tetrabromide. The complex $ReBr_3(n\text{-}C_3H_7CN)(PPh_3)_2$ (0.5 g.) and carbon tetrabromide (0.5 g.) in dichloromethane (20 ml.) were boiled under reflux for 30 min., then carefully concentrated to 1 ml. Carmine-red (almost black) crystals separated (0.2 g., 40%), whose visible spectrum in dichloromethane was identical with that of an authentic specimen of the complex $ReBr_4(PPh_3)_2$. The infra-red spectrum of the mother liquor showed bands attributed to triphenylphosphine and free n-butyronitrile (ca. 0.5 mole per mole of reactant). The g.l.c. on Carbowax at 130° showed n-butyronitrile to be the only volatile product.

(d) Reaction of trichloro(acetonitrile)bis(triphenylphosphine)rhenium(III) with carbon tetrabromide. The compound $ReCl_3(MeCN)(PPh_3)_2$ (0.6 g., 0.7 millimole) and carbon tetrabromide (0.3 g., 0.9 millimole) were heated in benzene (25 ml.) for 10 min., and acetone was added to the cold solution to give carmine red crystals of trichlorobromobis(triphenylphosphine)rhenium(IV) (0.3 g., 48%), which were recrystallised from dichloromethane. When a threefold excess of carbon tetrabromide was used the yield was 40%.

(e) Reaction of tribromo(acetonitrile)bis(triphenylphosphine)rhenium(III) with chlorocarbons. The compound $ReBr_3(MeCN)(PPh_3)_2$ (0.4 g.) in benzene (15 ml.) was heated with (i) carbon tetrachloride (10 ml.) for 30 min. and (ii) benzotrichloride (2 ml.) for 15 min. In both cases red crystals of dichlorodibromobis(triphenylphosphine)rhenium(IV) (0.3 g., 80%) were obtained, and were recrystallised from dichloromethane.

Analytical data for the complexes $ReX_nY_{4-n}(PPh_3)_2$ are given in Table 1. The wavelength (λ) in the last column refers to the main peak in the visible spectrum of a dichloromethane solution ($\varepsilon \sim 2000$).

Table 1

Analytical data for $ReX_nY_{4-n}(PPh_3)_2$

Compound	C (%)		Weight of Ag(Cl,Br)/g.		λ(mμ)
	Found	Calc.	Found	Calc.	
$ReCl_4(PPh_3)_2$	50.0	50.7	0.675	0.673	488
$ReCl_3Br(PPh_3)_2$	48.4	48.2	0.689	0.689	494
$ReCl_2Br_2(PPh_3)_2$	46.1	45.9	0.701	0.703	500
$ReBr_4(PPh_3)_2$	-	-	-	-	511

Preparation of Tetrachlorobis(alkanonitrile)rhenium(IV) Complexes. - Rhenium pentachloride was prepared by chlorinating the metal (73). Acetonitrile was dried by distillation over

phosphorus pentoxide, then over potassium carbonate (74). Benzonitrile was dried by fractionation with benzene. The reactions were in dry air.

(a) Tetrachlorobis(acetonitrile)rhenium(IV). Rhenium pentachloride (3.7 g.) in acetonitrile (25 ml.) was gently heated to boiling for 5 min., then allowed to cool. Crystals began to separate, and the mixture was shaken with water at 0° for 5 min., then filtered immediately. The crystals were washed with cold water, methanol and ether, and recrystallised from acetonitrile-dichloromethane and acetonitrile-benzene to give the compound in greenish yellow prisms (2.5 g., 59%), sparingly soluble in ether, benzene, dichloromethane and water, but readily soluble in acetone, acetonitrile and sulpholan. The infra-red spectrum showed bands at 2985m (ν_2-CH_3), 2924s (ν_1-CH_3), 2314w (combination with ν-CN), 2293vs (ν-CN), 1399m (δ_2-CH_3), 1361m (δ_1-CH_3), 1025m, 962vw and 951vw. A solution of the complex (135 mg.) in acetone (2 ml.) was diluted with cold water, when 115 mg. (85%) of the complex crystallised out unchanged. The finely divided complex (100 mg.) was boiled with concentrated hydrochloric acid (20 ml.) for 30 min. and caesium chloride was added to the yellow solution. Crystals of caesium hexachlororhenate(IV) (130 mg., 80%) separated and the salt was identified by its physical properties. A solution of $ReCl_4(MeCN)_2$ (0.30 g.) in acetone (5 ml.) was heated with triphenylphosphine (1.0 g.) in acetone (5 ml.) for 5 min. Carmine red crystals of

tetrachlorobis(triphenylphosphine)rhenium(IV) (0.52 g., 83%) were formed [Found: C, 50.5; H, 3.8%. Calc. for $C_{36}H_{30}Cl_4P_2Re$: C, 50.7; H, 3.6%] and were identified by the physical properties.

(b) Tetrachlorobis(n-butyronitrile)rhenium(IV). Rhenium pentachloride (0.7 g.) was dissolved in n-butyronitrile (5 ml.) and the red-brown solution was allowed to stand for 3 days. The solution was then diluted with 50% aqueous ethanol (15 ml.) at 0° to give crystals of the compound (0.2 g., 22%). These were recrystallised from dichloromethane–ether and acetone–water to give lemon-yellow needles, insoluble in ether and water, but readily soluble in acetone, dichloromethane and n-butyronitrile to greenish yellow solutions.

(c) Tetrachlorobis(benzonitrile)rhenium(IV). Method A. Rhenium pentachloride (2.0 g.) was heated with benzonitrile (15 ml.) to 100° under reduced pressure for 1 hr., the solution cooled and diluted with ether. The brown solid separating was washed well with dry acetone to leave a yellow residue of the compound (1.4 g., 47%). This was recrystallised from dichloromethane–ether to give pale yellow crystals, sparingly soluble in ether, benzene and acetone, but moderately soluble in hot benzonitrile and dichloromethane.

Method B. Tetrachlorobis(acetonitrile)rhenium(IV) (1.0 g.) was evaporated with benzonitrile (50 ml.) at 100° under reduced pressure. When the volume was reduced to 10 ml., ether (30 ml.)

was added to give yellow crystals of the compound (1.15 g., 88%).

Tetrachlorobis(triphenylarsine)rhenium(IV). - The complex $ReCl_4(MeCN)_2$ (0.3 g.) was heated with triphenylarsine (1.0 g.) in sulpholan (20 ml.) to 100° under reduced pressure for 1 hr., during which period 5 ml. of solvent distilled off. Scarlet crystals of the compound (0.45 g., 65%) separated out, and were washed with acetone and recrystallised from dichloromethane. Fusion of $ReCl_4(MeCN)_2$ with triphenylarsine led to a yield of only 10% of product.

Tetrachlorobis(triphenylstibine)rhenium(IV). - The complex $ReCl_4(MeCN)_2$ (0.1 g.) was fused with triphenylstibine (1.0 g.) at 100° under vacuum for 20 min. The cool melt was extracted with acetone to leave royal blue crystals of the compound (0.06 g., 24%), sparingly soluble in dichloromethane to a purple solution.

Trimethylammonium Tetrachlorobis(acetonitrile)rhenate(III). - The complex $ReCl_4(MeCN)_2$ (0.5 g.) in acetone (15 ml.) was shaken with 40% ethanolic trimethylamine (2 ml.) in acetone (5 ml., containing 10% of water) for 5 min., to give orange needles of the salt (0.4 g., 70%) which were washed with acetone and dried [Found: C, 19.4; Cl, 29.9; N, 9.1%. $C_7H_{16}Cl_4N_3Re$ requires C, 17.9; Cl, 30.2; N, 8.9%]. The solid was insoluble in acetone, ethanol and dichloromethane, sparingly soluble in hot acetonitrile, and readily soluble in water. To a solution of the salt (0.2 g.) in water (10 ml.) was added a solution of sodium tetraphenylborate

(0.25 g.) in water (10 ml.) to give a white precipitate of trimethylammonium tetraphenylborate (1.7 g., 105%), identical with an authentic specimen. When the filtrate was evaporated to dryness and the residue triturated with ethanol, orange crystals of crude sodium tetrachlorobis(acetonitrile)rhenate(III) remained, and were freely soluble in water and acetonitrile

Cadmium Di[tetrachlorobis(acetonitrile)rhenate(III)]. - The complex $ReCl_4(MeCN)_2$ (0.5 g.) in acetonitrile (30 ml.) was shaken with freshly purified cadmium amalgam for 2 min. The bright orange solution was decanted off the amalgam, centrifuged immediately, filtered and allowed to stand overnight to give large orange prisms. The solid was kept over phosphorus pentoxide under vacuum for 6 days to give the pure salt. The solid was extremely soluble in water to a clear orange solution, which darkened on warming. The equivalent conductivity of a fresh millimolar solution at 20° was 133 mhos $cm.^{-2}mole^{-1}$, but increased on standing. The infra-red spectrum of the dry salt showed only one band at 1020 $cm.^{-1}m$ (present in all acetonitrile complexes) in the range 4000-650 $cm.^{-1}$, but additional intense bands appeared at 3390vs and 1063vs after brief exposure to the atmosphere, owing to the absorption of water.

A stabilised solution of ascorbic acid was standardised against "Analar" potassium iodate via potassium iodide to a starch-iodine end-point (86). A solution of ferric ammonium sulphate in 0.05 N sulphuric acid was standardised against the

ascorbic acid to a variamine blue end-point (75,86). A solution of the cadmium salt (0.1195 g.) in cold water (20 ml.) was titrated with the ferric solution to a variamine blue end-point, and required 7.64 ml. of 0.0327 N ferric solution. The solution was then cooled to 0° for 10 min. and filtered to give tetrachlorobis-(acetonitrile)rhenium(IV) (0.0893 g., 85%) which was identified by its physical and chemical properties [Found: Cl, 34.4%. Calc. for $C_4H_6Cl_4N_2Re$: Cl, 34.6%].

Caesium Tetrachlorobis(acetonitrile)rhenate(III). - The complex $ReCl_4(MeCN)_2$ (0.5 g.) in acetonitrile (20 ml.) was reduced with cadmium amalgam as above, and the bright orange reduced solution poured into hot acetonitrile (80 ml.) saturated with caesium perchlorate (0.3-0.4 g.). The mixture was cooled immediately and shaken to give orange crystals of the pure salt (0.2 g., 30%) which were washed thoroughly with anhydrous acetonitrile and dried. Attempts to obtain a second crop by concentrating the solution gave a product contaminated with cadmium. The same compound could be obtained by adding excess of caesium chloride to aqueous $Me_3NH^+[ReCl_4(MeCN)_2]^-$ or by reducing $ReCl_4(MeCN)_2$ with ascorbic acid, but it was not obtained as pure as from acetonitrile. The salt was readily soluble in water to an orange solution (Λ_o = 103 mhos $cm.^2 mole^{-1}$). On titration with standard ferric solution, 0.1090 g. of the salt required 6.30 ml. of 0.0327N ferric solution to the variamine blue end-point, or 1.03 equivalents per mole.

Tetrachlorobis(N-p-tolyacetamidine)rhenium(IV). - The complex $ReCl_4(MeCN)_2$ (1.0 g.) in acetone (10 ml.) was shaken with p-toluidine (1.5 g.) in acetone (10 ml.) for 3 min. in the cold, and ether (120 ml.) was added in portions to the orange solution. Bright orange crystals of the compound (1.4 g., 92%) separated and were recrystallised from dichloromethane. The solid was insoluble in benzene and ether, moderately soluble in dichloromethane, and readily soluble in acetone and acetonitrile to orange solutions. The infra-red spectrum showed bands at 3356w and 3306m (ν-NH), 1613sh and 1599vs (ν-C = N overlapping ν-C = C of Ph), 1570sh [ν-C = C of Ph overlapping Amidine II (δ-NH)], 1506s (ν-C = C of Ph?), 1412s (ν-C = C of Ph), 1385s (ν-C — N of Acyl — N overlapping δ_1-CH_3), 1297s (ν-C — N of Alkyl — N), 1034m, 1021sh, 845m, 810ms, 773mw.

Tetrachlorobis(N-p-tolyacetoamidine)rhenium(IV) (0.5 g.) was heated to reflux for 5 min. with methanol (20 ml.) saturated with hydrogen chloride, when it dissolved to a pale green solution. The solution was evaporated to dryness in vacuo, dissolved in water and extracted with ether. The aqueous layer was then rendered alkaline with sodium carbonate and extracted with ether once more. The second ether extract was washed, dried with sodium sulphate and evaporated to dryness. The residue was recrystallised from hot petrol (b.p. 60-80°) to give white, glistening leaflets (100 mg., 42%), whose melting point (106°), mixed melting point, and infra-red

spectrum were identical with those of an authentic specimen of N-p-tolylacetamidine. The latter was prepared by heating thioacetamide and p-toluidine with mercuric chloride. The literature value of the melting point is incorrect (87).

Tetrachlorobis(N-p-methoxyphenylbenzamidine)rhenium(IV). - A suspension of $ReCl_4(PhCN)_2$ (0.3 g.) in dichloromethane (7 ml.) was shaken with p-anisidine (0.3 g.) and soon dissolved to a deep orange solution. Orange crystals of the compound (0.4 g., 91%) separated on adding ether (50 ml.) and were recrystallised from dichloromethane-benzene to give bright orange needles, sparingly soluble in ether and benzene, but readily soluble in dichloromethane. The infra-red spectrum (cf. ref. 54 and 76) showed bands at 3308s and 3284s (ν-NH), 3058vw (ν-CH of Ph), 2959vw (ν_2-CH_3), 2833vw (ν_1-CH_3), 1602vs (ν-C = N), 1562vs [ν-C = C overlapping amidine II (δ-NH)], 1506vs (ν-C = C of ϕ), 1480w, 1462w (δ_2-CH_3), 1445vw (δ_1-CH_3), 1421mw (ν-C = C of Ph), 1389mw (ν-Aryl — N), 1302sh and 1291s (ν- Alkyl — N), 1247vs and 1222sh (ν_2-C — O — C), 1179m, 1170sh, 1164m, 1157w, 1020vs (ν_1-C — O — C), and 921m.

Tetrachlorobis(N-m-fluorophenylacetamidine)rhenium(IV). - The complex $ReCl_4(MeCN)_2$ (0.2 g.) in acetonitrile (5 ml.) was shaken with m-fluoroaniline (0.5 g.) for 10 min., then diluted with ether to precipitate the compound (0.25 g., 80%). It was recrystallised from acetone-ether to give small mango orange crystals.

Tetrachlorobis(N-p-carbethoxyphenylacetamidine)rhenium(IV). -

Powdered $ReCl_4(MeCN)_2$ (0.15 g.) was heated under reflux with a solution of benzocain (0.5 g.) in dichloromethane (25 ml.) for 2 hr. The solid slowly dissolved to a yellow solution, and a precipitate of the compound (0.1 g., 37%) was obtained on adding ether. It was recrystallised from dichloromethane as orange yellow microcrystals. The infra-red spectrum showed bands at 3257ms (ν-NH), 2320w, 1674s (ν- C = O), 1617s, 1592s, 1558s, 1511m, 1416s, 1391m, 1319s, 1277vs, 1179s, 1126ms, 1015m, 935w, 854s, 769vs, 703s, 676m.

Tetrachlorobis(methyl acetimidate)rhenium(IV). - The complex $ReCl_4(MeCN)_2$ (1.0 g.) was gently heated to reflux with anhydrous methanol (20 ml.) for 15 min. (but no longer), during which period it dissolved to a pale green, then brown solution. There was no evolution of hydrogen chloride. The solution was concentrated to 10 ml. at the pump and allowed to stand overnight, when pale green crystals of the compound (0.3 g., 26%) slowly separated. They were washed with methanol, acetone and ether. The solid was insoluble in methanol, acetone and water, but slightly soluble in acetonitrile. The infra-red spectrum showed bands at 3268s (ν-NH), 3006mw, 2967w, 2950w and 2905w (ν-CH_3), 1596vs (ν- C = N), 1495s, 1459w (δ_2-CH_3), 1430m (δ_2-CH_3 of OMe), 1408s, 1366m (δ_1-CH_3), 1248vs (ν_2 - C —O — O) and 1059vs (ν_1-C — O —O).

Tetrachlorobis(ethyl acetimidate)rhenium(IV). - A solution of $ReCl_4(MeCN)_2$ (0.5 g.) in acetonitrile (20 ml.) was allowed to stand with ethanol (10 ml.) for 1 hr., then evaporated repeatedly

with ethanol at room temperature to give green crystals of the compound (0.1 g., 16%), insoluble in benzene and water, sparingly soluble in cold ethanol, moderately soluble in hot ethanol and dichloromethane, and very soluble in acetonitrile and acetone (ca. 170 g./l.). The infra-red spectrum was similar to the complex from methanol.

Trichloro[4-(dicyanomethylene)azetid-2-imine]bis(triphenylphosphine)rhenium(III). - Method A. Reagent grade malononitrile was freshly sublimed in vacuo. Trans-$ReOCl_3(PPh_3)_2$ (5.0 g.) and malononitrile (5.0 g.) were refluxed in benzene (200 ml.) for 2 hr. Hydrogen chloride (but no hydrogen cyanide) was evolved and the dark reaction mixture was filtered to give a black solid and a bluish grey solution (rejected). The solid was extracted with a large volume of dichloromethane (ca. 200 ml.) and the black residue (2.2 g.) rejected. The brownish-red extract was concentrated, diluted with methyl cellosolve and the dichloromethane distilled off to give red crystals in a brown solution. The crystals were recrystallised from dichloromethane-cellosolve in the same way, until the mother liquors were nearly colourless (2-3 times; no loss of compound), then once from dichloromethane-benzene to give carmine red prisms of the compound (0.6 g., 11%). The solid was insoluble in water, ether, benzene, methyl cellosolve and acetone, sparingly soluble in dichloromethane and acetonitrile, and moderately soluble in sulpholan and dimethylformamide [in

dimethyl phthalate: λ 540, 505, 393, and 357 mμ (ε shoulder, 1800, 5000, 7000)].

Method B. Trans-$ReOCl_3(PPh_3)_2$ (1.0 g.), malononitrile (1.0 g.) and triphenylphosphine (1.0 g.) were refluxed in benzene for 2 hr. The product was treated as above to give the compound (0.2 g., 18%).

Method C. Malononitrile dimer (MND) was prepared by method A in ref. 89 to give a pale yellow product [Found: C, 54.7; H, 3.1; N, 42.2%; M (Rast), 134. Calc. for $C_6H_4N_4$: C, 54.5; H, 3.1; N, 42.4%; M, 132], sparingly soluble in cold water, cold benzene and dichloromethane, readily soluble in hot water, methyl cellosolve and acetone. The infra-red spectrum was as reported(89). Trans-$ReOCl_3(PPh_3)_2$ (1.0 g.) and MND (0.32 g , 2 molar excess) were refluxed in benzene (80 ml.) for 2 hr. Hydrogen chloride was evolved and a black solid separated, which was treated as in method A to give the compound (0.35 g., 31%).

Method D. Trans-$ReOCl_3(PPh_3)_2$ (1.0 g.), MND (0.32 g.), and triphenylphosphine (1.0 g.) were refluxed with benzene (80 ml.) for 2 hr. The dark solid was almost completely soluble in dichloromethane, and when the extract was treated as in method A it gave red crystals of the compound (0.61 g., 53%).

The infra-red spectrum of the compound showed bands at 3311mw (ν-NH), 3058mw (ν-CH of Ph), 2189vs (ν-C≡N of conjugated nitrile), 1589w (ν-C=N?), 1576vw (PPh_3), 1484s (PPh_3), 1439vs (PPh_3), 1404ms, 1397ms and 1256m (ν-C—N?), 1107s, 1100s and 1094s (first

P-sensitive vibration of PPh_3), 1029vw (PPh_3), 992mw (PPh_3), 956vw, 803m, 758s, 745vs, 731s, 729s, 695vs, and 691vs. The magnetic susceptibility of the solid was 0.91×10^{-6} c.g.u.g.$^{-1}$ at 17°.

Table 2

Analytical data for new carboxylato complexes of rhenium

Compound	Found (%)							Calculated (%)						
	C	H	Hal	O	P	Re	M	C	H	Hal	O	P	Re	M
$Re_2Cl_3(Et.CO_2)_2(PPh_3)_2$	44.0	3.8	-	5.7	-	-	1180*	43.9	3.5	-	5.6	-	-	1150
$Re_2Cl_3(n\text{-}C_3H_7.CO_2)_2(PPh_3)_2$	45.0	4.0	-	5.6	-	-	1206*	44.85	3.8	-	5.4	-	-	1178
$Re_2Cl_3(Me_2CH.CH_2.CO_2)_2(PPh_3)_2$	45.7	4.4	-	5.2	-	-	1260*	45.8	4.0	-	5.3	-	-	1206
$Re_2Cl_3(MeCH_2.CHMe.CO_2)_2(PPh_3)_2$	45.5	4.3	-	5.5	-	-	1222*	45.8	4.0	-	5.3	-	-	1206
$Re_2Cl_3(Me_3C.CO_2)_2(PPh_3)_2$	45.6	4.1	-	5.2	-	-	1192*	45.8	4.0	-	5.3	-	-	1206
$Re_2Cl_3(n\text{-}C_5H_{11}.CO_2)_2(PPh_3)_2$	46.7	4.4	8.6	5.2	-	-	1250*	46.7	4.3	8.6	5.2	-	-	1234
$Re_2Cl_3(n\text{-}C_7H_{15}.CO_2)_2(PPh_3)_2$	47.8	4.9	8.2	4.5	-	28.6	1330*	48.4	4.7	8.2	5.0	-	28.9	1290
$Re_2Cl_3(n\text{-}C_{11}H_{25}.CO_2)_2(PPh_3)_2$	51.6	5.9	-	4.75	4.5	-	1419†	51.4	5.5	-	4.6	4.4	-	1404
$Re_2Cl_3(Ph.CH_2.CO_2)_2(PPh_3)_2$	48.9	4.3	-	5.25	-	-	1179†	49.0	3.5	-	5.0	-	-	1274
$Re_2Cl_3(C_6H_{11}CO_2)_2(PPh_3)_2$	47.5	4.4	-	5.3	-	-	-	47.75	4.2	-	5.1	-	-	-
$Re_2OCl_5(Me.CO_2)(PPh_3)_2$	40.0	2.9	15.5	4.5	5.3	32.6	1123†	39.7	2.9	15.4	4.2	5.4	32.4	1149
$Re_2OCl_5(EtCO_2)(PPh_3)_2$	40.3	3.3	-	-	-	-	-	40.3	3.0	-	-	-	-	-
$Re_2OCl_5(Me_2CH.CH_2.CO_2)(PPh_3)_2$	41.4	3.4	-	4.1	-	-	1202†	41.3	3.3	-	4.0	-	-	1192
$Re_2OCl_5(MeCH_2.CHMe.CO_2)(PPh_3)_2$	41.2	3.5	-	-	-	-	-	41.3	3.3	-	-	-	-	-

(Cont.)

Table 2 (Continued)

Compound	Found (%)							Calculated (%)						
	C	H	Hal	O	P	Re	M	C	H	Hal	O	P	Re	M
$Re_2OCl_5(n\text{-}C_7H_{15}.CO_2)(PPh_3)_2$	42.6	3.8	-	4.05	-	29.7	1143†	42.8	3.7	-	3.9	-	30.3	1234
$Re_2OCl_5(n\text{-}C_9H_{19}.CO_2)(PPh_3)_2$	44.4	4.4	14.2	4.4	5.1	28.8	1183†	43.8	3.9	14.1	3.8	4.9	29.5	1262
$Re_2OCl_5(n\text{-}C_{11}H_{23}.CO_2)(PPh_3)_2$	45.1	4.4	-	3.5	-	-	1278*	44.7	4.1	-	3.7	-	-	1290
$Re_2OCl_5(n\text{-}C_{15}H_{31}.CO_2)(PPh_3)_2$	46.3	4.6	-	-	-	-	1392*	46.4	4.6	-	-	-	-	1346
$Re_2OCl_5(Ph.CH_2.CC_2)(PPh_3)_2$	43.8	3.6	-	4.5	-	-	1225†	43.1	3.1	-	3.9	-	-	1227
$Re_2OCl_5(Ph.CO_2)(PPh_3)_2$	42.2	2.9	14.7	4.0	-	-	1064†	42.6	2.9	14.6	4.0	-	-	1212
$Re_2OCl_5(p\text{-}MeO.C_6H_4.CO_2)(PPh_3)_2$	42.4	3.2	-	5.1	-	-	1287†	42.6	3.0	-	5.2	-	-	1242
$Re_2Cl_2(Ph.CH_2.CO_2)_4$	39.3	3.3	-	13.2	-	-	-	39.1	2.9	-	13.0	-	-	-
$Re_2OBr_5(Me.CO_2)(PPh_3)_2$	33.2	2.5	-	3.6	-	-	1232†	33.3	2.4	-	3.5	-	-	1372
$Re_2OBr_5(n\text{-}C_5H_{11}.CO_2)(PPh_3)_2$	35.2	3.2	28.4	3.2	-	-	1495†	35.2	2.9	28.0	3.4	-	-	1428
$Re_2Br_2(Me.CO_2)_4$	12.3	1 9	-	16.75	-	-	-	12.5	1.6	-	17.0	-	-	-
$Re_2Br_2(Et.CO_2)$	17.3	2.6	-	15.4	-	-	815†	17.5	2.45	-	15.5	-	-	825
$Re_2Br_2(n\text{-}C_3H_7.CO_2)_4$	22.3	3.1	18.7	-	-	-	-	21.8	3.2	18.1	-	-	-	-

* Determined in benzene

† Determined in chloroform

Table 3

Analytical data for new rhenium(III) complexes*

Compound	Found (%)							Calculated (%)						
	C	H	Hal	N	P	Re	M[a]	C	H	Hal	N	P	Re	M
$ReCl_3(MeCN)(PPh_3)_2$	53.1	3.8	12.1	1.6	7.1	21.4	800	53.2	3.9	12.4	1.6	7.2	21.7	858
$ReCl_3(Pr^nCN)(PPh_3)_2$	53.7	4.2	-	-	-	-	-	54.2	4.2	-	-	-	-	-
$ReCl_3(Bu^iCN)(PPh_3)_2$	54.0	4.5	-	1.5	-	-	800[b]	54.7	4.4	-	1.6	-	-	900
$ReCl_3(n\text{-}C_7H_{15}CN)(PPh_3)_2$	55.6	4.7	-	-	-	-	900	56.1	4.8	-	-	-	-	943
$ReCl_3(PhCN)(PPh_3)_2$	56.5	4.1	-	1.6	-	-	-	56.1	3.8	-	1.5	-	-	920
$ReBr_3(MeCN)(PPh_3)_2$	45.9	3.4	-	1.5	-	-	1000	46.0	3.4	-	1.4	-	-	989
$ReBr_3(Pr^nCN)(PPh_3)_2$	47.4	3.7	23.7	1.3	-	-	1100	47.1	3.7	23.5	1.4	-	-	1020
$ReCl_3py_2(PPh_3)$	46.9	3.5	-	3.9	-	-	700	47.15	3.5	-	3.9	-	-	713
$ReCl_3py_3$	34.45	3.0	19.8	7.8	nil	-	560	34.0	2.9	20.1	7.9	nil	-	530
$ReCl_3(dipy)(PPh_3)$	46.8	3.2	-	3.8	-	-	-	47.3	3.3	-	3.9	-	-	-
$ReCl_3(Ph.CO.CO.Ph)(PPh_3)$	50.5	3.1	13.9	nil	3.6	-	800	50.2	3.3	13.9	nil	4.0	-	765
$ReCl_3(phenquin)(PPh_3)$	50.5	3.2	-	-	-	-	600	50.4	3.0	-	-	-	-	763
$Cd[ReCl_4(MeCN)_2]_2$	11.1	1.8	29.7	6.2	-	-	-	10.3	1.3	30.4	6.0	-	-	-
$CsReCl_4(MeCN)_2$[c]	9.8	1.1	26.2	5.3	-	33.8	-	8.8	1.1	26.1	5.2	-	34.3	-
$ReCl_3(C_6H_4N_4)(PPh_3)_2$	53.4	3.8	10.9	6.2	6.2	18.7	800[d]	53.1	3.6	11.2	5.9	6.5	19.6	950

* Except carboxylate complexes

[a] In chloroform, unless otherwise stated [b] In benzene

[c] Found: Cs, 24.6%; Calc. Cs, 24.5% [d] Cryoscopic in sulpholan.

Table 4

Analytical data for new rhenium(IV) complexes *

	Found (%)						Calculated (%)					
	C	H	N	Cl	Re	M	C	H	N	Cl	Re	M
$ReCl_4(MeCN)_2$	11.7	1.5	7.1	34.6	45.4	380[a]	11.7	1.5	6.8	34.6	45.4	410
$ReCl_4(n\text{-}C_3H_7CN)_2$	21.0	3.5	6.3	-	-	480[b]	20.6	3.0	6.0	-	-	470
$ReCl_4(PhCN)_2$	31.6	2.2	5.3	-	-	-	31.5	1.9	5.3	-	-	-
$ReCl_4(py)PPh_3$	41.0	3.0	2.1	-	-	610[c]	41.3	3.0	2.1	-	-	670
$ReCl_4(AsPh_3)_2$	46.0	3.1	-	-	-	-	46.0	3.2	-	-	-	-
$ReCl_4(SbPh_3)_2$	41.6	2.9	-	-	-	-	41.8	2.9	-	-	-	-
$ReCl_4[MeC(:NH).NH.C_6H_4Me]_2$	34.9	-	9.0	22.7	-	710[b]	34.6	-	9.0	22.7	-	620
$ReCl_4[PhC(:NH).NH.C_6H_4.OMe]_2$	43.3	-	6.9	-	-	810[b]	43.1	-	7.2	-	-	780
$ReCl_4[MeC(:NH).NH.C_6H_4.CO_2Et]_2$	34.9	3.7	7.7	-	-	-	35.7	3.8	7.6	-	-	-
$ReCl_4[MeC(:NH).NH.C_6H_4F]_2$[d]	30.3	3.0	8.7	-	-	-	30.4	2.9	8.9	-	-	-
$ReCl_4[MeC(:NH).OMe]_2$	15.1	2.9	5.8	29.9	-	-	15.2	3.0	5.9	29.9	-	-
$ReCl_4[MeC(:NH).OEt]_2$	19.2	3.4	5.3	-	-	-	19.1	3.6	5.6	-	-	-

* Except carboxylate complexes and the complexes $ReX_nY_{4-n}(PPh_3)_2$

[a] In acetonitrile [b] In acetone [c] In chloroform.

[d] Found: F, 5.6%; Calc. F, 6.0%.

ABBREVIATIONS

Unless otherwise stated, the abbreviations used in the text should be interpreted as follows:

X	A halogen or pseudohalogen
L	A neutral monodentate ligand
LL'	A neutral bidentate ligand
py	Pyridine
dipy	$\alpha\alpha'$-Dipyridyl
acacH	Acetylacetone
phenquin	9,10-Phenanthraquinone
diphos	1,2-Bis(diphenylphosphino)ethane
diars	o-Bis(dimethylarsino)benzene
MND	Malononitrile dimer (2-amino-1,3,3-tricyano-2-propane)

The following notation is used in conjunction with infra-red data:

ν_1	symmetric stretch	mw	medium to weak
ν_2	asymmetric stretch	ms	medium to strong
δ_1	symmetric bend	s	strong
δ_2	asymmetric bend	vs	very strong
vw	very weak	sh	shoulder
w	weak	β-CH	in plane deformation of Ph
		γ-CH	out of plane deformation of Ph.

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