

SOME STUDIES OF THE HYDRIDES OF
TRANSITION METAL COMPLEXES.

A Thesis submitted
by
John Anthony Osborn, B.A.,
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of the University of London.

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Royal College of Science,
South Kensington, London S.W.7.

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ABSTRACT.

Convenient rapid preparations of a number of compounds of rhodium(III) with nitrogen ligands are described involving the use of catalytic amounts of reducing agents. Spectroscopic data on certain of these complexes are presented and the structures of such complexes discussed. A mechanism for the catalysis is tentatively proposed involving transient hydrido-species.

The polarographic reduction of some aminerrhodium(III) complexes shows the primary reduction to involve a two-electron step indicating the formation of a rhodium(I) or hydridorhodium(III) species. The significance of this result to the above catalysis is discussed.

The preparation of two hydrido-complexes of rhodium(III) stabilised by weak-field ligands is described, i.e. hydridopentamminerrhodium(III) sulphate and hydrido-aquatetramminerrhodium(III) sulphate. The activation of molecular hydrogen by some rhodium(III) complexes and the use of such complexes as homogeneous catalysts is investigated. Intermediate hydrido-complexes, e.g. $\text{Rh}[\text{MePh}_2\text{As}]\text{Cl}_2\text{H}$ have been isolated from the catalytic solutions.

The preparation and properties of new complexes of rhodium(I), $\text{Rh}(\text{PPh}_3)_3\text{X}$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}.$) are described. These have been found to be extremely effective homogeneous catalysts

for the hydrogenation of olefins and acetylenes. The probable intermediates in this catalysis have been isolated and a mechanism proposed.

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INTRODUCTION.

At the outset of this work, in 1964, a good deal was known about transition metal hydride complexes.¹ Most of the significant advances, however, had taken place in the preceding ten years. The only hydrido-complexes known previous to this were those such as $\text{H}_2\text{Fe}(\text{CO})_4$ ² and $\text{HCo}(\text{CO})_4$ ³ formed from the corresponding carbonyls; these are very unstable and were regarded somewhat as curiosities. In 1955 the discovery⁴ of $(\text{C}_5\text{H}_5)_2\text{ReH}$ led to an upsurge of interest in the field for the existence of this compound showed that not only were ligands other than carbonyls able to stabilise hydrido-complexes but also led to the establishment of a physical test diagnostic for transition metal hydrides, i.e. that of the high field shift in the proton magnetic resonance spectrum. There followed the preparations of many hydrido-complexes stabilised by various π -bonded ligands such as tertiary phosphines and arsines, the cyanide ion, and the cyclopentadienyl anion. These preparations were carried out by means of protonation, reduction or reverse carbonylation; it was found that several compounds previously formulated with the metal in a low valence state contain, in fact, metal-hydrogen bonds, e.g. $\text{Rh}(\text{AsPh}_2\text{Me})_3\text{HCl}_2$,⁵ $[\text{Co}(\text{CN})_5\text{H}]^{3-}$.⁶ Complex hydrides have now been prepared for nearly all transition metals and overall show considerable variations in their chemical properties, e.g. in

basicity, thermal stability and reactivity. However, two important properties of hydrides generally encountered must be mentioned here. (a) their ability to enter into hydride transfer reactions, e.g. most hydrides react with carbon tetrachloride to give chloroform. (b) their reaction with olefins to give transition metal alkyl derivatives, e.g. trans-PtHCl(PEt₃)₂ reacts⁷ reversibly with ethylene to yield trans-PtClEt(PEt₃)₂. This is known as an insertion reaction.

While considerable attention has concentrated on the preparation of stable transition metal hydrides, little interest has hitherto been shown in those catalytic systems in which transient hydrido-species have been postulated, often on kinetic evidence⁸ Moreover, it has long been known that certain transition metal complexes can activate molecular hydrogen and catalyse its reactions in homogeneous solution.⁹ One such system which has received particular attention is that involving aqueous solutions of cobalt salts with excess (5:1) cyanide present. This system has been found to be an effective catalyst¹⁰ for the reduction of certain organic substrates with molecular hydrogen. The transition metal hydrido-species [HCo(CN)₅]³⁻ has been detected⁶ in such solutions and is the most likely intermediate in the reduction process. Despite the difficulties inherent in studying this system, it provides one of few bridges between homogeneous catalysis and hydride chemistry. The related complex, HCo(CO)₄, which has been isolated as the intermediate in 'Oxo' process for hydro-

formylation of olefins, has also been well studied¹¹ and the mechanism of its behaviour in the catalytic process elucidated.

The purpose of this work was to investigate other systems where transient metal hydrides are likely to be present. It was hoped that with our present knowledge of transition metal hydride chemistry, suitable changes of ligands in these systems would make them easier to study or more efficient in their action. Also by taking into account certain well-established chemical properties of hydrides such as the insertion and transfer reactions, a greater insight into these catalytic processes could be achieved.

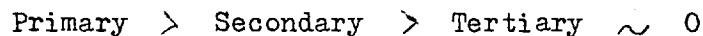
The work is described in four chapters. The first two are concerned with the preparation of rhodium(III) complexes catalysed by reducing agents and the mechanism by which this occurs. Chapter three deals with the activation of molecular hydrogen by complexes of rhodium(III) and the preparation of some weak-field rhodium(III) hydrides. The last chapter describes the preparation of some new rhodium(I) complexes, their properties and their behaviour as homogeneous catalysts.

CHAPTER I.

PREPARATION OF RHODIUM(III) COMPLEXES USING CATALYTIC QUANTITIES OF REDUCING AGENTS.

Introduction.

The study of the co-ordination chemistry of rhodium has been hampered by the slow and often inconvenient preparative methods required, and by the inert nature of the complexes formed. It has long been known that ethanol and several other alcohols can catalyse the formation of certain rhodium(III) complexes. Delépine¹², in 1929, in the synthesis of chloropyridine complexes of rhodium(III) by addition of pyridine to an aqueous solution of Na_3RhCl_6 , noted that small quantities of ethanol vastly increased the rate of production of trans- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}$. Further he found that the catalytic activity of the alcohol decreased in the series



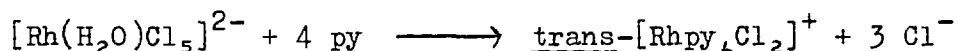
and that ethers, dioxan and acetone were ineffective. Again, in 1935, Poulenc¹³ noted the catalytic effect of alcohol in the formation of complexes of rhodium(III).

In 1943, Dwyer and Nyholm⁴ studied the action of reducing agents such as hypophosphorous acid on rhodium(III) compounds containing pyridine. The products were originally formulated as complexes of rhodium(II) but a recent re-examination of these reactions has shown most of the products to be rhodium(III) complexes. In particular it was shown that the hypophosphorous

acid behaved as a catalyst in the formation of trans-[Rhpy₄Cl₂Cl.

More recently, similar catalytic effects of ethanol have been noted in the formation of malonato- and diethyldithiocarbamate-complexes¹⁶ of rhodium(III) and in the preparation of amino-acid derivatives¹⁷ of rhodium(III) complexed with ethylenediamine.

While this work was in progress, a kinetic study¹⁸ was reported on the reaction

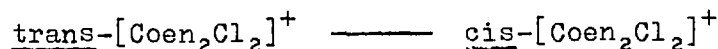


with and without ethanol as a catalyst. This paper will be discussed later in conjunction with the results of this present work.

Other reasonably rapid preparations of rhodium(III) species reported in the literature (e.g. [Rh(bipy)₂Cl₂]⁺ and [Rh(DMGH)₂Cl₂]⁻) have involved ethanol as a solvent for the ligand, and it therefore seemed possible that once again these preparations were assisted by ethanol catalysis.

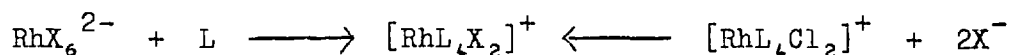
The rate of nucleophilic substitution in trans-[Rhen₂Cl₂]⁺ by halide ions has been found to be markedly increased when such reducing agents as hypophosphorous acid, hydrazinium chloride or sodium borohydride (even in the cold) are present. It is noteworthy that these reagents are not only typical reducing agents but also those which give rise to complex metal hydrides. In particular the borohydride reduction^{19,20} of trans-[Rhen₂Cl₂]⁺ has been shown to yield hydridic species. In the analogous cobalt system, borohydride does not produce a hydrido-complex but catalyses the

isomerism,²¹ viz.,



This catalysis is also effected by hypophosphorous acid, hydrazinium chloride, formic acid and zinc amalgam while other reducing agents such as sulphite, nitrite or quinol give rise to immediate formation of cobalt(II). It has been suggested²¹ that the isomerisation occurs through a cobalt monohydrido-intermediate and it seems possible that the hydride forming reagents can initiate a different mechanistic course in certain substitutions, often with an apparent rate increase. They may also give rise to products inaccessible by the usual substitution methods. This catalysis might thus arise from the ease of formation of the hydridic intermediates relative to that of the usual aquo-intermediate. Substitution in the position trans to the hydride ion is then rapid, followed by replacement of the labile hydride ligand.

This chapter is concerned with the possibility of synthesising rhodium(III) complexes by hydride catalysis under conditions where the hydride formed is likely only to be transient. These syntheses have been approached from two directions, viz.,



This approach has led to extremely convenient and quickly performed syntheses of ammine and related complexes of rhodium.

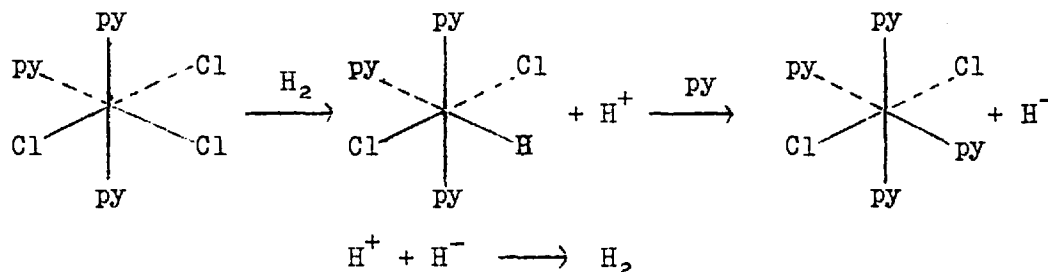
(a) Preparation and some reactions of pyridine complexes of rhodium(III).

(i) trans-Dihalogenotetrapyridinerhodium(III) Salts. - By

refluxing hydrated rhodium trichloride with aqueous pyridine in excess using alcohols as catalysts, Delépine¹² obtained trans- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl} \cdot 6 \text{H}_2\text{O}$. It has previously been shown by several authors^{12,22} that hot solutions of this kind in the absence of catalysts contain trichlorotrispyridinerhodium(III) only and it is now found that a complete conversion into the tetrapyridine compound is catalysed by hypophosphorous acid, sodium hypophosphite, or hydrazinium chloride when a small amount is added to the hot solutions. Sodium borohydride or zinc amalgam catalytically convert such solutions to the trans- $[\text{Rhpy}_4\text{Cl}_2]^+$ cation in the cold. Care must be exercised with the preparation using borohydride since an excess of the reagent will attack the required product. However, gentle warming of the resultant solution gives a good yield of the required product. In a mixture of ethanol and 2-methoxyethanol, hydrated rhodium trichloride and pyridine form trans- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}$ immediately on reaching ebullition. The product is precipitated by adding ether, and is recrystallised from water in extremely good yield. When an aqueous solution of rhodium trichloride containing pyridine is treated with a little hydridodichlorotris(triphenylphosphine)iridium(III), (dissolved in acetone or pyridine), as hydride-transfer agent, and the resulting solution warmed to 55° , the $[\text{Rhpy}_4\text{Cl}_2]^+$ cation is rapidly formed in solution, and can be obtained as shiny yellow feathery crystals of its chloride pentahydrate on cooling and standing.

Significantly, however, it has been found that molecular hydrogen can also serve as a catalyst for this reaction. If a warm

aqueous solution of rhodium trichloride and pyridine are treated with molecular hydrogen no net uptake of hydrogen is observed and trans-[Rhpy₄Cl₂]Cl can be isolated in quantitative yield from the solution. This catalysis can be explained in the following mechanism:



Support for this proposed mechanism is found in that on treating 1,2,6-Rhpy₃Cl₃ in ethanol with molecular hydrogen under a pressure of 50 atmospheres at 20°C in the absence of pyridine, a transition metal hydride species could be detected in the solution by n m r. spectroscopy. A strong doublet was found, centred at high field ($\tau \sim 25.6$) splitting 23.5 c/sec. [by interaction with ¹⁰³Rh ($s = 1/2$, relative abundance 100%)] and although the species was too unstable to be isolated, the proposed intermediate above is the most likely species to be present. As is shown in a later chapter, treatment of certain complexes of formula RhL₃X₃ with molecular hydrogen under mild conditions yields isolable hydrido-complexes of the type RhL₃X₂H. Moreover, ethanolic solutions of 1,2,6-Rhpy₃Cl₃ containing hex-1-ene, slowly take up molecular hydrogen at room temperature and pressures up to one atmosphere, the olefin being converted into n-hexane. This catalytic reduction of the olefin can be accelerated by use of higher hydrogen

pressures. These reactions are discussed in more detail later, but it must be noted that such reactions are characteristic of transition metal hydrides.

trans-Dibromotetrapyridinerhodium(III) Bromide can be simply prepared by treatment of $[\text{RhBr}_6]^{3-}$ (made in situ by refluxing rhodium trichloride with excess aqueous potassium bromide solution) with excess pyridine and hypophosphorous acid in the usual way. However, on boiling a solution of trans- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}$ with an excess of potassium bromide in the presence of hypophosphorous acid, the solution darkens and suddenly precipitates a very insoluble fawn compound. This is $[\text{Rhpy}_4\text{Br}_2][\text{Rhpy}_2\text{Br}_4]$ which was obtained by Poulenc¹³ by boiling $[\text{Rhpy}_4\text{Br}_2]\text{Br}$ with concentrated hydrobromic acid, or¹⁵ hypophosphorous acid. On heating a solution of trans- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}$ in the presence of an excess of potassium iodide with a little hypophosphorous acid, halide exchange is again catalysed, since $[\text{Rhpy}_4\text{I}_2]^+$ cation is formed rapidly in solution; however, the solution soon precipitates dark brown tri-iodotripyridinerhodium(III), the di-iodo cation being stable only in the presence of excess of pyridine

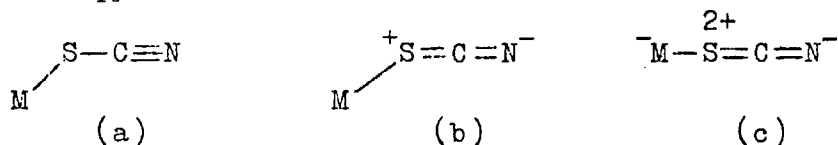
(ii) Thiocyanato-complexes. - The reaction of $[\text{Rh}(\text{SCN})_6]^{3-}$ with pyridine has previously been investigated.²³ The product after refluxing was described as trithiocyanatotripyridinerhodium(III); this product is found to be the nearly pure orange isomer described below, though there is always a small amount of the pale yellow isomer present, which can be removed by recrystallising from

dichloromethane. If a drop of hypophosphorous acid is added to the reaction mixture, the cation $[\text{Rhpy}_4(\text{SCN})_2]^+$ is not formed. The product is again a mixture of the two isomers, containing appreciably more of the pale yellow one. These isomers [both having the stoichiometry $\text{Rhpy}_3(\text{SCN})_3$] can be separated by their differing solubilities in dichloromethane, the orange isomer being very soluble, the pale yellow isomer virtually insoluble; it can, however, be recrystallised from aqueous pyridine.

The electronic spectra of both yellow and orange isomers show bands around $375 \text{ m}\mu$, supporting S-bonded rather than N-bonded thiocyanate. By comparison with the analogous formation of the isomers of trihalogenotripyridinerhodium(III) from the hexachlororhodate(III) or hexabromorhodate(III) ions, where the major products (85%) are the 1,2,6-isomers, 1,2,6-structure is tentatively assigned to orange $[\text{Rhpy}_3(\text{SCN})_3]$ and 1,2,3-structure to yellow $[\text{Rh}(\text{py})_3(\text{SCN})_3]$. Properties which distinguish between the isomers are given in Table 1.

In both isomers absorption occurs in the infrared spectrum at about 840 cm^{-1} , the orange isomer showing one band, and the pale yellow isomer three in this region, which has been said²⁴ to indicate N-bonded thiocyanate in complexes of the type $[\text{M}(\text{NCS})_6]^{3-}$. Since there appears to be no doubt that the hexathiocyanatorhodate(III) ion contains S-bonded thiocyanate, there would have to be a complete rearrangement during the reaction with pyridine if N-bonded thiocyanate were present in either isomer of $[\text{Rhpy}_3(\text{SCN})_3]$. Such a

rearrangement is unlikely, so it is preferred to assign the weak bands at 840 cm.^{-1} to overtones of the NCS bending vibrations. No absorption was apparent in either isomer between the pyridine bands at 700 and 750 cm.^{-1} , even when mulls in carbon disulphide were examined (to avoid the paraffinic absorption at 720 cm.^{-1}). However, the intense band around 700 cm.^{-1} due to pyridine may well obscure the weak C-S absorption due to the co-ordinated SCN^- . There is, of course, the further possibility that, of the possible forms of sulphur-co-ordinated thiocyanate shown, the normally favoured (a) no longer predominates in these tripyridine compounds, because of modification of the d-orbitals of the rhodium by the co-ordinated pyridine.



The formation of only tripyridine complexes in the thiocyanate system is reminiscent of the reaction of dichlorotetrapyridine-rhodium(III) chloride with iodide ion; either with or without added hypophosphorous acid, the product is tri-iodotripyridinerhodium(III), the tetrapyridine species $[\text{Rhpy}_4\text{I}_2]^+$ being stable only when excess of pyridine is present. It has been pointed out²⁵ that in the trans-dichlorotetrapyridinecobalt(III) cation, the molecules of pyridine must adopt a twisted configuration about the Co-N bond, the whole ion resembling a four-bladed propeller. The trans-dichlorobisbipyridylcobalt(III) cation is, so far as the four nitrogen atoms and the rings are concerned, however, genuinely

planar. In view of the existence of the $[\text{Rh}(\text{bipy})_2\text{I}_2]^+$ cation, the instability of $[\text{Rhpy}_4\text{X}_2]^+$, where $\text{X} = \text{I}^-$ or SCN^- may be due to steric factors arising from compression of the propeller in the xy-plane about the metal by the large axial ligands.

(b) Bipyridyl and o-phenanthroline complexes of rhodium(III).

(i) trans-Dichlorobisbipyridylrhodium(III) Salts. - Numerous attempts have been made²⁶ to prepare pure salts of the $[\text{Rh}(\text{bipy})_2\text{Cl}_2]^+$ cation; products described in the literature are notoriously difficult to separate from other reaction products. In these early preparations, alcohol was used as solvent for the bipyridyl and the formation of small amounts of $[\text{Rh}(\text{bipy})_2\text{Cl}_2]^+$ in these cases is mainly due to the catalytic effect of this alcohol. When acetone is used to dissolve the bipyridyl, the bisbipyridyl complex is formed only very slowly, in extremely low yield. However, on addition of a few drops of ethanol, the $[\text{Rh}(\text{bipy})_2\text{Cl}_2]^+$ cation begins to appear rapidly in solution. In a more recent preparation,²⁷ using the fusion of hydrated rhodium trichloride with bipyridyl, the bulk product is impure trisbipyridylrhodium(III) chloride. The bisbipyridyl compound, which is a by-product, is recovered as its slightly soluble nitrate. Recent interest in these complexes arises from the observation²⁸ that rhodium trichloride in methanol which contains bipyridyl gives a purple colour on shaking with zinc amalgam. This was later found²⁹ to be due to a reduction of the required bipyridyl complex and oxidation of such purple

solutions in the presence of chloride ion might be expected to give rise to the $[\text{Rh}(\text{bipy})_2\text{Cl}_2]^+$ cation. Although dark yellow solutions are obtained in this way, they do not contain the desired salt. However, several other catalysed processes give rise to the dichlorobisbipyridylrhodium(III) cation. When hydrated rhodium trichloride is dissolved in a 1 : 1-ethanol-2-methoxyethanol mixture, bipyridyl dissolved in ethanol added, and the mixture slowly brought to the boil, $[\text{Rh}(\text{bipy})_2\text{Cl}_2]\text{Cl}$ is precipitated as a bright yellow powder. Its solution in hot water when treated with sodium nitrate or perchlorate gives the required salts as pale yellow crystals. Yields are high, the loss being incurred during recrystallisation. Interestingly enough, when an aqueous alcoholic solution of rhodium trichloride and bipyridyl is treated with a little hypophosphorous acid and allowed to stand in the cold, yellow needles of $[\text{Rh}(\text{bipy})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ crystallise out over a few days. However, the preferred method is to add a small quantity of hydrazinium chloride to a hot ethanolic solution of rhodium trichloride and bipyridyl, when there is an extremely rapid colour change and on cooling beautiful crystals of $[\text{Rh}(\text{bipy})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ are obtained. The identity of the products with those prepared by literature methods has been shown by electronic and infrared spectra.

Although hypophosphorous acid slowly gives the required compound in the cold, when the solutions are boiled the product is contaminated by phosphorus-containing products. If molar amounts

of hypophosphorous acid are added to boiling mixtures of rhodium trichloride and bipyridyl in aqueous ethanol a **yellow**, highly insoluble product is obtained. It contains phosphorus and its infrared spectrum shows modes due to P-H (ca 2350 cm^{-1}) and P-O (ca. 890 cm^{-1}) as well as the characteristic bonded bipyridyl frequencies. It appears that this is a hypophosphite complex; no chlorine was present. More interesting, however, was the behaviour of the complex in aqueous solution. Insoluble in cold water, it dissolves in hot water to give a dark brown solution which, if cooled rapidly, shows a high-field line in the proton-resonance spectrum characteristic of hydrogen bonded to rhodium directly. On cooling, the solution gradually lightens to a pale yellow from which the original complex can be recovered. This cycle can be performed many times with only a gradual loss in efficiency. It is relevant that the same cycle can be initiated by treating $[\text{Rh bipy}_2\text{Cl}_2]\text{Cl}$ in aqueous solution with sodium hypophosphite.

trans-stereochemistry has been assigned to the rhodium(III) bisbipyridyl cations from a consideration of their electronic spectra in aqueous solution. These have not been previously reported and are recorded in the Experimental section. Previous assignments of stereochemistry were based firstly²⁹ on the splitting of the in-phase out-of-plane CH vibrations of the bipyridyl, allegedly due to the cis-configuration, and later on the formation³⁰ of an adduct with hydrogen chloride, indicating the trans-configuration.

(ii) trans-Dichlorobis-1,10-phenanthroline-rhodium(III)

Chloride. - This salt is new. The preparation is analogous to that of the bipyridyl derivative; the hydrazine-catalysed reaction is again the simplest, and gives a very good yield. Salts vary from bright to pale yellow; spectroscopic data are recorded in the Experimental section. Again if hypophosphorous acid is used in molar quantities in hot aqueous ethanolic solutions of rhodium trichloride and 1,10-phenanthroline a hypophosphite complex is formed entirely analogous to that described in the previous section. Again trans-stereochemistry has been assigned to this compound because of the similarity of its electronic spectra to that of the trans-bisbipyridyl complex.

(iii) Other Bisbipyridylrhodium(III) Compounds. - Related compounds containing the bisbipyridylrhodium(III) moiety can be prepared by similar methods; when hexabromorhodate(III) ion is allowed to react with bipyridyl in aqueous ethanol a fawn precipitate is given on heating. This contains co-ordinated bipyridyl and analysis yields the empirical formula $\text{Rh}_2\text{dipy}_3\text{Br}$. This compound is insoluble in dichloromethane but soluble in boiling hydrobromic acid or after prolonged boiling in water. It can be recovered unchanged from hydrobromic acid but gives a yellow solution in hot water, suggesting that hydrolysis has taken place. If hydrazinium chloride is added to the hot bipyridyl-hexabromorhodate reaction mixture, a little fawn precipitate is given but on cooling and standing beautiful plate-like orange crystals grow in the solution.

These are $[\text{Rh bipy}_2\text{Br}_2]\text{Br}\cdot 2\text{H}_2\text{O}$. The replacement of chloride in $[\text{Rh bipy}_2\text{Cl}_2]^+$ cation by bromide even in the presence of hydridic catalysts is slow and the above synthesis is the most convenient. This is not so in the case of $[\text{Rh bipy}_2\text{I}_2]^+$ cation. There is fairly ready replacement of the chloride in $[\text{Rh bipy}_2\text{Cl}_2]^+\text{Cl}$ with excess of iodide present in solution, and the rate of this replacement is increased by catalysis, especially by hypophosphorous acid. $[\text{Rh bipy}_2\text{I}_2]\text{I}$ is sparingly soluble in water and comes out of solution as a brick-red precipitate. If bipyridyl in ethanol is added to a hot solution of $[\text{RhI}_6]^{3-}$ anion, a black precipitate is found, which cannot be substituted further, presumably because of its extreme insolubility. Analyses were inconclusive. In attempts to prepare the bithiocyanatobispyridylrhodium(III) cation by either of the possible routes, both catalysed and uncatalysed, a red compound is formed, usually as an oil, which has not been characterised further.

(c) Complexes of Rhodium(III) with Ethylenediamine and Ammonia. -

Earlier preparations of trisdiaminerhodium(III) salts utilised the slow reaction of the diamine with rhodium tri-iodide. However, when an excess of ethylenediamine is added to a warm alcoholic solution of rhodium trichloride trihydrate, $[\text{Rhen}_3]\text{Cl}_3$ precipitates immediately. Propylenediamine behaves identically. Yields of these reactions are virtually quantitative. It has not been possible to make complexes containing the bisethylenediaminerhodium(III)

moiety catalytically. However, the rate of nucleophilic substitution by bromide and iodide in the trans-dichlorobisethylenediamine-rhodium(III) cation is enormously enhanced by catalytic amounts of hydridic reagents such as sodium borohydride or hypophosphite.

Although the ammine complexes of rhodium(III) are well known, their preparation³¹ has been laborious and the separation of products somewhat difficult. This is especially true of the hexammine and chloropentammine cations. However, on using alcohol as a catalyst they are readily accessible.

The hexammine complex is prepared in an identical way to that of the trisethylenediaminerhodium(III) cation, i.e. a warm concentrated solution of rhodium trichloride trihydrate in ethanol is treated with a few drops of concentrated (.88) ammonia and then gently refluxed for two minutes. The required product $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ precipitates from the solution in good yield.

However, if a warm concentrated aqueous solution of rhodium trichloride trihydrate with only a few drops of ethanol present is treated with .88 ammonia and refluxed for two minutes, $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is the major product.

(d) Rhodium Complexes with Dimethylglyoxime. -

Several complexes of rhodium(III) with dimethylglyoxime have been reported. The dichlorobisdimethylglyoxime-rhodium is readily formed from aqueous alcoholic solutions of the reactants.³² However, if acetone-water is used to dissolve the reactants little reaction is noted even after boiling for some time. However, on

addition of a few drops of alcohol, the reaction goes quickly to completion. Again alcohol serves both as solvent and catalyst. Even in this alcohol-catalysed reaction the addition of a little hypophosphorous acid or hydrazinium chloride greatly increases the rate.

The synthesis of the dichlorobiscyclohexadionedioximato-rhodium(III) anion cannot readily be achieved by boiling aqueous solutions of the ligand and rhodium trichloride, but on addition of alcohol the required product is quickly formed in solution.

Similarly the analogous bromide and iodide complexes of the bisdimethylglyoximato-rhodium(III) moiety can be prepared by the catalysed reaction in aqueous solution of the $[\text{RhX}_6]^{3-}$ ion (made in situ by heating an aqueous solution of rhodium trichloride with excess of potassium bromide or iodide) with the alcoholic solution of the ligand. Substitution in the trans-dichlorobisdimethyldioximato-rhodium(III) anion by other halides, except iodide, is slow even with hydridic catalysts present.

Although the formation of anionic compounds of the type $[\text{Rh}(\text{DMGH})_2\text{XCl}]^-$ has been claimed³³ by refluxing the dichloro-compound with the ammonium salt of the anion, X^- , the sole product obtained in this work when such reactions were repeated has been the ammonium salt of the starting material $(\text{NH}_4)[\text{Rh}(\text{DMGH})_2\text{Cl}_2]$. In particular, the infrared spectrum of the product when ammonium thiocyanate is refluxed with the dichloro-compound shows the absence of co-ordinated thiocyanate. It has not been possible to

prepare a pure thiocyanato-complex either by catalysed substitution in the $[\text{Rh}(\text{DMGH})_2\text{Cl}_2]^-$ anion or by the catalysed action of dimethylglyoxime on $[\text{Rh}(\text{SCN})_6]^{3-}$ anion.

It was claimed³⁴ that when dimethylglyoxime reacts with $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}$, chlorobisdimethylglyoximatopyridinerhodium(III) is formed. Pyridine is indeed displaced, but the sole complex containing dimethylglyoxime produced is the dichlorobisdimethylglyoximatorhodate(III) ion, as its pyridinium or trans-dichlorotetrapyridinium(III) salts. Both $[\text{Rhpy}_4\text{Cl}_2]^+$ and $[\text{Rh}(\text{DMGH})_2\text{Cl}_2]^-$ react with reducing agents, and the presence of hydridic species has been demonstrated for both "reduced" complexes under certain conditions^{20,21}. However, no combinations of solvent (water or ethanol), reducing agent, or temperature gave the desired compound, the most common product on allowing the reduced reaction mixture to oxidise being pyridinium dichlorobisdimethylglyoximatorhodate(III). It was finally found that when pyridinium dichlorobisdimethylglyoximatorhodate(III), suspended in hot pyridine, was heated with a little H_3PO_2 , a clear solution forms, which rapidly deposits needle-like crystals of chlorobisdimethylglyoximatopyridinerhodium(III).

The best-known complex of rhodium(III) with dimethylglyoxime is that formulated³² as "hydrogen dichlorobisdimethylglyoximatorhodate(III)". This formulation is undoubtedly correct in aqueous solution, as shown (Table 2) by the coincidence of the ultraviolet spectra of the monobasic acid and its salts. However, the formulation is incorrect for the solid state of the acid, since

an O-H stretching mode is apparent at 3400 cm^{-1} . This had been noted previously,³⁵ but not discussed. It leads to the formulation of the compound in the solid state as "dichloro(dimethylglyoximato)-dimethylglyoximerhodium(III)", as in the analogous compound of cobalt(III).³⁶ This formulation is confirmed by (a) the shift of ν_{OH} to 2400 cm^{-1} on deuteration, giving $\nu_{\text{OH}} : \nu_{\text{OD}} = 1.38$, and (b) the disappearance of ν_{OH} when the silver salt is formed. The hydrogen-bonded O-H...O frequency has been located in the original acid, and in its silver salt; in a strong mull, an extremely broad band occurs, centred at 2440 cm^{-1} , which, in the acid, on deuteration (by several recrystallisations from heavy water) shifts; $\nu_{\text{O-D...O}}$ occurs as a very broad, weak band centred at 1840 cm^{-1} , giving $\nu_{\text{O-H...O}} : \nu_{\text{O-D...O}} = 1.33$.

Infrared spectra for dihalogenobisdimethylglyoxime complexes with rhodium(III) are collected in Table 4. It is clear that all the solid dihalogeno-acids must be reformulated as $[\text{Rh}(\text{DMGH}_2)(\text{DMGH})\text{X}_2]$. Although dichloro(dimethylglyoximato)dimethylglyoximerhodium(III) is fairly soluble in dimethylformamide, giving beautiful crystals by slow evaporation of the solution, no proton resonance signal due to an intramolecular hydrogen bond was observed in the solution, suggesting hydrogen transfer to give $\text{Me}_2\text{NCONH}_3^+$, i.e., the dimethylglyoxime compound is a weaker base than dimethylformamide. It was further found that, for chlorobisdimethylglyoximatopyridinerhodium(III), the intramolecular hydrogen bond is by no means so obvious as that in analogous complexes of the first transition row. For example

in complexes of cobalt(III), the intramolecular hydrogen bond gives a resonance at $\tau \sim -8.5$,³⁶ and in complexes of nickel(II), at $\tau \sim -8$.³⁷ Nor is the infrared absorption, ca. 1800 cm.^{-1} , found in the complexes of cobalt(III) observed; the corresponding absorption for the rhodium complex is at $\sim 2400 \text{ cm.}^{-1}$. The spectroscopic properties of the cobalt(III) and rhodium(III) complexes are compared in Table 3.

The proton resonance due to $\text{O-H} \cdots \text{O}$ is observed at $\tau \sim -2$ in the rhodium(III) complex; its position varies slightly with dilution. Presumably, the hydrogen bond in the rhodium complex is longer and therefore weaker than that in the cobalt analogue, as a consequence of the larger radius of rhodium. The resonance spectrum due to the co-ordinated pyridine molecule is very similar to those observed in other complexes containing pyridine. In work using platinum(II) complexes, it was found³⁸ that the chemical shift of the β -protons of co-ordinated pyridine varied only very slightly from one square-planar complex to another. In this work, the chemical shifts of the β -protons are strikingly different in the octahedral cobalt(III) and rhodium(III) complexes, possibly owing to differences in π -bonding between pyridine and cobalt(III) or rhodium(III).

TABLE 1.

Properties of isomers of $[\text{Rhpy}_3(\text{SCN})_3]$

Isomer	Colour	$\lambda_{\text{max.}}$	$\epsilon_{\text{max.}}$	CH_2Cl_2	Infrared
1,2,3-	Yellow	372 ^a	1750	Insol.	853, 846, 838
1,2,6-	Orange	380 ^b	1650	Sol.	841

^a In pyridine. ^b In dichloromethane.

TABLE 2.

Electronic spectra of salts of the $[\text{Rh}(\text{DMGH})_2\text{Cl}_2]^-$ anion
(in water; λ in $\text{m}\mu$)

Compound	λ	ϵ	λ	ϵ
" $\text{H}[\text{Rh}(\text{DMGH})_2\text{Cl}_2]$ "	292	5×10^3	273	7×10^3
$(\text{NH}_4)[\text{Rh}(\text{DMGH})_2\text{Cl}_2]$	292	5×10^3	273	7×10^3
$(\text{GH})[\text{Rh}(\text{DMG})\text{H}_2\text{Cl}_2]^{\text{a}}$	292	5×10^3	274	7.1×10^3

^a (GH) = guanidinium.

TABLE 3.

Spectroscopic data for $[\text{M}(\text{DMGH})_2\text{pyCl}]$ (M = Co or Rh)

Compound	$\nu_{\text{O-H}\cdots\text{O}}$	$\tau_{\text{O-H}\cdots\text{O}}$	τ_{py}		τ_{CH_3}	Ref.
			β	α		
$[\text{Co}(\text{DMGH})_2\text{pyCl}]$	1710	-8.01	$\begin{Bmatrix} 1.04 \\ 0.82 \\ 0.54 \end{Bmatrix}$	$\begin{Bmatrix} -1.11 \\ -1.13 \end{Bmatrix}$	6.86	a
$[\text{Rh}(\text{DMGH})_2\text{pyCl}]$	2450	-2.05	$\begin{Bmatrix} 2.67 \\ 2.55 \\ 2.46 \end{Bmatrix}$	$\begin{Bmatrix} 1.49 \\ 1.38 \end{Bmatrix}$	6.76	b

^a Gillard and Wilkinson, J., 1963, 6041. ^b This work.

TABLE 4.

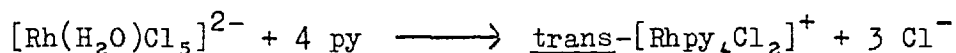
Infrared spectra of dimethylglyoxime complexes of rhodium(III) (cm^{-1})

	"H[Rh(DMGH) ₂ Cl ₂]"	Ag[Rh(DMGH) ₂ Cl ₂]	NH ₄ [Rh(DMGH) ₂ Cl ₂]	a	b
ν_{OH}	3400m	---	---	3280w	3300m
			3460		
ν_{NH}	---	---	3246	---	---
			3135		
ν_{CH}	---	2900w	2874w	---	---
ν_{OHO}	2440w, b	2480w, b	---	2420w	2400w
	---	---	---	---	---
ν_{NH_2}			1616	---	---
ν_{OH}	1600m, b	---	---	1598m	1598m
ν_{NO}	1508m	1515s	1520	1520w	1530m
	---	1420m	1424		
ν_{CH} {		1362m			
	1328m	1321m		1333w	---
	1240s	1241s	1245	1221s	1227s
	1129m	1129m	1124m	1121m	1121m
	1078s	1075s	1074s	1066s	1076s
$\nu_{\text{OHX?}}$	1019w	---	---	1000m	1008w
	986w	---	977	965m	970m
	---	---	---	---	---
	860m, vb	---	---	842w	855wb
$\nu_{\text{NH}_4^+}$	---	---	839	---	---
	737s	733s	734s	730w	728s

a = H[Rh(DMGH)₂Br₂].b = H[Rh(DMGH)₂I₂].

Discussion

It can be seen that the preparation of complexes by reductive catalysis appears to be a general phenomenon of rhodium(III) chemistry. The most likely catalytic intermediate is a reduced rhodium species and it has also been noted here and elsewhere¹⁸ that the reducing agents which generally promote this behaviour are those used for preparing hydrido-complexes. In the kinetic study of the ethanol catalysed conversion



it was found that only catalytic quantities and not stoichiometric quantities of ethanol were required. Moreover, only the rate of formation of trans- $[\text{Rhpy}_4\text{Cl}_2]^+$ cation was increased by the presence of ethanol and not the rate of disappearance of $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$. From these present studies the rate of formation of trichlorotripyridinerhodium(III) even in the absence of ethanol is fast and the conversion of this complex into the dichlorotetrapyridine-rhodium(III) cation is the rate determining and ethanol catalysed step. It was concluded in the kinetic study that the catalytic intermediate was the rhodium(I) species, $[\text{Rhpy}_4]^+$. However, only rather peripheral evidence supported this proposal, although the suggested³⁹ mechanism is analogous to that put forward to explain the Pt^{II} catalysis of the reactions of Pt^{IV} complexes.

It is also possible that $\text{Rh}(\text{II})$ could function in the catalysis in a way similar to the Co^{II} catalysis of Co^{III} . However, the divalent oxidation state plays little or no part in

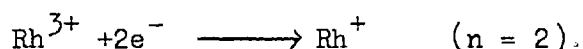
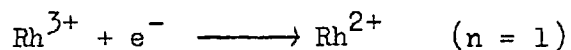
the chemistry of rhodium and it is shown in the following chapter that there is no evidence for rhodium(II) as an intermediate in the polarographic reduction of a series of rhodium(III) complexes

It is suggested in this work that a hydrido-species promotes the catalysis by an intermolecular hydride ion transfer process. The fact that hydride producing reagents, and, in particular, molecular hydrogen, are used in the catalysis considerably favours this concept.

CHAPTER II.

POLAROGRAPHIC REDUCTION OF RHODIUM(III) COMPLEXES.

From the preceding chapter it is clear that more data on the nature of the reduced species of rhodium with nitrogenous ligands would be desirable. The polarographic method is capable, in principle, of distinguishing between the primary processes



However, reduction to a monohydrido-rhodium(III) species would also be equivalent to a two electron step, and thus whether Rh^{I} or $\text{Rh}^{\text{III}} - \text{H}$ is formed, cannot be decided by polarographic methods. Several halogenoamminorhodium(III) complexes have been examined by means of polarography to determine the primary electron transfer process.

Rhodium(III) complexes have previously been studied on several occasions polarographically. However, in the light of the present knowledge of the chemistry of rhodium, it is quite clear that in most cases the solutions used contained mixtures of several complexes, despite the usual assumption that a single species only was present. For example, even refluxed solutions of rhodium trichloride and pyridine contain only the isomers of trichlorotripyridinerhodium(III), and not the hexakispyridinerhodium(III) cation, as was assumed.⁴⁰ Values of n in much previous work have therefore rested on diffusion coefficients which are greatly in

error, since the assumption as to the nature of the electro-active species have usually been incorrect. Polarographic data on well-characterised complexes of rhodium(III) are collected in Table 5.

TABLE 5.

Polarographic results for complexes of rhodium(III)

Complex	Supporting electrolyte	$E_{\frac{1}{2}}^*$	n	Ref.
$[\text{Rh}(\text{SCN})_6]^{3-}$	KSCN (0.9M)	-0.39	2	40
$[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$	NaNO_3 (1M)	-0.96	2	40
	K_2SO_4 (0.5M)	-0.96	2	40
	NH_4Cl (1M)	-0.93	2	40
	NH_3 (1M)	-0.93	2	40
	NH_4Cl (1M)	-0.93	2	40
$[\text{Rh}(\text{CN})_6]^{3-}$	KCN (1M)	-1.54	2	41
" RhCl_3 "	HClO_4 (0.5M)	-0.39	2	42
$[\text{Rh}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{3-}$		-0.43	2	42
$[\text{Rh}(\text{C}_2\text{O}_4)_3]^{3-}$	$\text{H}_2\text{C}_2\text{O}_4$ (0.5M)	-0.83	2	42

* v relative to S.C.E.

Chlororhodium(III) species in particular have given rise to variable conclusions. Cozzi and Pantani⁴³ found fairly large variation of $E_{\frac{1}{2}}$ with the concentration of the supporting electrolyte, hydrochloric acid, suggesting that more species were present in solution than they considered. Recently, Magee and Douglas,⁴⁴ using larger chloride-ion concentrations, studied solutions which still contained a large fraction of mixed chloro-aquo-species. The presence of such species is obvious from the comparison of the quoted electronic spectra⁴⁴ with those of well-characterised

complexes.⁴⁵ Because of the probable presence of polymeric complexes in solutions of rhodium(III) in chloride media, manifested by the strong electronic absorption bands observed in the near-ultraviolet region, the reduction of hexachlororhodate(III) ion was re-investigated, using sodium hexachlororhodate(III) dissolved in sodium chloride solution; the complex does not aquate detectably during the experiment. $E_{\frac{1}{2}}$ was -0.19v (relative to the S.C.E.) with $\underline{n} = 2$. It is relevant that, in reductions of ferric ion with molecular hydrogen, catalysed by solutions containing $[\text{RhCl}_6]^{3-}$, it has been suggested,⁸ on kinetic grounds, that the intermediate responsible is $[\text{HRhCl}_5]^{3-}$; such an ion could certainly form from the further reaction of the first reduction product of the polarographic process.

The validity of results obtained by using the coulombic method⁴³ is questionable, since for the chloropentamminerhodium(III) cation the coulombic method gave $\underline{n} = 3$, while an accurate polarographic determination⁴⁶ on this cation showed it to undergo a two-electron reduction. Moreover, the hydridopentamminerhodium(III) cation has been isolated by zinc reduction of the corresponding chloro-complex (Chapter III), thus indicating that a two-electron reduction step has taken place.

Analytical methods for determining rhodium by means of polarography have repeatedly recommended^{40,47} use of a pyridine medium. The assumption^{40,44} has been, incorrectly, that dissolving rhodium trichloride in aqueous pyridine gave the

hexakispyridinerhodium(III) cation.

Some recent studies⁴⁸ on 1,2,6-trichlorotripyridine-rhodium(III) in pyridine solution have shown a two-electron step to take place, which is equivalent to the formation of a Rh^{I} or $\text{Rh}^{\text{III}} - \text{H}$ species. Significantly, as discussed earlier, both these species have been postulated as catalytic intermediates in the preparation of $\text{trans-}[\text{Rhpy}_4\text{Cl}_2]^+$ from 1,2,6-Rhpy₃Cl₃.

In this work, using trans-dichlorotetrapyridinerhodium(III) chloride, $E_{\frac{1}{2}}(\text{I})$ was found to be -0.39 with $n = 2$, under varying conditions. It is noteworthy that on treatment with hydride ion, this complex cation yields²⁰ a hydrido-species, as in



A second polarographic wave is observed for this salt with $E_{\frac{1}{2}}(\text{II}) = -0.95$; however, this is probably not a simple electron step between two stable species. Although n is approximately 1, $i_{\text{d}}(\text{II})$ does not bear a constant relation to $i_{\text{d}}(\text{I})$. This second step is due to the further reduction, possibly of the ligand, of a reduced species formed in step I, e.g., $[\text{Rhpy}_4\text{HCl}]^+$, particularly since the high $E_{\frac{1}{2}}$ observed is characteristic⁴⁹ of hydridic species. Similar results were obtained for the cation $\text{trans-}[\text{Rhpy}_4\text{Br}_2]^+$; data are collected in Table 6. The polarographic behaviour of the trans-dichlorobisbipyridylrhodium(III) cation is not as simple as that of its pyridine analogue; a polarographic wave is observed, but accurate measurements were not obtained because the pronounced maxima, due probably to the unsaturated ligand, could not be

TABLE 6.

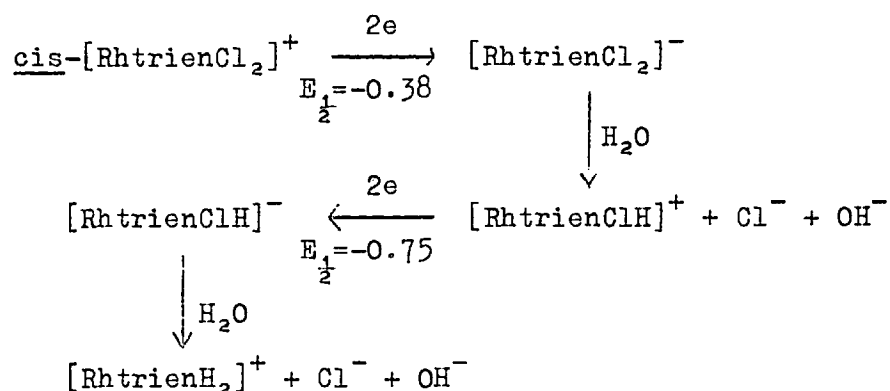
Polarographic results for trans-[Rh(amine)₄XY]

Complex	Concn. (mm./l.)	$E_2(I)^+$	$\frac{i_d}{(\mu A)}$	$\frac{m_2}{m_1} \frac{t_1}{t_2}$	$\underline{n}$	$\lambda_{max.}$	$E_2(II)^*$
Rhen ₂ Cl ₂ ⁺	1	-0.79	6.7	2.2	2	406	--
	0.2	-0.79	1.4	2.2	2		
Rhen ₂ I ₂ ⁺	0.47	-0.70	2.8	2.2	2	462	--
Rhen ₂ BrCl ⁺	1	-0.77	5.8	2.3	2	417	--
Rhpy ₄ Cl ₂ ⁺	0.62	-0.39	3.5	2.2	2	411	-0.95
Rhpy ₄ Br ₂ ⁺	1	-0.28	3.0	2.2	2	425	-0.92

* v relative to S C E

suppressed.

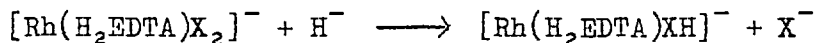
For complexes of the type trans-[Rhen₂XY]⁺, where X and Y are halides, similar results were obtained for the first reduction step. Again, $\underline{n}$ is 2, in line with observations²⁰ on the chemical reductions of such complexes.. For these trans-cations, no second wave derived from further reduction of the monohydride could be found. For the cis-isomers of these cations, [Rhen₂X₂]⁺, where X = halide, only ill-defined polarographic waves could be obtained and no accurate measurements were possible. However, with cis-dichlorotriethylenetetraminerhodium(III) chloride, two waves were observed, with $E_2 = -0.38$ and -0.75 , both having $\underline{n}$ approximately 2. The existence²⁰ of both the mono- and di-hydridic species, [RhtrienClH]⁺ and [RhtrienH₂]⁺ has previously been demonstrated, and it seems likely that the two waves observed may be accounted for by the scheme:



The only other case where two polarographic waves were observed was for the dichloro(ethylenediaminediacetatodiacetic acid)rhodate(III) anion, $[\text{Rh}(\text{H}_2\text{EDTA})\text{Cl}_2]^-$. This was previously studied by Russian workers,⁵⁰ who claimed that $\text{E}_{\frac{1}{2}} = -0.75$ with $\underline{n} = 3$. This work shows this to be a two-step reduction, with $\text{E}_{\frac{1}{2}}(\text{I}) = -0.73$, and $\text{E}_{\frac{1}{2}}(\text{II}) = -0.97$. The two steps are approximately equal, $\underline{i}_d(\text{I}) \simeq \underline{i}_d(\text{II})$. Using a value for the diffusion coefficient derived from the conductivity of potassium ethylenediaminetetraacetatocobaltate(III), whereby $D^{\frac{1}{2}} = 2.5 \times 10^{-3}$, gives $\underline{n} = 4$, so that $\underline{n}_{\text{I}} = \underline{n}_{\text{II}} = 2$. The diffusion coefficient derived from the rhodium complex itself is not useful, because of the presence of ionisable protons in the complex, the pK value being about 4. The electronic spectra of the dichloro-complex and of its dibromo-analogue show shifts of the longest wavelength band to shorter wavelengths when the complexes are treated with borohydride ion. Isosbestic points are observed for the reactions. It has been previously found²⁰ for rhodium(III) compounds of this type that in the spectrochemical series, $\text{H}^- > \text{Cl}^- > \text{Br}^-$, and the data collected in Table 7 for these systems agree with the formation

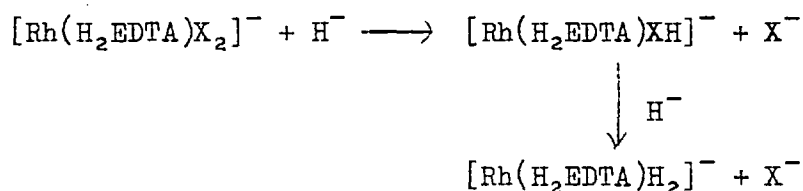
TABLE 7.

Spectra data for reactions



X	[Rh(H ₂ EDTA)X ₂] ⁻		Isosbestic point	X	[Rh(H ₂ EDTA)XH] ⁻	
	λ _{max.}	ε			λ _{max.}	ε
Cl	402	400	377	Cl	370	360
Br	418	460	392	Br	375	500

of hydrido-species, as in



However, it has not been possible to establish the presence of rhodium-hydrogen bonds by means of proton magnetic resonance.

Vlček^{46,49} has pointed out that the process $\text{M}^{n+} \longrightarrow \text{M}^{m+}$ (where $\underline{n} > \underline{m}$) involves addition of electrons to the lowest unoccupied orbitals of the metal, and that the half-wave potential should be related to the lowest energy $\underline{d}-\underline{d}$ electronic transitions for similar complexes. An attempt was made recently⁴⁴ to interpret polarographic results for complexes of rhodium(III) in this way. However, examination of the quoted⁴⁴ electronic spectra shows that the assumption that the solutions used contained complexes of the type $[\text{RhX}_6]^{n+}$, where $\text{X} = \text{Cl}^-$, SCN^- , py , NH_3 , or CN^- , is unjustified. If spectrophotometric and polarographic results are to be meaningfully correlated, it is essential that clearly defined complexes must be used.

When, in the complexes of the type trans-[Rhen₂XY]⁺, E_g is plotted⁴⁶ against Δν (the difference between the observed frequencies of ¹T_{1g} ← ¹A_{1g} in [Rh(NH₃)₆]³⁺ and ¹E_g ← ¹A_{1g} of the complex), a straight line is obtained with slope -3.3 x 10⁻⁵ v cm.⁻². The relationship between ease of reduction and the energy of the lowest unoccupied orbital is similarly clear in the case of trans-[Rhpy₄X₂]⁺, where X = Cl or Br. Unfortunately, the di-iodo-complex is thermodynamically unstable, readily losing pyridine.

The present results show that, in these ammine complexes, rhodium(II) is not formed as a stable intermediate during the polarographic reduction. It seems probable that this valence state cannot be responsible for the catalysis in such systems. The remaining question of whether the catalytic species is Rh^I or Rh^{III} - H is not settled although the existence of hydrido-species in many complexes of rhodium(III) containing non-π-bonding ligands supports the hydride concept.

CHAPTER III.

THE ACTIVATION OF MOLECULAR HYDROGEN BY COMPLEXES OF RHODIUM(III);
THE PREPARATION OF SOME RHODIUM(III) HYDRIDES.

Introduction.

The activation of molecular hydrogen by transition metal ions or complexes in homogeneous solution is well known.⁵¹ Only a few systems, however, have proved to be useful for the catalytic homogeneous hydrogenation of unsaturated compounds. One of the most versatile catalysts is the cobalt(II)-cyanide system⁹ which allows the reduction of conjugated double bonds but not isolated ethylenic linkages.⁵² The hydrido-species, $[\text{Co}(\text{CN})_5\text{H}]^{3-}$, has been proposed as the active intermediate in this system. It has also been observed⁹ that molecular hydrogen can reduce certain organic substrates such as quinone in the presence of soluble rhodium(III) complexes, e.g. rhodium trichloride trihydrate and dichlorotetramminerrhodium(III) ~~dichloride~~. More recently, the reduction of ferric ion by hydrogen in the presence of hexachlororhodate(III) ion has been studied^{8,53} kinetically, and it was suggested⁸ that the hydrido-species, $[\text{RhCl}_5\text{H}]^{3-}$, was the catalytic intermediate.

The first part of this chapter is concerned with the preparation and properties of hydrido-complexes of rhodium(III) stabilised by weak field ligands, i.e. hydridopentamminerrhodium(III) sulphate and hydrido-aquo-tetramminerrhodium(III) sulphate. The

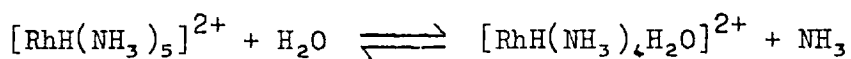
second part deals with the activation of molecular hydrogen by complexes of rhodium(III) and the catalytic properties of such complexes.

(a) Hydridopentamminerhodium(III) sulphate and hydrido-aquotetramminerhodium(III) sulphate.

A number of cationic chloroamine rhodium(III) complexes undergo ²¹ nucleophilic displacement of chloride by hydride in aqueous solution, the borohydride ion serving as a source of hydride. The resulting hydrido-complexes were detected by observation of the high field proton resonance absorption. In several cases impure tetraphenylborate salts could be precipitated which show a band at ca. 2100 cm.⁻¹ in the infrared assignable as a metal-hydrogen stretching frequency. No pure hydridoamine-rhodium(III) complexes could be isolated because successive reductions²⁰ were occurring and/or rhodium metal was readily deposited.

However, if chloropentamminerhodium(III) sulphate is treated with zinc dust in ammoniacal solution, hydridopentamine-rhodium(III) sulphate is obtained as a white precipitate on addition of excess concentrated ammonia. This salt is stable in air indefinitely although readily oxidised in solution. The infrared spectrum shows an intense band at 2073 cm.⁻¹ ($\nu_{\text{Rh-H}}$) as well as modes due to co-ordinated ammonia and ionic sulphate. The proton magnetic resonance spectrum in water shows a high field doublet centred at $\tau = 27.1$, ($J_{\text{Rh-H}} = 14.5$ c/sec.). The electronic

absorption spectrum taken as a mull in spectroscopic n-hexane shows a band at 307 μ which confirms previous conclusions²⁰ on the position of the hydride ion in the spectrochemical series. If hydridopentamminerhodium(III) sulphate is repeatedly re-precipitated from a large volume of water by addition of acetone, the white air-stable hydrido-aquotetramminerhodium(III) sulphate can be separated out. The infrared spectrum of this salt shows bands due to bound water as well as a band at 2145 cm^{-1} ($\nu_{\text{Rh-H}}$). Dissolution of the hydrido-aquotetrammine complex in D_2O followed by immediate acetone precipitation shows that exchange of hydride and bound water occurs much faster than the exchange with ammonia. The n.m.r. in water shows a doublet at high field centred at τ 32.0, ^{103}Rh splitting 25 c/sec. If one drop of concentrated ammonia is added to this solution in the n.m.r. tube, the doublet at τ 32.0 immediately decays while the doublet at τ 27.1 grows up. Hence in solution the following equilibrium is set up, viz.



The ready loss of one ammonia molecule is a striking example of the strong trans labilizing effect of the hydride ion; the resulting hydrido-aquotetrammine complex must then be formulated as the trans isomer. It is noteworthy that the recently isolated⁵⁴ hydrido-tetracyanoaquaorhodium(III) anion showed trans-stereochemistry.

The two hydrido complexes, although very stable in the solid state, are very reactive in solution readily undergoing oxidation, anation and insertion reactions. However, the unexpected

stability of these complexes would indicate that many hydrido-species stabilised by weak field ligands can have a definite if short-lived existence in certain catalytic processes. This combination of thermodynamic stability with chemical reactivity is, of course, a critical factor in catalytic behaviour.

(b) Activation of molecular hydrogen by complexes of rhodium(III)

(i) Rhodium trichloride trihydrate - Iguchi⁹ studied the absorption of molecular hydrogen by aqueous solutions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of reduceable organic substrates such as sodium cinnamate and quinone. However, aqueous or alcoholic solutions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ do not contain only simple monomeric species. The visible spectrum of the deep red solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ dissolved in water taken after 5 minutes at 20°C shows absorption bands at $506 \text{ m}\mu$ ($\epsilon \sim 130$) and $380 \text{ m}\mu$ ($\epsilon \sim 1000$). This spectrum results presumably from a polymeric species since the spectra of the monomeric species have been measured⁵⁵ and show no comparable band in the near ultraviolet. Moreover, it has been claimed⁵⁶ that complexes of the type $(\text{Me}_4\text{N})\text{Rh}_2\text{Cl}_9$ can be precipitated from such solutions. If these solutions are gently warmed or let stand under nitrogen for several hours, the colour lightens and the band at $506 \text{ m}\mu$ shifts to shorter wavelengths while a decrease in intensity at $380 \text{ m}\mu$ is observed. Jørgensen has shown⁵⁷ the final product of this hydrolysis to be the $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ cation.

When the initial red solution is treated with molecular

hydrogen at atmospheric pressure and room temperature, a rapid colour change takes place yielding a yellow solution which if treated further with hydrogen quickly deposits rhodium metal. The yellow solution shows no high field line in the n.m.r. spectrum. However, the visible spectrum (λ_{max} 447, $\epsilon \sim 60$; λ_{max} 350, $\epsilon \sim 50$) is practically identical to that recorded for the ~~trans-~~ $[\text{Rh}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ cation.⁵⁵ Furthermore, no net uptake of hydrogen occurs, the catalysis being very similar to that of the catalysed formation of trans- $[\text{Rhpy}_4\text{Cl}_2]^+$ cation. A mechanism can be proposed involving heterolysis of molecular hydrogen by the polymeric chloro-rhodium species, the resultant hydride replacing chloride nucleophilically with the eventual displacement of the labile hydride ion by water.

Similar behaviour is found in methanolic solutions. The initial red solution (λ_{max} 500, $\epsilon \sim 160$; λ_{max} 380, $\epsilon \sim 1000$) when treated with molecular hydrogen rapidly turns yellow (λ_{max} 470, $\epsilon \sim 100$; λ_{max} 375, $\epsilon \sim 110$). This same solution is obtained on refluxing the red solution for about 10 minutes (λ_{max} 470, $\epsilon \sim 105$; λ_{max} 375, $\epsilon \sim 115$). Once again the initial solution contains a polymeric species which is catalytically cleaved and solvated by molecular hydrogen.

The proposal that the above reactions are catalysed by intermediate hydrido-species is supported by observations that solutions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ can act as homogeneous hydrogenation catalysts. It was found that an ethanolic solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$

containing hex-1-ene takes up molecular hydrogen at room temperature and pressures up to one atmosphere, the olefin being converted into n-hexane.

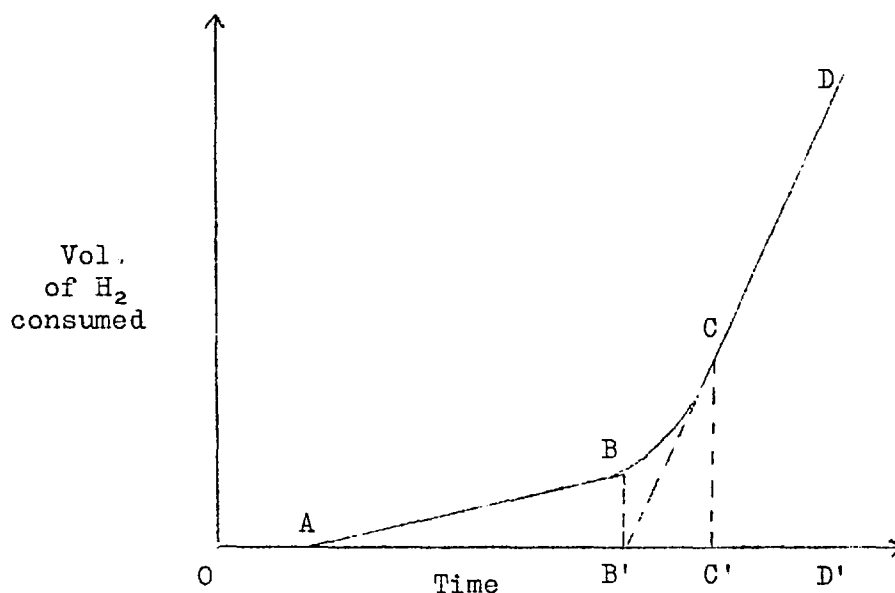


Figure 1.

Rate of hydrogen uptake for ethanolic solutions
of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ containing hex-1-ene.

The main features of this reaction are represented diagrammatically in Fig. 1, where the volume of hydrogen consumed is plotted against time. The following points are noteworthy.

(a) After the initial saturation of the solution there follows an induction period, OA, in which no absorption takes place. This induction period varies with the catalyst concentration but bears no simple relationship to it.

(b) A smooth homogeneous take-up of hydrogen then occurs, AB. Analysis of the solution at B shows the presence of n-hexane. However substantial isomerisation also occurs⁵⁸ since cis- and

trans-hex-2-ene can also be detected on the gas-liquid chromatograph. The rate of reduction during this period is found to be approximately proportional to the catalyst concentration.

(c) At C, rhodium metal can be seen in the solution and the marked increase in the rate of hydrogen absorption along CD results presumably from the intervention of heterogeneous catalysis.

Clearly this is not a simple reaction. The hydrido-intermediate has not been detected spectroscopically and appears to be too unstable to be able to maintain homogeneous behaviour. Thus it was found necessary to investigate the catalytic behaviour of other complexes of rhodium(III) where the hydrido species, if formed, would be sufficiently stable to be detected or even isolated.

(ii) Other complexes of rhodium(III). - The conversion of 1,2,6 Rhpy₃Cl₃ to trans-[Rhpy₄Cl₂]⁺ in aqueous pyridine solution is found to be very effectively catalysed by molecular hydrogen (Chap. I). This observation implies that activation of molecular hydrogen takes place in this solution and it is postulated that the hydrido-species, Rhpy₃Cl₂H, is formed. Moreover, if an ethanolic solution of 1,2,6 Rhpy₃Cl₃ is treated with hydrogen under pressure at 25°C, the n.m.r. spectrum of the resultant solution shows a doublet at high field (centred at $\tau \sim 25.6$, $J_{\text{Rh-H}} \sim 23.5$ c/sec.) which is characteristic of a direct rhodium-hydrogen bond. The hydrido-complex is thus stabilised by the presence of pyridine

ligands, no rhodium metal being formed. It has not been possible to characterise the complex further since it is extremely readily oxidised. However, ethanolic solutions of 1,2,6 Rhpy_3Cl_3 containing hex-1-ene at 25°C are found to take up molecular hydrogen slowly at ca. atmospheric pressure or more rapidly at higher pressures, n-hexane being identified as the product by vapour phase chromatography.

When a concentrated solution of $\text{Rh}(\text{MePh}_2\text{As})_3\text{Cl}_3$ in ethanol/benzene containing hex-1-ene is treated with molecular hydrogen at room temperature and atmospheric pressure, there is an initial induction period followed by a slow absorption of gas. Analysis of the hydrogenated solution after some time shows n-hexane to have been formed. After several hours, however, a yellow complex precipitates from solution. This compound has an Rh-H stretching frequency at 2075 cm^{-1} in the infrared spectrum, a high field doublet centred at $\tau\ 27.4$ ($J_{\text{Rh-H}}\ 10\text{ c/sec.}$) in the n.m.r. spectrum (taken in dichloromethane solution), and analyses for $\text{Rh}(\text{MePh}_2\text{As})_3\text{Cl}_2\text{H}$. This compound appears to be a different isomer to that described by Nyholm.⁵ The reduction of $\text{Rh}(\text{MePh}_2\text{As})_3\text{Cl}_3$ with hypophosphorous acid gives a yellow hydride of the same stoichiometry but with a different n.m.r. spectrum. The high field doublet measured in dichloromethane is centred at $\tau\sim 26.3$. Recently⁵⁹ an orange isomer has also been prepared by the stannous chloride reduction of the parent trichloro-complex. This latter hydride when dissolved in ethanol/benzene also takes up hydrogen

when hex-1-ene is present. Interestingly enough, however, very little induction period is observed and the rate of reduction is identical to that observed for solutions of $\text{Rh}(\text{MePh}_2\text{As})_3\text{Cl}_3$. After some hours the yellow hydrido-isomer again precipitates from the solution.

It appears that during the induction period gradual formation of the reactive hydrido-species takes place without appreciable hydrogen absorption. The function of ethanol as co-solvent is to assist this reaction by solvating the proton released in the heterolysis of the hydrogen molecule. Presumably, the catalysis then follows the conventionally accepted mechanism, i.e. insertion of the olefin into the metal-hydrogen bond to give a metal-alkyl followed by molecular hydrogen attack on the alkyl to regenerate the hydrido-species and give the required paraffin

Similarly $(\text{Et}_2\text{PhP})_3\text{RhCl}_3$ and $(\text{Bu}_3^{\text{n}}\text{P})_3\text{RhCl}_3$ behave as low-activity hydrogenation catalysts in ethanol-benzene solution. Moreover, on concentrating the solution of $(\text{Et}_2\text{PhP})_3\text{RhCl}_3$ after hydrogenation, a yellow solid is obtained. This compound has a Rh-H stretching frequency at 2105 cm^{-1} and in benzene solution the n.m.r. spectrum shows a high field doublet centred at $\tau\ 27.4$ ($J_{\text{Rh-H}}\ 19\text{ c/sec.}$). Analyses were not good, but indicated a stoichiometry of two chlorine atoms per rhodium and (by analogy with the above arsine complex) the probable formula of the complex is $(\text{Et}_2\text{PhP})_3\text{RhCl}_2\text{H}$. When the hydrogenated solution of $(\text{Bu}_3^{\text{n}})_3\text{RhCl}_3$ was concentrated, an air-sensitive yellow solid could be isolated.

The infrared spectrum showed a single band at 2100 cm.^{-1} ($\nu_{\text{Rh-H}}$) but the n.m.r. spectrum in benzene showed two high field doublets centred at τ 27.7 and τ 33.0 respectively ($J_{\text{Rh-H}} \sim 15\text{ c/sec.}$ in each case). No analysis corresponding to a particular composition has been obtained for this complex. These are, however, the first hydrido-complexes of rhodium(III) stabilised by phosphines yet recorded. Previous attempts⁶⁰ at their preparation have involved the conventional methods of reducing the trichlorotriphosphine-rhodium(III) complexes, e.g. by borohydride or hydrazine.

Several complexes of transition metals are now known to activate molecular hydrogen under mild conditions but few hydrido-complexes have been prepared or even detected in this way. Undoubtedly the preparative chemist has been deterred from using molecular hydrogen as a reagent because of its high dissociation energy ($\sim 103\text{ kcal/mole}$). This present work shows that activation of molecular hydrogen is more widespread than was previously thought, particularly in octahedral complexes. At room temperature and atmospheric pressure of hydrogen, the activation process is slow and needs a basic solvent to promote it. Both the activation process and the hydrogen transfer mechanism which follows it in the catalysis are undoubtedly kinetically slow, at least in part, due to the complexes being co-ordinatively saturated. This is further discussed in the next chapter.

CHAPTER IV.TRIS(TRIPHENYLPHOSPHINE)HALOGENORHODIUM(I) COMPLEXES AND
THEIR CATALYTIC BEHAVIOUR.A. Introduction.

Square planar d^8 complexes⁶¹ have long been known to add, often reversibly, molecules of the type RX , e.g. CH_3I , HCl . Vaska has recently⁶² shown that chlorocarbonylbis-(triphenylphosphine)-iridium(I) adds molecular hydrogen to form a dihydrido-iridium(III) complex; this reaction is also readily reversible. While this present work was in progress Vaska has extended his studies and in preliminary notes reports that ethylene, propylene and acetylene can be slowly hydrogenated at $40-60^\circ C$ by use of $IrCl(CO)(PPh_3)_2$ or at $20-40^\circ C$ by $IrH(CO)(PPh_3)_3$ and $OsHCl(CO)(PPh_3)_3$.

During the studies on rhodium(III) complexes, it was found that if excess triphenylphosphine were used in attempting to prepare the rhodium(III) complex, a rhodium(I) complex, $RhCl(PPh_3)_3$, results. This rhodium(I) complex and the corresponding bromide and iodide have proved to be most effective catalysts yet discovered for the homogeneous hydrogenation at normal temperatures and pressures of a variety of unsaturated compounds with both double and triple bonds. Moreover, these particular complexes have proved more convenient than any other catalyst systems for allowing the mechanism of the catalytic process to be studied.

B. Tris(triphenylphosphine)chlororhodium(I) and its properties.(a) Preparation and physical properties: -

When rhodium(III) chloride hydrate and an excess (ca 6

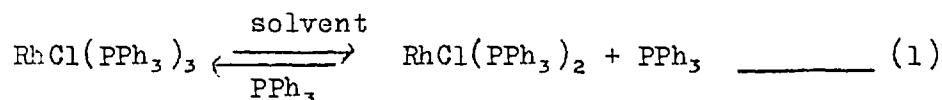
moles) of triphenylphosphine are dissolved in boiling ethanol reduction occurs and the dark, burgundy red, crystalline complex, $\text{RhCl}(\text{PPh}_3)_3$, is obtained. A large excess of PPh_3 is essential to prevent formation of a bridged dimer (see below) and to further the reduction of the rhodium(III) species formed initially. Since reduction does not occur in refluxing ethanol unless excess triphenylphosphine is present, and since acetone - water mixtures can be used in place of ethanol as solvent, the PPh_3 is without doubt the actual reducing agent. The initial product is probably PPh_3Cl_2 which then undergoes solvolysis to form OPPh_3 ; the latter is detectable in the residual solutions. If insufficient ethanol solvent is used, an orange crystalline material is first precipitated, which gives the red complex on continued refluxing. This orange complex has an analysis identical to that of the red $\text{RhCl}(\text{PPh}_3)_3$ and may be another crystalline form.⁶³ The corresponding bromide, prepared by addition of excess lithium bromide to the reaction mixture, can also be isolated in two crystalline forms. The iodide has been prepared similarly but the conditions are somewhat more critical, as described in the experimental section.

The above reaction involving triphenylphosphine appears to be unique. By contrast the interaction of other tertiary aryl alkyl phosphines and arsines with hot ethanolic solutions of rhodium trichloride gives mono- or binuclear rhodium(III) complexes.⁶⁰ Although the interaction of rhodium chloride with triphenylphosphine has been reported,⁶⁴ stoichiometric quantities were used in order

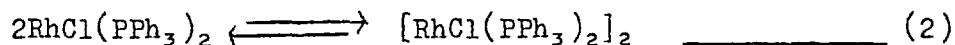
to obtain $\text{RhCl}_3(\text{PPh}_3)_3$; it has not been possible to reproduce this preparation and although orange materials are obtained, they appear to be mixtures which, on repeated crystallisation give some $\text{RhCl}(\text{PPh}_3)_3$.

At 25°C , the chloride complex is moderately soluble in CHCl_3 or CH_2Cl_2 (ca. 20 g/l.), slightly soluble in benzene (ca. 2 g/l.) or toluene, and considerably less soluble in acetic acid, acetone and other ketones, methanol, ethanol and other alcohols. It is virtually insoluble in light petroleum and cyclohexane. The bromide and iodide are somewhat more soluble in organic solvents. The complexes dissolve and react with donor solvents, (L), such as pyridine, dimethyl sulphoxide, and acetonitrile, to yield complexes of the type $\text{RhCl}(\text{PPh}_3)_2\text{L}$. The solutions in CH_2Cl_2 or benzene quite rapidly absorb oxygen to give an oxygen complex⁶⁵ (see later) which is more soluble in organic solvents than is $\text{RhCl}(\text{PPh}_3)_3$; the higher solubilities reported for $\text{RhCl}(\text{PPh}_3)_3$ ⁶³ may be due to inadequate de-gassing of solvents. It is essential for the determination of molecular weights in solution that air be rigorously excluded; there are difficulties in ensuring this when the Mechrolab Osmometer is used, but freezing point depression studies are in agreement with the osmometric values (see Experimental).

The tristriphenylphosphine halides dissociate in solution, e.g.



and the solution species may dimerise:



It appears that the dissociation in equation (1) is essentially complete in chloroform or benzene solution, where the apparent molecular weight remains constant at about half the undissociated value over an appreciable concentration range.

On refluxing benzene solutions of the chloride, the orange pink complex of stoichiometry $\text{RhCl}(\text{PPh}_3)_2$ is obtained; over long periods (> 24 hrs.) precipitation of the dimer occurs even from cold concentrated solutions in benzene. The dimer is very sparingly soluble in organic solvents but molecular weights of this substance in solution under hydrogen (see later) agree with a dimeric formula. A dimeric halogen bridged structure is the most likely, considering the well established behaviour of closely related rhodium(I) complexes of the type $(\text{RhClL}_2)_2$. The dimer can be readily converted to $\text{RhCl}(\text{PPh}_3)_3$ by heating with a 10 molar excess triphenylphosphine in ethanol. It may be mentioned here that although $\text{RhCl}(\text{PPh}_3)_3$ is stable indefinitely in air in the solid state, the crystalline dimer is not. Oxygen is taken up and the infrared spectrum of the product shows a strong band at ca. 1150 cm^{-1} attributable to triphenylphosphine oxide.

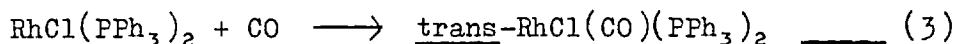
At the present time, no information is available concerning the structure of the dissociated solution species $\text{RhCl}(\text{PPh}_3)_2$ (A). If it is assumed that $\text{RhCl}(\text{PPh}_3)_3$ has the square configuration common for Rh^{I} , then on trans effect considerations one would anticipate that one of the trans phosphine groups would be labile. However,

it seems unlikely that this can be the sole reason for this ready lability and steric repulsion due to overcrowding by the phenyl groups is likely to be a strong and probably decisive contributing factor. It seems unlikely that the formally three coordinate species, $\underline{\underline{A}}$, would retain the square configuration, with the fourth position occupied by solvent, especially in rather weakly donating solvents such as chloroform or benzene. Further, steric repulsion between the triphenylphosphine groups will tend to widen the P-Rh-P angle. The essential point is that $\underline{\underline{A}}$ has vacant coordination sites which can be occupied either by weakly bound solvent molecules or by other ligand atoms. The existence of vacant sites is essential to the catalytic activity of $\underline{\underline{A}}$ as shall be seen.

It is finally noted that $\text{RhCl}(\text{PPh}_3)_3$ gives non-conducting solutions in acetone and formdimethylamide.

(b) Chemical Properties:

1) Reaction with carbon monoxide and aldehydes: - The coordinative unsaturation of $\underline{\underline{A}}$ is demonstrated by its formation of adducts with donor molecules, as noted above, but especially by its affinity for carbon monoxide, whereupon the well known complex trans-bis(triphenylphosphine)carbonyl chlororhodium(I) is formed. Thus on saturation of benzene or chloroform solutions of $\underline{\underline{A}}$ with carbon monoxide, essentially immediate and quantitative reaction occurs, the solutions changing in colour from red to yellow:



It appears to be impossible to reverse this reaction and even the

action of molten PPh_3 at 100° on the carbonyl complex does not displace CO.

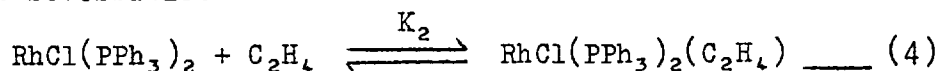
The high affinity of A for CO is also shown by its rapid reaction with aldehydes under mild conditions, when CO is abstracted. Thus a benzene solution of A reacts with n-heptaldehyde or valeraldehyde in the cold, or more rapidly on warming, to give quantitative yields of trans- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. From heptaldehyde, gas-liquid chromatography (g.l.c.) shows that the other products are ca. 80% n-hexane and ca. 20% hexenes. Benzaldehyde gives only the complex and benzene. The latter reactions may be regarded as a reverse of the hydroformylation reaction.

2) Interaction with ethylene: - Ethylene, like carbon monoxide, reacts rapidly with benzene or chloroform solutions of A, and the bright yellow crystalline complex, bis(triphenylphosphine)-ethylenechlororhodium(I), $\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$, can be readily isolated. Although dipole moment measurements cannot be made, it seems that this square complex has trans triphenylphosphine groups like the corresponding ^{*} complex; the ^{19}F n.m.r. spectra of the corresponding tetrafluoroethylene complex⁶⁶ show that the C_2F_4 group is trans to Cl and cis to two mutually trans PPh_3 groups.

The chloride and also the bromide complexes are stable in the solid state but in solution lose ethylene rapidly. This dissociation can be accelerated by sweeping the solution with nitrogen, but regeneration is quantitative on resaturating the solution with ethylene. Thus, unlike the carbon monoxide reaction,

insert 'carbonyl'

this one is reversible:



The n.m.r. spectrum of the ethylene chloro complex has been measured in deuteriochloroform solution in presence of varying amounts of ethylene (Table 8). The spectra show only a single line

TABLE 8.

Nuclear magnetic resonance spectra of $\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ in
chloroform

C_2H_4 (free) C_2H_4 (coord.)	Line ^a position	Approx. half-width
0	262	25
0.5	282	20
1.5	300	5
3.0	300	5
∞ b	300	5

^a c/sec. on low field side of Me_4Si

^b Free C_2H_4 value $\gamma = 4.69$ in CHCl_3

due to ethylene, whose position depends on the ethylene-rhodium concentration ratio. At low ethylene concentrations the peak is broad, half width ca. 25 c/sec., and even on cooling to -50°C , no sharpening or splitting was observed, although a slight downfield shift (ca. 7 c/sec.) occurs due to the greater solubility of ethylene at lower temperatures. With increasing ethylene concentration, the line sharpens and moves downfield towards the position of resonance for uncoordinated ethylene in the solvent. As in other

ethylene complexes, it is clear that rapid exchange between free and coordinated ethylene is occurring in solution, even at -50°C . A mean lifetime for residence of ethylene on the metal atom can be estimated as less than ca. 10^{-2} sec., a value comparable to those found by Cramer.⁶⁷

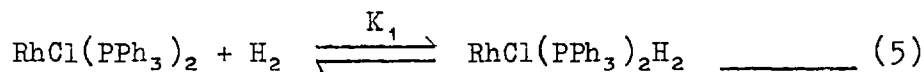
By contrast, ^{19}F n.m.r. spectra show that at 25°C there is no ligand exchange with the corresponding complex of tetrafluoroethylene.⁶⁶

No complexes could be prepared using propylene or but-1-ene. However, readily isolable complexes are obtained with chelating olefins,⁶³ hexafluorobut-2-yne⁶⁶ and diphenylacetylene.

3) Reaction with molecular hydrogen; dihydrido complexes: -

When saturated solutions of A in solvents such as benzene, chloroform, ethyl acetate, or glacial acetic acid are shaken with molecular hydrogen, the colour changes from red to pale yellow. Manometric studies indicate that in all of these solvents one mole of hydrogen is absorbed per mole of rhodium complex. In chloroform and benzene the dihydrido species is more soluble than $\text{RhCl}(\text{PPh}_3)_3$; the dihydrido species in glacial acetic acid and ethyl acetate have about the same low solubility as $\text{RhCl}(\text{PPh}_3)_3$. Hence, depending on the concentration, pale yellow or white crystals of the dihydrido complex may separate as the hydrogen uptake proceeds. N.m.r. spectra of these solutions, which contain one equivalent of displaced phosphine of course, show three high field lines due to hydrogen atoms bound to rhodium. On sweeping the solutions with

nitrogen, the high field lines disappear and the solution regains its initial red colour. Re-saturation with hydrogen restores the yellow colour and the n.m.r. signals. The cycle can be repeated, evidently indefinitely, showing a reversible equilibrium of the type:



Analogous behaviour was observed for solutions of $\text{RhBr}(\text{PPh}_3)_3$ and $\text{RhI}(\text{PPh}_3)_3$.

Absorption of molecular hydrogen has not been previously reported for a rhodium complex but the uptake of hydrogen at room pressure by the iridium complex $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ is well known.⁶² The solubility of this hydrido species was too low for n.m.r. study, but the corresponding bromide and iodide have been quoted⁶⁸ as having sufficient solubility to yield n.m.r. spectra which are consistent with an octahedral species with cis-hydrido groups, in confirmation of infrared data. It has been reported⁶⁸ that the dihydrido derivatives of the corresponding rhodium and cobalt complexes could not be obtained. The uptake of hydrogen by the carbonyl species and their ability to act as hydrogenation catalysts is discussed later.

The nature, spectra and structure of dihydrido species:

There is no change in the non-conductance of acetone solutions of the chloro and bromo complexes $\text{RhX}(\text{PPh}_3)_3$ ($\text{X} = \text{Cl}, \text{Br}$) when they are saturated with hydrogen; this indicates that the halide ion remains coordinated, as also confirmed by the analysis of the

isolated solids. Although crystalline solids can be obtained fairly readily from hydrogen-saturated solutions, their characterization has not been easy, due to the ease of aerial oxidation of, and ready loss of hydrogen from the solutions.

The microcrystalline white solid isolated from hydrogen saturated chloroform solutions of A analyses for $\text{RhCl}(\text{PPh}_3)_2\text{H}_2$; the molecular weight under hydrogen is normal. The species may possibly be 5-coordinate in the solid but in solution 6-coordination with solvation by CHCl_3 is most likely. The formation of solvates with chlorinated hydrocarbons is confirmed by the isolation from dichloromethane solutions of a stable yellow crystalline complex $[\text{RhCl}(\text{PPh}_3)_2\text{H}_2]_2 \cdot \text{CH}_2\text{Cl}_2$, which evidently contains quite firmly held and, it is proposed, coordinated bridging dichloromethane. Using ethyl acetate, glacial acetic acid and formdimethylamide as solvents for $\text{RhCl}(\text{PPh}_3)_3$, white solids may again become isolated. The analyses, whilst not entirely satisfactory, show that two triphenylphosphine ligands are present per rhodium atom, and that coordinated solvent is present. The latter is also clearly shown by the presence of coordinated solvent bands in the infrared spectra of the complexes. Dissolution of these solvated complexes (which are very sparingly soluble in the parent solvent) in deuterochloroform gives an n.m.r. spectrum identical with that given by hydrogenation of $\text{RhCl}(\text{PPh}_3)_3$ in deuterochloroform. Hence these solvates appear to have the same basic stereochemistry as the "5-coordinate" species in chloroform solution.

The high field n.m.r. spectra (Fig. 2 and Table 9) at 56.4 Mc/sec. consist of three peaks (a weak shoulder may occasionally be observed on the highest field line - this is due to the tetra-

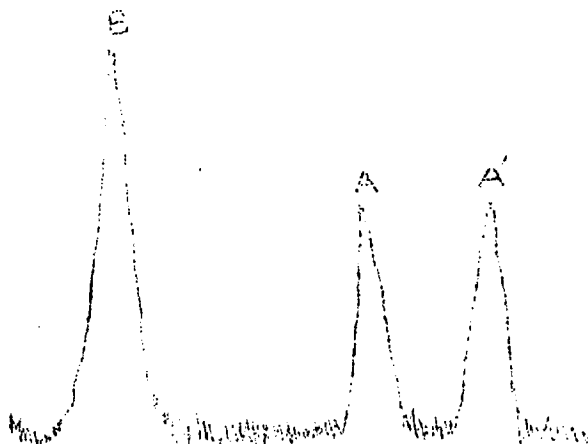


Figure 2.

hydrido complex of the dimer discussed later). The peaks A, A' are of equal intensity and half that of the peak B. At 40 Mc/sec., the A, A' separation remained constant, showing that these lines are attributable to the spin-spin interaction of H with ^{31}P . Additional confirmation that this is so, comes from study of the corresponding triphenylarsine complex,⁶⁹ which has only two lines of equal intensity in positions similar to those in the phosphine complex. The absence of fine structure on the lines is discussed below.

The spectra are most readily interpreted in terms of an octahedral cis-dihydrido complex (I) of Rh^{III} formed from A by addition of H_2 to give two Rh-H bonds.

TABLE 9.

N.m.r. and i.r. data on hydrido complexes of $\text{Rh}(\text{PPh}_3)_3\text{X}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$: high field lines and Rh-H modes only. N.m.r. relative intensities in parentheses

parentheses

Solvent	τ ^a	ν cm. ⁻¹	
		solution ^b	solids ^c Rh-H str.; Rh-H bend
<u>Chloride</u>			
CDCl ₃	28.2(2), 21.5(1), 18.8(1)	2095m, 2050m	2078m, 2013m; 785m.
C ₆ H ₆	26.5(2), 20.4(1), 17.8(1)	2066sh, 2035m	2066sh, 2051m; 805m.
C ₅ H ₅ N	28.6(1), 27.7(1) ^d	2078sh, 2052m	2143m, 2075m ^e ; 838m, 812m
CH ₂ Cl ₂	-	-	2099m ^f , 2065m ^e ; 845s
MeCO ₂ Et	28.2(2), 21.5(1), 18.8(1)	-	2075m, 2088m ^e ; 840m, 775m.
MeCONH ₂	28.2(2), 21.5(1), 18.8(1)	-	2137m, 2081m ^e .
<u>Bromide</u>			
CDCl ₃	28.2(2), 21.5(1), 18.8(1)	2177sh, 2057m	- -
C ₆ H ₆	26.5(2), 20.4(1), 17.8(1)	2066sh, 2035m	- -
C ₅ H ₅ N	29.2(1), 28.4(1) ^d	2081sh, 2049m	2144m, 2099m ^e ; 845m, 830m.
CH ₂ Cl ₂	-	-	2103m, 2068m ^e ; 847m, 838m.
<u>Iodide</u>			
CDCl ₃	26.2(2), 23.1(1), 20.5(1)		

^a Measured in CDCl_3 except where indicated; values relative to Me_4Si as internal reference.

^b Measured in parent solvent.

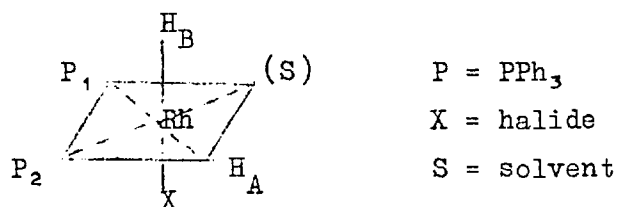
^c Spectra taken in nujol mulls.

^d In pure pyridine: for both chloride and bromide, $\tau = 28.1(1), 27.8(1)$.

^e Bands due to coordinated solvent are also present.

^f For deuteride, 1507 cm.⁻¹.

Note: The n.m.r. spectra of highly concentrated solutions may show lines due to $[\text{RhX}(\text{PPh}_3)_2\text{H}_2]_2$. For the Cl: in CDCl_3 , $\tau = 27.4$; in C_6H_6 , $\tau = 28.9$. For the Br: in CDCl_3 , $\tau = 29.1$; in C_6H_6 , $\tau = 25.6$.

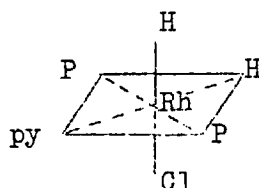


For a number of octahedral hydrido phosphine complexes it has been found that $H - {}^{31}P$ coupling constants are of the order 80-150 c/sec. for H trans to P, while the couplings for H cis to P are ca. 15 c/sec. Further the γ values for H trans to P are generally lower than when H is trans to a halide or similar ligand.⁷⁰ The observed spectrum is consistent therefore with I; a similar spectrum would result if X and S in I were interchanged and at present the exact dispositions cannot be determined.

It is possible that in chloroform or benzene solution, there is an unsolvated 5-coordinate species which could have a spectrum very close to that of solvated species but we believe that solvent occupancy of the vacant site always occurs in solution. The solution species are in any case likely to be distorted from true octahedral geometry. In order to have the observed trans coupling it is only necessary that the H shall experience the presence of the P atom in the trans position and this is possible even if slow ligand exchange is proceeding.

The pyridine solutions of A after hydrogenation, the isolated dihydrido pyridine complex, and the dihydrido pyridine cleavage product of the dihydrido dimeric species discussed below

all have identical spectrum consisting of two rather broad lines. This is consistent with trans phosphines and cis dihydrides as in II; the γ values are in the region for cis H-P groups, in agreement



II

with infrared data. Although we have not isolated an acetonitrile complex, the n.m.r. spectra of hydrogenated acetonitrile solutions of A are identical with those of the pyridine complex. It is of interest that the re-organisation of the hydrido complexes in chloroform solution on addition of pyridine or acetonitrile can be followed via the growth and decay of the respective high field lines.

The infrared spectra (Table 9) of the various species in both the solid state in mulls and in solution generally show two broad Rh-H stretching frequencies in the normal region, ca. 2000 cm^{-1} for transition metal and hydrogen bonds. This is to be expected for cis dihydrido groups. The dideutero complex, $[\text{RhCl}(\text{PPh}_3)_2\text{D}_2]_2 \cdot \text{CH}_2\text{Cl}_2$ obtained from dichloromethane solution shows only one Rh-D stretching frequency ($\nu_{\text{Rh-D}} = 1507 \text{ cm}^{-1}$; $\nu_{\text{H}}/\nu_{\text{D}} = 1.39$), the other presumably being obscured by triphenylphosphine absorption.

A final word concerning the broad nature (45-70 c/sec.)

of the high field lines must be made. Fine structure should have been expected to arise (a) from $H-^{103}\text{Rh}$ coupling (ca. 20-30 c/sec.), (b) from H_A-H_B coupling and (c) from additional cis ^{31}P coupling with the trans H_A as in I. Although such couplings will appear under the envelope of the broad high field lines, no resolution could be obtained. There was no detectable change in the appearance of the lines (a) on cooling to -70°C or (b) on exerting a pressure of 100 atmos. of hydrogen on the solution in an n.m.r. tube. In the pressurised solution the proton resonance of dissolved hydrogen⁷¹ at τ 5.57 was readily observed in addition to all three high field lines, which were unchanged in position. Clearly the broadening cannot be due to exchange processes although on addition of excess PPh_3 , the line breadth is apparently reduced, suggesting some inhibition of ligand dissociation is taking place. However, the main and unexpected cause of line broadening is due to the presence of trace quantities of a paramagnetic species in the starting material. It has not been possible to prepare a sample of the catalyst not contaminated in this way.

4) Other reactions : - Solutions of $\text{RhCl}(\text{PPh}_3)_3$ interact with a variety of ligands in a way similar to the reactions of square complexes. Methyl iodide gives the complex $\text{RhClI}(\text{CH}_3)(\text{PPh}_3)_2-\text{ICH}_3$ where CH_3I acts as a donor. Allyl chloride adds to give allylic complexes of stoichiometry⁷² $\text{RhCl}_2(\text{PPh}_3)_2\text{C}_3\text{H}_5$. It is also noted in solution both $\text{RhCl}(\text{PPh}_3)_3$ and the corresponding arsine complex take up one mole of oxygen and that solid adducts can be isolated.⁷³

C. Catalytic hydrogenation of olefins and acetylenes.

In benzene or similar solvents, the tris(triphenylphosphine)halogenorhodium(I) complexes are extremely efficient catalysts for the homogeneous hydrogenation of non-conjugated olefins and acetylenes at ambient temperatures and pressures of 1 atmos. or below. The reaction appears to be specific since functional groups such as keto, hydroxy, nitrile, nitro, chloro, azo, ether, ester or carboxylic acid are not reduced under these conditions.

The rates of reduction of terminal olefins such as hex-1-ene compare favourable with those obtained by heterogeneous catalysts such as Raney nickel or Adam's catalyst. Indeed, if the reaction mixture is not efficiently thermostatted, using 10^{-3} M solutions of the catalyst in benzene with hydrogen pressures of ca. 1 atmos., the hydrogenation of olefins may proceed so rapidly that the temperature of the solution is raised to boiling point.

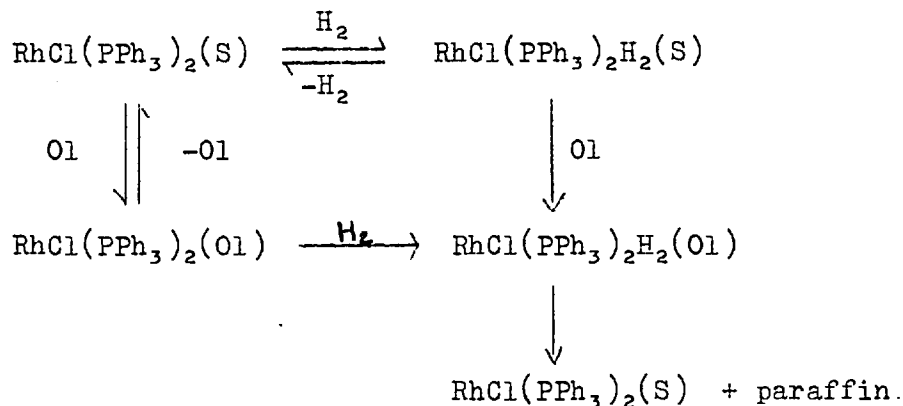
Generally terminal olefins are reduced more rapidly than internal olefins although ethylene itself is not catalytically hydrogenated (vide infra). The catalysis is inhibited very effectively by the addition of donor molecules such as triphenylphosphine, pyridine, thiophen, or dimethylsulphoxide.

An insight into the mechanism is given by a n.m.r. study of the direct transfer of hydrogen using high concentrations of dihydrido-species. A hydrogen saturated deuteriochloroform solution of $\text{RhCl}(\text{PPh}_3)_3$ in an n.m.r. tube was frozen and a suitable quantity

of ethylene condensed. On allowing the tube to warm up slowly in a low temperature probe, both the high field lines of the dehydrido-species and the line due to uncoordinated ethylene were readily observable at -50°C . At about 0°C , the intensities of both lines decreased, while a new line at $\tau \sim 9.69$, due to ethane, appeared. No lines due to the intermediate containing a $\text{Rh-C}_2\text{H}_5$ groups produced by ethylene insertion into the Rh-H bond was observed. Similar direct transfer experiments were carried out in benzene solutions of the complex and with the injection of hex-1-ene. The same behaviour is also indicated by the colour changes in the solutions, the yellow of dihydrido-species being replaced by the red-brown of $\text{RhCl(PPh}_3)_2(\text{S})$ or $\text{RhCl(PPh}_3)_2(\text{Ol})$. These are identical to the changes observed in the catalytic experiments, but due to the low concentrations of catalyst used in the latter, it has not been possible to demonstrate a standing concentration of the dihydrido-species by either n.m.r. or infrared methods. However, the electronic absorption spectra of these solutions are nearly identical with that of the dihydrido-species. A similar experiment was made by adding hex-1-ene to solutions of the pyridine hydrido-complex, $\text{RhCl(PPh}_3)_2\text{pyH}_2$, but the high field lines remained unchanged, showing hydrogen transfer does not occur.

D. Discussion.

From the chemical evidence presented earlier the following reaction scheme can be proposed:



Which of the two possible reaction paths occurs, i.e. the attack of hydrogen on the olefin complex or the attack of olefin on the dihydrido-species, cannot be easily determined. The latter mechanism, however, seems intuitively more feasible although the problem is discussed more fully elsewhere.⁷⁴ However, it must be noted that catalytic reduction of ethylene does not readily take place because the complex, $\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$, has a large formation constant and is inert to hydrogen attack under mild conditions. However, the ready reduction of ethylene when it is added to the previously formed dihydrido-species indicates that the latter path is the most likely general mechanism of the catalysis.

Whether there is an actual intermediate species, $\text{RhCl}(\text{PPh}_3)_2\text{H}_2(\text{olefin})$, has not been ascertained. It may be noted that the lifetime of the dihydrido-species is quite long so that attack by the olefin can occur. The inhibition of the catalysis

by donor molecules which form coordinatively saturated complexes, e.g. $\text{RhCl}(\text{PPh}_3)_2\text{H}_2\text{py}$ indicates that a vacant site on the dihydrido-species at which the substrate olefin can be activated is necessary for efficient catalysis. Those substrates which cannot approach the activating site because of steric factors, e.g. internal olefins, are not readily reduced. It is also clear why certain species, although being able to activate molecular hydrogen readily, e.g. $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ can only hydrogenate olefins very slowly at 25°C and 1 atmosphere. On the dihydrido-species formed in this case there is no vacant site for olefin coordination, i.e. they are coordinatively saturated.

Thus the evidence presented here is in agreement with the initial formation of $\text{RhCl}(\text{PPh}_3)_2\text{H}_2(\text{solvent})$, displacement of solvent competitively by olefin, and transfer of bound hydrogen to the olefin in an actual intermediate or in an activated complex. Diffusion of the saturated substrate away from the transfer site leaves the complex ready again to activate dissolved hydrogen molecules. As to the precise manner in which the two hydrogen atoms are transferred to the olefin, it appears that essentially simultaneous transfer occurs without the formation of an alkyl intermediate.

Experimental.

Microanalyses, molecular weight determinations (Mechrolab Osmometer, 37°C and Freezing Point method) and microhydrogenations by the Microanalytical Laboratory, Imperial College.

N.m.r. spectra were obtained using a Varian Associates Model 43100 spectrometer at 56.45 Mc/sec. and 40 Mc/sec., and e.s.r. spectra on a Varian Associates V-4502-15 spectrometer. Infrared spectra were taken on a Grubb-Parsons Grating "Spectromaster", and electronic spectra on a Perkin-Elmer Model 350 spectrometer.

Melting points (uncorrected) were determined on a Kofler hot-stage microscope. Conductivities were determined with a Mullard E7576 conductivity bridge, with a dipping all. Polarograms were obtained using a Tinsley Mark 19 recording instrument with a dropping mercury electrode. G.L.C. measurements were made on a Perkin-Elmer Model F-11 chromatograph with flame ionisation detector and 2m. columns. The stationary phase was squalene or silver nitrate-diethyleneglycol; calibrations were made using standard samples.

Catalytic hydrogenation experiments were carried out using a 250 ml. flask with outer jacket adapted to accommodate a magnetic stirrer. It was attached to a vacuum system with storage bulbs, manometer, sampling tubes etc.

For most experiments water was pumped through the jacket to maintain a constant temperature in the hydrogenating solutions. The teflon coated magnetic stirrer was rotated at the gas-liquid

interface to saturate efficiently the hydrogenating solutions. The standard quantities used for catalytic runs were 10^{-4} moles catalyst in 50 ml. of solvent. Solvents were carefully degassed before experiments. Olefins were cleaned of peroxides in the usual way before use, i.e. washed with acid FeSO_4 , dried over CaCl_2 and stored under nitrogen in the dark.

The rhodium chloride, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was from Johnson Matthey Ltd.; triphenylphosphine (Albright and Wilson Ltd.) was recrystallised from benzene ethanol before use.

trans-Dichlorotetrapyridinerhodium(III) Chloride. - Catalytic preparations were performed as follows: with hypophosphorous acid as described earlier,¹⁵ in this work, sodium hypophosphite has been used equally effectively; with ethanol as described by Delépine.¹²

With zinc amalgam. Hydrated rhodium trichloride (0.26 g., 1 mmole) and pyridine (1 ml.) in methanol (7 ml.) were shaken in air, with 5% zinc amalgam (1 g.) Immediately, a pale yellow solution was formed, containing only the $[\text{Rhpy}_4\text{Cl}_2]^+$ ion, as shown by the spectral maximum at 410 m μ . The spent amalgam was removed, and the yellow solution was evaporated on a steam-bath, when needle-like crystals of trans- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl} \cdot 5\text{H}_2\text{O}$ were obtained, identified by infrared and electronic spectra (yield 0.58 g.; 94%).

With hydrazinium chloride. Hydrated rhodium trichloride (0.264 g., 1 mmole), sodium chloride (0.3 g.), and pyridine (1 ml.)

in water (5 ml.) were heated; a warm, 10% aqueous, solution (0.1 ml.) of hydrazinium chloride was added, and an immediate colour change occurred. On cooling, yellow crystals (0.5 g.; 81%) of $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}\cdot 5\text{H}_2\text{O}$ were obtained.

With 2-methoxyethanol-ethanol. Hydrated rhodium trichloride (0.26 g., 1 mmole) in 1:1 2-methoxyethanol-ethanol (4 ml.) containing pyridine (1 ml.) was heated to boiling. Immediately, the solution became pale yellow; it was cooled, and treated with diethyl ether, whereupon trans- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}$ was precipitated. This was collected, washed with ether, sucked dry, and recrystallised from water (yield 0.53 g.; 85%).

With hydridodichlorotris(triphenylphosphine)iridium(III). Rhodium trichloride (0.31 g., 0.5 mmole) in water (5 ml.) containing pyridine (2 ml.) was warmed to 50° , and a solution of hydridodichlorotris(triphenylphosphine)iridium(III) (0.005 g.) in pyridine (2 ml.) or acetone (3 ml.) added, and the resultant solution warmed slightly (to ca. 55°). In either case, the solution rapidly became pale yellow, showing the electronic spectrum of the trans- $[\text{Rhpy}_4\text{Cl}_2]^+$ cation, and, on cooling the solution in ice, crystals of trans- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl}\cdot 5\text{H}_2\text{O}$ were obtained, identified by electronic and infrared spectra (yield ca. 90%).

With molecular hydrogen. Rhodium trichloride (0.26 g., 1 mmole) in water (5 ml.) with pyridine (1 ml.) were heated to 50°C ; molecular hydrogen was bubbled through the warm solution for one minute. On cooling, yellow crystals of the complex (ca. 0.5 g., 80%) were obtained

trans-Dibromotetrapyridinerhodium(III) Bromide. - The following is a more convenient preparation than those given in the literature. Rhodium(III) chloride trihydrate (1 g., 4×10^{-3} mole) in water (5 ml.) was added to a solution of potassium bromide (1.5 g., 1.5×10^{-2} mole) in water (5 ml.). Pyridine (2 ml.) was added and the mixture heated until just boiling. At this point, hypophosphorous acid (0.5 ml.) was carefully added dropwise, whereupon the solution turned yellow. On cooling, yellow-orange crystals of the salt appeared, which were recrystallised from water. Yield 1.8 g. (70%) (Found: C, 36.3; H, 3.15; N, 8.6. Calc. for $C_{20}H_{20}Br_3N_4Rh$: C, 36.5; H, 3.05; N, 8.5%).

Reactions of the trans-Dichlorotetrapyridinerhodium(III) Ion. -

With bromide. trans-Dichlorotetrapyridinerhodium(III) chloride pentahydrate (0.31 g., 0.5 mmole) in water (6 ml.) containing excess of potassium bromide (1 g.) was treated with hypophosphorous acid (0.5 ml.), and the mixture boiled. After 2 min. a fawn precipitate of the known¹³ trans-dibromotetrapyridinerhodium(III trans-tetrabromodipyridinerhodate(III)) appeared. This was collected, washed with water, and dried in vacuo [Found: C, 30.7; H, 2.40; N, 7.3. Calc. for $C_{30}H_{30}Br_6N_6Rh_2$: C, 30.8; H, 2.58; N, 7.18%] (yield 0.28 g.,; 97%).

With iodide. trans-[Rhpy₄Cl₂]Cl₂·5H₂O (0.31 g., 0.5 mmole) in water (5 ml.) was treated with excess of potassium iodide (1 g.), the mixture (containing much crystallised $[Rhpy_4Cl_2]I$) heated, and hypophosphorous acid (2 drops) added. The solution

became clear, and then rapidly deposited a dark brown precipitate of 1,2,6-tri-iodotripyridinerhodium(III), identical with that formed¹⁵ by removing coordinated pyridine from trans-di-iodo-tetrapyridinerhodium(III) iodide.

Trithiocyanatotripyridinerhodium(III). -

(a) Uncatalysed, following the literature method.²³

Rhodium trichloride trihydrate (0.26 g., 1 mmole) in water (10 ml.) was treated with potassium thiocyanate (1 g.) and the solution refluxed for 10 min. Pyridine (2 ml.) was added, and the mixture again refluxed for 10 min. The yellow solid which had formed was collected, washed with water, and dried at the pump. It is a mixture of the 1,2,3- and 1,2,6-isomers of $[\text{Rhpy}_4(\text{SCN})_2]$ (Found: C, 42.1; H, 3.18; N, 16.51. Calc. for $\text{C}_{18}\text{H}_{15}\text{N}_6\text{RhS}_3$: C, 42.1; H, 2.94; N, 16.35%). It was taken up in dichloromethane (5 ml.) giving an orange solution (S) and a residual pale yellow solid, which was removed and washed with dichloromethane, the washings being discarded. The solid was recrystallised from aqueous pyridine (yield ca. 5%). It is 1,2,3-trithiocyanatotripyridine-rhodium(III) (Found: C, 41.8; H, 3.40; N, 16.85. $\text{C}_{18}\text{H}_{15}\text{N}_6\text{RhS}_3$ requires C, 42.1; H, 2.94; N, 16.35%). The solution (S) was concentrated until crystals of 1,2,6-trithiocyanatotripyridine-rhodium(III) were obtained; these were collected and recrystallised from ethanol, as orange-yellow plates (yield ca. 80%) (Found: C, 42.5; H, 2.95; N, 16.06%).

(b) Catalysed. The directions under (a) were followed

except that a drop of hypophosphorous acid was added immediately after the pyridine, and the resultant mixture was boiled for 1 min. only. In this case, a little more of the pale yellow 1,2,3-isomer was obtained [Found (1,2,3-isomer): C, 42.4; H, 3.02; N, 16.5; (1,2,6-isomer): C, 41.7; H, 3.12; N, 16.6%]. The infrared spectra of the two isomers were as follows: 1,2,6-: 2079s, 1605m, 1302w, 1239w, 1215m, 1168sh, 1156m, 1062s, 1018m, 841m, 760s, and 691s; 1,2,3-: 2081s, 1603m, 1491sh, 1240w, 1216m, 1157m, 1064s, 1017m, 853sh, 846m, 838w, 768sh, 760s, 691sh, and 689s. The region normally concealed by the absorption due to Nujol (ca. 720 cm^{-1}) was examined by preparing mulls in carbon disulphide as follows. The solid (ca. 0.004 g.) was ground with carbon disulphide (ca. 3 ml.) as usual. At an ambient temperature of 22° , the ground powder was nearly dry after 3 min. It was then rapidly transferred to a rock-salt plate, six drops of carbon disulphide were rapidly added, and a second rock-salt plate was immediately pressed on with a rotary motion, re-forming a mull. Without special precautions, this mull was sufficiently stable to give good spectra in the relevant region for about 10 min. After this, the solvent began to be lost from the centre of the mull as detected both by direct observation of dry powder, and by the apparently increased background absorption.

trans-Dichlorotetrapyridinerhodium(III) Thiocyanate. - As described by Meyer and Kienitz,²³ this was prepared for comparison purposes, by double decomposition. The infrared spectrum showed bands

(cm.^{-1}) at: 2060s, 1601m, 1211m, 1157m, 1073m, 1061m, 772sh, 768s, 751m, 737m, 708m, 697s, and 689s.

trans-Dihalogenobisbipyridylrhodium(III) Salts - Electronic spectra, measured in aqueous solution (ca. 10^{-3}M for the visible region and ca. 10^{-5}M for the ultraviolet) are in Table 10. Infrared spectra, taken on mulls, are in Table 11.

trans-Dichlorobisbipyridylrhodium(III) salts. (1) The nitrate was prepared by the more recent literature method,²⁷ fusion of rhodium trichloride and bipyridyl, and recrystallisation of the nitrite. We find it to be a dihydrate. (2) The chloride was prepared by a modification of an earlier literature method;²⁶ rhodium trichloride trihydrate (0.26 g., 1 mmole) in ethanol (5 ml.) was treated while hot with bipyridyl (0.343 g., 2.2 mmole) in ethanol (5 ml.) The mixture was heated, when the colour changed (ca. 3 min.) from red to yellow. At this stage, on cooling, crystals of $[\text{Rh}(\text{bipy})_2\text{Cl}_2]\text{Cl}$, $2\text{H}_2\text{O}$ were obtained, which were recrystallised from water (yield 0.5 g., 89%) (Found: C, 42.4; H, 3.53; N, 9.6. Calc. for $\text{C}_{20}\text{H}_{20}\text{Cl}_3\text{N}_4\text{O}_2\text{Rh}$: C, 43.0; H, 3.61; N, 10.0%).

This preparation was repeated with acetone in place of ethanol. The red colour of the original mixture lightened only very slowly. However, on addition of ethanol (2 ml.), the colour changed to yellow during 1 min., and the desired $[\text{Rh}(\text{bipy})_2\text{Cl}_2]\text{Cl}$, $2\text{H}_2\text{O}$ was obtained.

The preparation was repeated in 1:1 ethanol-2-methoxyethanol. Immediately on ebullition, the desired complex (anhydrous) began to

TABLE 10.

Electronic spectra of trans-[Rh(AA)₂X₂]⁺ salts (AA = bipy or 1,10-phenanthroline;
λ in mμ)

Compound	λ	ε	λ	ε	λ	ε	λ	ε
[Rh(bipy) ₂ Cl ₂] ⁺ ^a	383	110	312	1.2 x 10 ⁴	301	9.8 x 10 ³	-	-
" ^b	384	112	312	1.1 x 10 ⁴	301	9.3 x 10 ³	-	-
[Rh(bipy) ₂ Br ₂] ⁺	395	415	311	2.7 x 10 ⁴	302	2.25 x 10 ⁴	-	-
[Rh(bipy) ₂ I ₂] ⁺	402	1400	312	2.4 x 10 ⁴	301	2.25 x 10 ⁴	238	7 x 10 ⁴
[Rh(o-phen) ₂ Cl ₂] ⁺	385	110	350	2.5 x 10 ³	333	2.6 x 10 ³	318sh	4.1 x 10 ³
					300sh	1.3 x 10 ⁴	272	5.6 x 10 ⁴

^a Prepared following ref. 27.

^b Catalytically prepared.

TABLE 11.

Infrared spectra of $[\text{Rh}(\text{bipy})_2\text{X}_2]\text{X}, 2\text{H}_2\text{O}$

$\text{X} = \text{Cl}^{\text{a}}$	Cl^{b}	Br	I^{c}	$\text{X} = \text{Cl}^{\text{a}}$	Cl^{b}	Br	I^{c}
3400s, b	3410s, b	3350m, b	-	1063w	1064sh	1063w	1062w
1651m, b	1650m, b	1647w, b	-	1045w	1046sh	1046w	-
1608s	1608s	1601s	1601m	1040m	1040m	1040m	1036m
1493sh	1493sh	1492w	1495w	1028m	1029m	1028w	1029w
1315w	1316w	1316m	1309m	968	969w	970w	972m
1280w	-	1280w		898m	899w	901m	895w
1244m	1244m	1243m	1241w			883sh	
		1173sh	1170	805w	-	805w	803w
1160s	1160m	1164sh		778s		780sh	778sh
		1158s	1159m		772s	773s	771sh
1106m	1106w	1106m	1105m	769s		768sh	767s
1078m	1077m	1079m	1074m	729s	729s	729s	728s

^a As nitrate, prepn. (1); nitrate bands occurred at 1350sb and 832m.

^b As chloride, prepn. (2) - (6). ^c Anhydrous.

precipitate, and, on cooling, it was recovered in 93% yield. It could be dissolved in hot water and the sparingly soluble nitrate or perchlorate salts obtained by treating the hot solution with a concentrated solution of sodium nitrate or perchlorate. The nitrate dihydrate (Found: C, 41.0; H, 3.65; N, 11.8 Calc. for $C_{20}H_{20}Cl_2 \cdot N_5O_5Rh$: C, 41.1; H, 3.45; N, 12.0%) was identical with that prepared by method (1) above. The perchlorate (Found: C, 40.1; H, 2.99. Calc. for $C_{20}H_{16}Cl_3N_4O_4Rh$: C, 40.0; H, 2.72%) was identical with the literature product.²⁰ (3) With hydrazine as catalyst: rhodium trichloride trihydrate (0.26 g., 1 mmole) in water (5 ml.) was treated with bipyridyl (0.34 g., 2.2 mmole) in warm ethanol (5 ml.) and the mixture heated; to the hot mixture (60°), hydrazinium chloride (0.02 g.) was added, and the mixture brought to boiling. Immediately, the mixture gave a clear yellow solution, which, on cooling, deposited the desired complex as small yellow needles (0.48 g.; 87%). (4) Using hypophosphorous acid: the preparation was performed as described under (3), except that hypophosphorous acid (0.05 ml.) was added in place of hydrazinium chloride. Again, immediate formation of $[Rh(bipy)_2Cl_2]Cl$ occurred, which was collected after cooling and recrystallised from water.

With larger amounts of hypophosphorous acid present, the reaction took a different course; rhodium trichloride trihydrate (0.26 g., 1 mmole) in water (5 ml.) was mixed with bipyridyl (0.34 g., 2.2 mmole) in ethanol (5 ml.), and the mixture kept at 60° while hypophosphorous acid (1 ml.) was added. A clear yellow

solution at once resulted; this was heated briefly to boiling, when it became brown. On cooling (even in the absence of air) yellow crystals are formed (0.53 g.). Phosphorus was present, but chlorine absent. The infrared spectrum showed bands at 3380m,b, 2350m (PH), 1650w,b, 1605m, 1311m, 1248m, 1161m, 1139sh, 1126sh, 1113sh, 1075w, 890s, vb (PO), 773s, and 729s cm^{-1} . The compound can be recovered apparently unchanged from hot hydrochloric acid. When the yellow crystals are heated with water, a brown solution was formed, which rapidly became yellow; at this stage a definite high-field line was observed in the n.m.r. spectrum, at 1130 c/sec. relative to H_2O , showing the presence of an Rh-H bond. On cooling and standing, pale yellow crystals are formed, apparently identical with those above.

Exactly similar behaviour was observed with the analogous *o*-phenanthroline complex, and it is relevant that when dichloro-bispyridylrhodium(III) chloride was treated in aqueous solution with sodium hypophosphite, the product after heating is apparently identical with that from rhodium trichloride and bipyridyl described above.

Dibromo-salt. When solutions of $[\text{RhBr}_6]^{3-}$ in water and bipyridyl in ethanol are mixed, a fawn precipitate is at once obtained; this is formulated $\text{Rh}_2\text{bipy}_3\text{Br}_6$ (Found: C, 31.0; H, 2.52; N, 7.3. Calc. for $\text{C}_{30}\text{H}_{24}\text{Br}_6\text{N}_6\text{Rh}_2$: C, 31.2; H, 2.08; N, 7.3%). However, the desired salt was obtained as follows: rhodium trichloride trihydrate (0.26 g., 1 mmole) in aqueous solution (10 ml.) was

heated with excess of potassium bromide (1.0 g.); the solution was boiled for 2 min., then bipyridyl (0.34 g., 2.2 mmole) in hot alcohol (6 ml.) was added to the hot aqueous solution (60°). 0.02 g. of hydrazinium chloride was added and the mixture brought to boiling. The solution rapidly changed colour and a little fawn precipitate was given immediately. The solution was filtered when hot and allowed to cool slowly to crystallise. The salt trans-[Rh(dipy)₂Br₂]Br, 2H₂O was collected as orange plate-like crystals (yield 0.58 g.; 84%) (Found: C, 35.0; H, 3.29; Br, 35.6.

C₂₀H₂₀Br₃N₄O₂Rh requires C, 34.8; H, 2.92; Br, 34.8%).

Di-iodo-salt. trans-Dichlorobisbipyridylrhodium(III) chloride dihydrate (0.28 g., 0.5 mmole) was dissolved in hot water (8 ml.) and a solution of potassium iodide (0.33 g., 2 mmole) in water (2 ml.) was added. To the hot mixture hypophosphorous acid (0.02 ml.) was added and the solution brought to boiling. A rapid deepening in colour was noted and trans-di-iodobisbipyridyl-rhodium(III) iodide crystallised as a brick-red solid. It was collected after cooling, washed with cold water, then ethanol, and air-dried (yield 0.36 g., 90%) (Found: C, 29.9; H, 2.50; N, 7.11. C₂₀H₁₆N₄I₃Rh requires C, 30.2; H, 2.03; N, 7.04%).

trans-Dichlorobis-1,10-phenanthroline-rhodium(III) Chloride Dihydrate - Rhodium trichloride trihydrate (0.26 g., 1 mmole) in water (5 ml.) was mixed with 1,10-phenanthroline (0.4 g., 2.2 mmole) in warm alcohol (7 ml.), and the mixture heated to 60°. Hydrazinium chloride (0.02 g.) was added and the mixture brought to boiling.

Immediately, the mixture gave a clear yellow solution which, on cooling, deposited the desired complex as its dihydrate, which was recrystallised from water (Found: C, 47.1; H, 3.62; N, 18.0. $C_{24}H_{20}Cl_3N_4O_2Rh$ requires C, 47.6; H, 3.33; N, 17.6%). The infrared spectrum showed bands (cm^{-1}) at 3400s,b, 1632m,b, 1601m, 1582m, 1501m, 1336w, 1301w, 1218w, 1201w, 1140m, 1102w, 1083w, 1027m, 880w, 850s, 749m, 729m, and 719s.

Trisethylenediaminerhodium(III) Chloride Dihydrate. - Hydrated rhodium trichloride (0.26 g., 1 mmole) in ethanol (5 ml.) at 60° was treated with ethylenediamine hydrate (1 ml.) in ethanol (5 ml.), when a white precipitate immediately formed, which was collected, washed with ethanol, and dried (0.36 g.). It was recrystallised from hot water-ethanol as the dihydrate (Found: C, 16.7; H, 6.8; N, 19.9. Calc. for $C_6H_{28}Cl_3N_6O_2Rh$: C, 16.9; H, 6.6; N, 19.7%).

Trispropylenediaminerhodium(III) Chloride. - In the same way as for the ethylenediamine complex, trispropylenediaminerhodium(III) chloride hydrate was obtained as white crystals (Found: C, 24.4; H, 6.96. Calc. for $C_9H_{32}Cl_3N_6ORh$: C, 24.05; H, 7.15%).

Hexamminerhodium(III) Chloride. - Hydrated rhodium trichloride (0.26 g., 1 mmole) in ethanol (10 ml.) at 60°C was slowly added to a gently refluxing solution of ethanol (10 ml.) and .88 ammonia (5 ml.). The white precipitate was collected, washed with ethanol, and recrystallised from water-ethanol (0.28 g.) (Found: N, 26.7; Cl, 34.2. Calc. for $H_6Cl_3N_6Rh$: N, 27.0; Cl, 34.2%). The compound can also be prepared by addition of .88 NH_3 to an alcoholic rhodium

trichloride solution at 60° but the product contains quantities of the chloropentammine salt. The above method gives the best yields.

Chloropentamminerhodium(III) Chloride. - Hydrated rhodium trichloride (0.26 g., 1 mmole) in water (5 ml.) and ethanol (1 ml.) at 60°C was treated with .88 ammonia solution (1 ml.). The solution was heated to boiling for two minutes and cooled. Pale yellow crystals are collected, washed with a little cold water, alcohol and air dried (0.25 g.). It was recrystallised from hot water. (Found: N, 24.0; Cl, 35.8. Calc. for $H_{15}Cl_3N_5Rh$: N, 23.8; Cl, 36.2%).

trans-Dichloro(dimethylglyoximato)dimethylglyoximerhodium(III). - This was prepared by the literature method,³² and recrystallised from copious hot water (Found: Cl, 18.3. Calc. for $C_8H_{15}Cl_2N_4O_4Rh$: Cl, 18.2%). In addition to the bands given in Table 2, a band with λ 345, ϵ 1130 was observed in aqueous solution ($\sim 10^{-3}M$). The ammonium and silver³² salts were prepared by literature methods.

Deuteration. - The complex $[Rh(DMGH_2)(DMGH)Cl_2]$ (0.1 g.) was suspended in deuterium oxide (3 ml.) and the suspension refluxed for 15 min., then filtered hot. On cooling the filtrate, yellow crystals were obtained which, from their infrared spectrum, were almost completely deuterated $[Rh(Dd_2)(Dd)Cl_2]$, where Dd_2 and Dd represent deuterated dimethylglyoxime and its anion, respectively

trans-Dichloro(cyclohexanedioximato)cyclohexanedioximerhodium(III). - Rhodium trichloride trihydrate (0.2 g.) in water (1 ml.) and ethanol (9 ml.) was treated with cyclohexane-1,2-dionedioxime

(0.3 g.) in ethanol (10 ml.). The mixture was boiled for 1 min., then cooled rapidly, whereupon yellow crystals appeared. These were collected, and recrystallised from copious hot water (yield 0.2 g.) (Found: C, 31.5; H, 4.3; N, 12.5. $C_{12}H_{18}Cl_2N_4O_4Rh$ requires C, 31.6; H, 3.9; N, 12.3%). The compound, though soluble in alcohol, reacts rapidly with it when hot. Its infrared spectrum shows bands (cm^{-1}) at 3215s, 1611m, 1572m, 1511s, 1340m, 1305m, 1252w, 1227s, 1047s, 978s, 932w, 915m, 810m, and 751m. When treated with sodium borohydride in water-ethanol (1:10), a very insoluble blue compound is obtained, analogous to the reaction²⁹ for the bisbipyridyl compound, and for other complexes of rhodium(III) of the type $[Rh(AA)_2Cl_2]^{+n}$, where AA is a chelating, π -bonding, nitrogenous ligand, such as 1,10-phenanthroline or dimethylglyoxime. Such blue compounds are, in fact, markedly red-blue dichroic, and we now attribute this, and their marked insolubility, to the presence of a columnar structure based on rhodium-rhodium bonds, the rhodium being present, formally, as Rh^I , with the d^8 electronic configuration. The analogy with the well-known structure of the isoelectronic species bisdimethylglyoximate nickel(II) is obvious.

Substitution Reactions. - With thiocyanate. According to the literature,³³ when $[Rh(DMGH)_2Cl_2]^-$ is refluxed in aqueous solution with an excess of ammonium thiocyanate, the product is $NH_4[Rh(DMGH)_2(SCN)Cl]$. This reaction was repeated, but the yellow-brown crystals obtained were actually $(NH_4)[Rh(DMGH)_2Cl_2]$,

identified by analysis and the identity of the infrared spectrum with that of an authentic sample; in particular, no absorption due to the thiocyanate group was found (Found: C, 22.7; H, 4.35; Cl, 17.1. Calc. for $C_8H_{18}Cl_2N_5O_2Rh$: C, 22.8; H, 4.26; Cl, 16.8%). Bands occur (cm^{-1}) at 3120, 2610w,b, 1848w,b, 1656w,b, 1520, 1235s, 1118s, 1074s, 998w, 976m, 840m, and 733s. When the product was warmed (70°) with 1:1 hydrochloric acid, crystals of the original $[Rh(DMGH)(DMGH)Cl_2]$ were obtained. When the preparation was repeated in the presence of hypophosphorous acid, once again the original dichloro-compound was recovered unchanged.

Chlorobisdimethylglyoximapyridinerhodium(III). (1) When $[Rh(DMGH_2)(DMEH)Cl_2]$ is refluxed with pyridine, the beautiful light brown crystals obtained are the pyridinium salt,³² $(pyH)[Rh(DMGH)_2-Cl_2]$, and again, on treatment with hydrochloric acid, $[Rh(DMGH_2)-(DMGH)Cl_2]$ is regenerated. Authentic pyridinium trans-dichlorobisdimethylglyoximatorhodate(III), originally described by Dwyer and Nyholm,³² is readily prepared by allowing a cold solution of $[Rh(DMGH_2)(DMGH)Cl_2]$ in pyridine to stand. After 14 days, the large brown crystals of the desired compound were collected (Found: C, 32.8; H, 4.2; N, 14.9. $C_{13}H_{20}Cl_2N_5O_4Rh$ requires C, 32.2; H, 4.1; N, 14.5%).

(2) The literature method³³ using the reaction of trans-dichlorotetrapyridinerhodium(III) chloride with dimethylglyoxime during 36 hr. in refluxing water was re-examined. The product, however, was not the desired compound, but a mixture of yellow-

orange 1,2,3-trichlorotripyridinerhodium(III) (Found: C, 39.9; H, 3.62; N, 9.45. Calc. for $C_{15}H_{15}Cl_3N_3Rh$: C, 40.3; H, 3.35; N, 9.40%) (λ 407 $m\mu$, ϵ 138. Lit.,²² λ 407 $m\mu$, ϵ 140) and a pale yellow powder (ca. 5 - 10% of the whole) insoluble in dichloromethane. This by-product contains rhodium, chlorine and, from its infrared spectrum, pyridine, but no dimethylglyoxime: bands occur at 1606, 1311, 1220, 1177, 1161, 1074, 1023, 770, and 698 cm^{-1} . Analytical data are inconclusive.

It is noteworthy that after refluxing the original mixture for 3 hr., the components could very readily be separated by virtue of the insolubility of dimethylglyoxime in water. No reaction appeared to have occurred at this stage, since the electronic spectrum of the soluble material showed it to be pure trans-dichlorotetrapyridinerhodium(III) cation.

(3) The literature method¹⁷ was modified in several ways: (a) $[Rhpy_4Cl_2]Cl \cdot 5H_2O$ (0.31 g., 0.5 mmole) and dimethylglyoxime (0.06 g., 0.5 mmole) in warm ethanol (6 ml.) were treated with sodium borohydride (0.01 g.) in water (1 ml.). Pyridine was at once evolved; the solution was concentrated to 3 ml. and allowed to cool, when the salt trans- $[Rhpy_4Cl_2]$ trans- $[Rh(DMGH)_2Cl_2]$ (0.30 g.) crystallised (Found: C, 37.3; H, 4.0; N, 11.8. $C_{28}H_{34}Cl_4N_8O_4Rh_2$ requires C, 37.6; H, 3.8; N, 12.5%).

(b) $[Rhpy_4Cl_2]Cl \cdot 5H_2O$ (0.31 g., 0.5 mmole) and dimethylglyoxime (0.14 g., 1.2 mmole) in warm ethanol (7 ml.) were treated with sodium borohydride (0.1 g.) in water (1 ml.). Pyridine was

lost, and, on concentrating the solution to half its bulk, yellow crystals of pyridinium trans-dichlorobisdimethylglyoximatorhodate(III) were obtained (Found: C, 32.7; H, 4.16; N, 15.1. Calc. for $C_{13}H_{19}Cl_2N_5O_4Rh$: C, 32.2; H, 4.13; N, 14.5%). In the absence of catalysts other than ethanol this salt was also the reaction product.

(c) The components as in (b) were heated in 2-methoxy-ethanol (50 ml.) on a steam-bath, the solution being evaporated to dryness. The resultant yellow solid was dissolved in warm water, the solution was filtered, and, on cooling the filtrate, yellow crystals were obtained of pyridinium trans-dichlorobisdimethylglyoximatorhodate(III) (Found: C, 31.7; H, 4.26; N, 14.2).

(d) When $[Rh(DMGH_2)(DMGH)Cl_2]$ is treated either in aqueous or ethanolic solution with sodium borohydride, a blue solid is obtained. This was allowed to re-oxidise in the presence of pyridine, but the sole product was pyridinium dichlorobisdimethylglyoximatorhodate(III). When hypophosphorous acid was used in the place of sodium borohydride, in aqueous-ethanolic media, the original acid was recovered unchanged.

(4) Chlorobisdimethylglyoximatopyridinerhodium(III). A hot suspension of dichloro(dimethylglyoximate)dimethylglyoxime-rhodium(III) (0.41 g., 1 mmole) in hot pyridine (5 ml.) was treated with hypophosphorous acid (0.1 ml.). The excess of solid at once dissolved, and on cooling the clear yellow solution acicular crystals of the desired compound were obtained, which were collected, washed with ice-water, and recrystallised from dichloromethane

(yield 0.40 g.; 89%) (Found: C, 35.45; H, 4.13; N, 15.8; Cl, 8.25. $C_{13}H_{19}ClN_5O_4Rh$ requires C, 34.87; H, 4.28; N, 15.6; Cl, 7.92%).

The infrared spectrum shows bands (cm^{-1}) at $\sim 2500s,b$, 1608s, 1561sh, 1519s, 1337m, 1261s, 1221m, 1150s, 1140sh, 1078s, 1069s, 1021m, 1004w, 980s, 848m, 780s, 739s, and 701s.

trans-Dibromo(dimethylglyoximato)dimethylglyoximerhodium(III). - Rhodium trichloride (0.26 g.) in aqueous solution (10 ml.) was treated with excess of potassium bromide (1.0 g.); the solution was boiled for 2 min., then dimethylglyoxime (0.2 g.) in hot ethanol (4 ml.) was added. The mixture was heated, with or without the addition of a small amount (1 drop) of hypophosphorous acid. In the absence of hypophosphorous acid, during about 2 min., the colour of the solution gradually fades, and crystals of the desired compound begin to appear. If hypophosphorous acid is added, there is almost immediately a rapid change of colour, and, if the solution is cooled at this stage, trans-dibromo(dimethylglyoximato)-dimethylglyoximerhodium(III) crystallises in very good yield (Found: C, 20.1; H, 3.36; N, 11.7. Calc. for $C_8H_{15}Br_2N_4O_4Rh$: C, 19.8; H, 3.0; N, 11.3%). The electronic spectrum in aqueous solution ($\sim 10^{-3}M$ for visible, $\sim 5 \times 10^{-5}M$ for ultraviolet) showed bands at 435 $m\mu$ (sh), ϵ 80; λ 335 $m\mu$, ϵ 5.8×10^3 ; λ 264 $m\mu$, ϵ 1.9×10^4 .

Strangely, dichloro(dimethylglyoximato)dimethylglyoximerhodium(III) can be recovered unchanged after refluxing for 5 min. in an aqueous solution containing excess of potassium bromide and hypophosphorous acid.

Di-iodo(dimethylglyoximate)dimethylglyoximerhodium(III). - (1) Rhodium trichloride (0.26 g.) in water (10 ml.) containing potassium iodide (1.6 g.) was boiled for 2 min., and the extremely dark solution produced was mixed with dimethylglyoxime (1.4 g.) in ethanol (5 ml.) and the mixture heated. Unlike the analogous bromo-system, no crystals were so obtained, dark brown polymer being formed. However, if a drop of hypophosphorous acid was added to the hot reaction mixture, a change of colour occurred, and, on cooling, the desired compound appeared as orange-brown, glistening, acicular crystals (0.53 g.) (Found: C, 16.8; H, 2.98; I, 43.0. $C_8H_{15}I_2N_4O_4Rh$ requires C, 16.3; H, 2.54; I, 43.05%).

(2) Dichloro(dimethylglyoximate)dimethylglyoximerhodium(III) (0.4 g., 1 mmole) in water (10 ml.) containing excess of potassium iodide (1.0 g.) was heated, and, while hot, treated with hypophosphorous acid (1 drop). The clear yellow solution at once became orange, and, on cooling, orange-brown needles (0.5 g.; 85%) of dio-iodo(dimethylglyoximate)dimethylglyoximerhodium(III) were obtained (Found: C, 16.5; H, 3.01; N, 9.72%). The electronic spectrum in water ($10^{-3}M$ for visible, 10^{-5} for ultraviolet) shows bands at $450 m\mu$ (sh), ϵ 135; $335 m\mu$, ϵ 1.25×10^4 ; $264 m\mu$, ϵ 4×10^4 .
trans-Bisdimehtylglyoximatodiamminerhodium(III) Chloride Pentahydrate.- Chloropentamminerhodium(III) chloride (0.56 g.), dimethylglyoxime (0.66 g.), ammonium acetate (1.2 g.), and water (14 ml.) were heated overnight at 150° in a sealed tube. After cooling, the solution was filtered to remove unchanged dimethylglyoxime (0.085 g.,

m.p. 240°) and the filtrate evaporated to dryness. The yellow product (0.6 g.) was recrystallised from water, collected, washed with a little ice-water, and dried in air at 100° (Found: C, 18.9; H, 5.8; N, 16.6. Calc. for $C_6H_{30}ClN_6O_9Rh$: C, 19.5; H, 6.1; N, 17.0%); Δ , 122 mhos ($10^{-3}M$ in water). The electronic spectrum ($3.1 \times 10^{-3}M$ in water) had λ 335, ϵ 2.1×10^3 ; λ 266, ϵ 1.2×10^4 .

The preparations of the complexes used in the polarographic work, e.g. $Rhen_2Cl_2^+$, are found in ref. 20. Other compounds such as $Rhpy_4Cl_2^+$, $Rhpy_4Br_2^+$ are described in this work.

Hydridopentamminerhodium(III) sulphate. - Chloropentamminerhodium(III) sulphate (0.30 g., 1 mmole) in cold water (5 ml.) with .88 ammonia added (0.5 ml.) was treated with ~~a~~stoichiometric quantity of zinc dust (0.07 g., 1 mmole) under nitrogen. After shaking for ten minutes, the solution was filtered free of any unchanged chloropentammine complex and zinc (under nitrogen), and ammonium sulphate added (0.5 g.). Then .88 ammonia was added to the solution until the required complex precipitated out as a white microcrystalline solid. It can be recrystallised by redissolving the white precipitate in a small quantity of cold water and adding .88 ammonia. The white solid is collected, washed with alcohol and dried under vacuum (0.20 g.) (Found: H, 5.6; N, 24.9; SO_4 , 32.7. $H_{16}N_5O_4RhS$ requires H, 5.3; N, 24.6; SO_4 , 33.7%).

Hydridoaquotetramminerhodium(III) sulphate. - Hydridopentamminerhodium(III) sulphate (0.5 g.) was dissolved in water (100ml.). Sufficient acetone was added until no more precipitation occurred.

The white solid was collected and redissolved in a further 100 ml. of water. This was repeated four times. The pure hydrido-aquo-tetramminerrhodium(III) sulphate was collected as a white solid, washed with a small quantity of ethanol and dried in a vacuum (0.2 g.) (Found: N, 19.6; SO_4 , 32.9. $\text{H}_{15}\text{N}_4\text{O}_5\text{RhS}$ requires N, 19.6; SO_4 , 33.6%).

Catalytic experiments of rhodium(III) complexes. -

(a) 1,2,6-Rhpy₃Cl₃ (0.5 g.) in ethanol (5 ml.) was placed in a stainless steel bomb (25 ml.) and the bomb evacuated. Hydrogen (50 atmos.) was let in and the system left for 6 hours at room temperature. On opening the bomb, the solution was quickly transferred to a n.m.r. tube under nitrogen.

(b) 1,2,6-Rhpy₃Cl₃ (0.05 g.) in ethanol (5 ml.) was placed in a stainless steel bomb (25 ml.) and hex-1-ene (4 ml.) added. Hydrogen (60 atmos.) was let in and the system left for 6 hours at room temperature. Analysis of the solution on opening the bomb showed ca. 95% conversion to n-hexane.

(c) Rh(MePh₂As)₃Cl₃ (0.25 g.) in benzene (15 ml.) and ethanol (35 ml.) containing hex-1-ene (5 ml.) was treated with molecular hydrogen (60 cm. pressure). After 5 hours, a yellow precipitate was filtered from the solution, washed with ethanol and dried. M.Pt. 162 - 163°C (decomp.) (Found: C, 51.3; H, 4.9; Cl, 6.9. Calc. for C₃₉H₄₀Cl₂As₃Rh: C, 51.6; H, 4.4; Cl, 6.8%).

(d) The same experiment as (c) was carried out for Rh(Et₂PhP)₃Cl₃ and (Buⁿ₃P)₃RhCl₃. The solutions, however, were

hydrogenated for ca. 24 hours, and then the solvent was removed under reduced pressure.

Tris(triphenylphosphine)chlororhodium(I). - To a solution of PPh_3 (12.0 g., 6 M excess, freshly recrystallised) in hot ethanol (350 ml.), was added a solution of rhodium trichloride trihydrate (2 g.) in hot ethanol (70 ml.) and the solution was refluxed (30 min.). The hot solution was filtered and the Burgundy-red crystals of the complex were washed with degassed ether (50 ml.) and dried in a vacuum. Yield 6.25 h., 88% based on Rh; m.p. $157 - 158^\circ\text{C}$ [Found: C, 70.1; H, 4.9; Cl, 3.9; O, 0.0. $\text{C}_{54}\text{H}_{45}\text{ClP}_3\text{Rh}$ requires C, 70.1; H, 4.9; Cl, 3.8; O, 0.0%]. The molecular weight data is given in Table 12.

If more concentrated solutions are used, i.e. using 200 ml. or less of ethanol in total, orange crystals of the complex are obtained after 5 min. refluxing; these often mixed with a small quantity of the above red complex [Found: C, 69.7; H, 4.9; Cl, 4.4%]. On continued refluxing, gradual conversion of these orange crystals to the deep red form occurs.

The infrared spectra of the two forms of the compound from 4000 cm^{-1} to 600 cm^{-1} showed no differences. Their chemical properties appear to be identical, and, in particular, there is no difference in catalytic behaviour when dissolved.

The preparation of the complex can also be carried out in aqueous acetone. Thus, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.1 g.) in water (5 ml.) is added to a hot solution of PPh_3 (0.6 g.) in acetone (25 ml.) and

TABLE 12.

Molecular weight data for $\text{RhCl}(\text{PPh}_3)_3$ (M required 924.9).

Mechrolab osmometer at 37° .

Solvent	Concentration g/l	<u>M</u> .	Solvent	Concentration g/l	<u>M</u> .
CHCl_3	5.654	471	C_6H_6 ^b	2.783	480
	13.856	440		4.025	473
	18.044	462		4.550	492
	23.534	461		a	

^a Above 4.6 g/l variable results are obtained but these are generally above 600.

^b Cryoscopic values: 2.575 g/l, M, 458; 2.321 g/l, M, 457.

refluxed. Orange crystals of the complex are deposited after a few minutes. [Found: C, 69.6; H, 4.6%].

The excess PPh_3 used in the preparations can be recovered by addition of water to the filtrates until precipitation begins; on standing 2-3 days, PPh_3 crystallises. Recrystallisation from ethanol and ethanol-benzene gives pure material.

Tris(triphenylphosphine)bromorhodium(I). - To a solution of PPh_3 (12 g., 6 M excess) in hot ethanol (250 ml.) was added a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (2 g.) in warm ethanol (70 ml.). After refluxing until the solution begins to lighten in colour (5 min.), LiBr (8 g.) in hot ethanol (50 ml.) was added and the mixture refluxed for 1 hour. Orange prisms of the complex were collected from the warm solution, washed with de-gassed ether (50 ml.) and dried in a vacuum. Yield 5.1 g., 64%; m.p., 133-134°. [Found: C, 66.8; H, 4.9; Br, 8.2 $\text{C}_{54}\text{H}_{45}\text{BrRh}$ requires C, 66.9; H, 4.7; Br, 8.2%].

A second form of the bromide can be prepared as follows: To a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.5 g.) in warm ethanol (75 ml.) was added LiBr (2 g.). After refluxing (5 min.), 75 ml. of hot ethanol containing PPh_3 (3 g.) were added and the mixture refluxed for 30 min. Deep brown crystals of the complex were collected from the warm solution, washed with de-gassed ether (25 ml.) and dried in a vacuum. Yield, 1.3 g., 69%; m.p., 129-130°. [Found: C, 66.7; H, 4.7; Br, 8.3%].

Again, no differences were found in the infra-red spectra of the two forms from 4000 cm^{-1} to 600 cm^{-1} and their chemical

properties are identical.

Tris(triphenylphosphine)iodorhodium(I). - To a solution of PPh_3 (6.0 g., 6 M excess freshly recrystallised from ethanol) in hot ethanol (200 ml.) was added a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1.0 g.) in warm ethanol (60 ml.) and the mixture brought to the boil. When lightening of the colour of the solution occurred and orange crystals began to be deposited (ca. 5-10 min.), a solution of LiI (4 g.) in hot ethanol (80 ml.) was added quickly dropwise, and the solution stirred. The mixture was refluxed for 3-4 hours and brown crystals collected from the warm solution. These were often contaminated with a material of higher iodine content, probably the dimeric species $[\text{RhI}(\text{PPh}_3)_2]_2$. The product was therefore dissolved in the minimum quantity of hot benzene containing excess PPh_3 , the solution filtered and allowed to stand for several hours under nitrogen. Deep red prisms of the complex were collected, washed with ether and dried in a vacuum. m.p., $118-120^\circ\text{C}$ (dec.). [Found: C, 64.1; H, 4.8; I, 12.3. $\text{C}_{54}\text{H}_{45}\text{IP}_3\text{Rh}$ requires C, 63.8; H, 4.4; I, 12.5%].

Tetrakis(triphenylphosphine)-~~rh~~'-dichlorodirhodium(I). - Saturated solutions or suspensions of $\text{RhCl}(\text{PPh}_3)_3$ in benzene, toluene or preferably methylethylketone when refluxed under nitrogen, give salmon-pink crystals of the complex in essentially quantitative yield. The collected material was washed with de-gassed ethanol and vacuum dried. [Found: C, 65.4; H, 4.8; Cl, 5.3. $\text{C}_{72}\text{H}_{60}\text{Cl}_2\text{P}_4\text{Rh}_2$ requires C, 65.1; H, 4.5; Cl, 5.4%].

The complex slowly absorbs oxygen from the air in the solid

state but most rapidly in suspension in organic solvents in which it is sparingly soluble. Storage should be in vacuo. The molecular weight (in CHCl_3 , saturated with H_2) is that for a dimer: $\underline{M}$ (found), 1263; $\underline{M}$ (calc.) 1324. If molecular weight measurements are carried out in aerobic conditions, low values are obtained, presumably because of the formation of the soluble oxygeno complex, $\text{RhCl}(\text{PPh}_3)_2\text{O}_2$. The dimer in suspension can be cleaved with carbon monoxide at 25°C , to give $\text{RhClCO}(\text{PPh}_3)_2$, which was identified by comparison of its infrared spectrum with an authentic sample. Crystallisation from benzene solution containing excess triphenylphosphine gives $\text{RhCl}(\text{PPh}_3)_3$.

Interaction of the complexes with carbon monoxide. - When CO is passed through a solution of $\text{RhCl}(\text{PPh}_3)_3$ (0.1 g.) in benzene (10 ml.) the solution rapidly turns yellow and after removal of solvent, crystals of $\text{RhClCO}(\text{PPh}_3)_2$ are obtained essentially quantitatively. The product was identical (i.r.) with the authentic material prepared from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. [Found: C, 64.3; H, 4.3; Cl, 5.3. Calc. for $\text{C}_{37}\text{H}_{30}\text{ClOP}_2\text{Rh}$, C, 64.4; H, 4.4; Cl, 5.1%].

Identical behaviour was found for the corresponding bromide and iodide complexes and the products were identified by their infrared spectra.

Interactions of the complexes with aldehydes. - A suspension of $\text{RhCl}(\text{PPh}_3)_3$ (0.5 g.) in benzene (10 ml.) was warmed (40°C) and n-heptaldehyde added (0.5 ml.). The solution rapidly turned pale yellow, and on cooling, crystals of $\text{RhClCO}(\text{PPh}_3)_2$ were deposited

from the solution (identified by i.r.). Analysis of the residual solution by g.l.c. shows the following yields of products: n-hexane, 80%; hex-1-ene, 10%; cis-hex-2-ene, 5%; trans-hex-2-ene, 5%.

Similar behaviour was found for propionaldehyde, formaldehyde, benzaldehyde, cinnamic aldehyde and formic acid.

The corresponding bromide and iodide were found to behave similarly, $\text{RhBrCO}(\text{PPh}_3)_2$ and $\text{RhICO}(\text{PPh}_3)_2$ being identified as the products.

Bis(triphenylphosphine)ethylene chlororhodium(I). - On bubbling ethylene through a solution of $\text{RhCl}(\text{PPh}_3)_3$ (0.1 g.) in de-gassed chloroform (10 ml.), the red colour rapidly changes to yellow and on concentration of the solution under an ethylene atmosphere, yellow crystals of the complex were obtained. They were collected rapidly, washed with a little ethylene-saturated chloroform and dried in air. Yield, ca. 70%. [Found: C, 65.5; H, 5.0; Cl, 4.9. $\text{C}_{38}\text{H}_{34}\text{ClP}_2\text{Rh}$ requires C, 66.0; H, 4.8; Cl, 5.1%].

The corresponding bromide complex is made in an identical way from $\text{RhBr}(\text{PPh}_3)_3$. [Found: C, 62.3; H, 4.7; Br, 10.5. $\text{C}_{38}\text{H}_{34}\text{BrP}_2\text{Rh}$ requires C, 62.0; H, 4.6; Br, 10.9%].

The complexes are readily soluble in benzene, CHCl_3 and CH_2Cl_2 . The solutions lose ethylene rapidly but regeneration is complete in presence of excess ethylene.

Absorption of hydrogen by $\text{RhCl}(\text{PPh}_3)_3$ and $[\text{RhCl}(\text{PPh}_3)_2]_2$. - In a standard micro-hydrogenation apparatus, 5 ml. of solvent (benzene, ethyl acetate, glacial acetic acid) were saturated with hydrogen at

1 atm. pressure. Then ca. 40-45 mg. of $\text{RhCl}(\text{PPh}_3)_3$ were tipped into the solvent from a bucket and the additional hydrogen uptake measured. The rate of uptake varied with each solvent, but no useful data could be obtained because of the differing solubilities of the complex and the dihydride product in each of the solvents. Generally uptake was complete after 1 hour. In all cases the absorption was found to correspond to 1 mole of hydrogen per mole of $\text{RhCl}(\text{PPh}_3)_3$. The dimer (37.45 mg.) in CH_2Cl_2 absorbed 1.30 ml. H_2 at STP. ($\cong 2.05$ moles H_2 per mole).

Bis(triphenylphosphine)dihydridochlororhodium(III). - On passing H_2 through a solution of $\text{RhCl}(\text{PPh}_3)_3$ (0.5 g.) in de-gassed chloroform (10 ml.) for a few min., the solution turns pale yellow. On concentrating the solution under a hydrogen atmosphere to small volume (~ 2 ml.) or by addition of a little de-gassed ether, pale yellow crystals of the complex are obtained. These are quickly collected, washed with a little hydrogen-saturated ether and dried under vacuum. [Found: C, 65.2; H, 5.1; Cl, 6.2. $\text{C}_{36}\text{H}_{32}\text{ClP}_2\text{Rh}$ requires C, 65.0; H, 4.8; Cl, 5.3%].

The molecular weight cannot be determined due to the rapid loss of hydrogen occurring in solution. The yellow crystals, even after storing in vacuo for several days, smell faintly of chloroform and the high chloride analysis reflects the retention of some weakly bonded chloroform. $[\text{RhCl}(\text{PPh}_3)_2(\text{H}_2)] \cdot \text{CHCl}_3$ requires Cl, 18.1%].

Di[bis(triphenylphosphine)dihydridochlororhodium(III)] methylene chloride. - This is prepared in the same manner as the possibly five coordinate species above except using dichloromethane as

solvent. Beautiful yellow crystals of the complex were obtained on concentrating the solution under hydrogen; they were filtered, washed with a little de-gassed ether and dried in vacuo for several days. [Found: C, 64.5; H, 5.0; Cl, 9.5. $C_7H_6Cl_4P_4Rh$ requires C, 64.8; H, 4.7; Cl, 10.0%].

The infrared mull spectrum shows bands due to the presence of dichloromethane. The corresponding dideutero complex was made in an analogous way.

Bis(triphenylphosphine)pyridine dihydrido chlororhodium(III). -

On passing hydrogen through a solution of $RhCl(PPh_3)_3$ (0.25 g.) in pyridine (10 ml.) for 20 min., the solution gradually turns pale yellow. On concentration under a hydrogen atmosphere to ca. 2 ml., crystals of the complex are obtained. These appeared to be yellow but after washing with ether (5 ml.) were white. Yield ca. 90%. [Found: C, 66.6; H, 5.1; Cl, 4.8. $C_4H_3ClNP_2Rh$ requires C, 66.2; H, 5.0; Cl, 4.8%].

The complex is stable in the solid state in absence of air but in solution, hydrogen is lost slowly; re-saturation with hydrogen restores the complex.

The corresponding bromide can be obtained in an analogous way from $RhBr(PPh_3)_3$. [Found: C, 62.4; H, 4.7; Br, 10.3. $C_4H_3BrNP_2Rh$ requires C, 62.4; H, 4.7; Br 10.2%].

As well as Rh-H frequencies ir. spectra of both compounds show bands due to both PPh_3 and pyridine.

Other solvent hydrido complexes. - Repetition of the preceding

experiments using benzene, ethyl acetate, glacial acetic acid or formdimethylamide gave pale yellow solutions, from which almost white crystals were obtained directly or by precipitation on concentration of the solution in a stream of H_2 . However, the solids were rather unstable, losing hydrogen. In addition to Rh-H bands (Table 9), ir. spectra of the ethyl acetate and formdimethylamide products had frequencies assignable to coordinated solvent at 1734 m and 1639 m $cm.^{-1}$ respectively.

Ethylene complex. - Deuteriochloroform (0.5 ml.) containing $RhCl(PPh_3)_2(C_2H_4)$ (0.05 g.) and one drop of $SiMe_4$ in an n.m.r. tube was attached to a vacuum line, frozen in liquid nitrogen, evacuated, and an appropriate measured amount of ethylene condensed in. After sealing, the tube was placed in a Varian low temperature probe for the 40 Mc/sec. spectrometer and the spectrum measured over the range -50° to $25^\circ C$. Repetition with varying quantities of ethylene led to the results given in Table 8.

Hydrogen pressure studies. - A deuteriochloroform (0.5 ml.) solution of $RhCl(PPh_3)_3$ (0.1 g.) containing one drop of $SiMe_4$ was saturated with H_2 and transferred to a thick-walled n.m.r. tube. The latter was sealed in to a brass adaptor by Ciba Araldite epoxy resin (type AY/HY111). The adaptor was connected to stainless steel pressure tubing (1 mm. o.d.) terminating in a needle valve and connection to pressure gauge and cylinder. The system was flushed with H_2 and thereafter the pressure slowly increased to ca. 100 atm. After a few minutes to allow equilibrium (and for safety

reasons) the tube arrangement was disconnected from the cylinder and the n.m.r. tube inserted in the spectrometer.

Hydrogen transfer to olefins. - A solution of $\text{RhCl}(\text{PPh}_3)_3$ (ca. 0.1 g.) in CDCl_3 (3.0 ml.) in an n.m.r. tube sealed to a vacuum line, was saturated with H_2 until yellow; after addition of a little Me_4Si , ethylene was condensed on. After sealing, the n.m.r. spectrum was followed from -70° to 25°C .

In similar experiments, liquid olefins such as hex-1-ene were injected into the hydrido complex solution with the tube in the probe.

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