

RHODIUM AND RUTHENIUM COMPLEXES IN
HOMOGENEOUS HYDROGENATION REACTIONS

A Thesis submitted

by

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for the Degree of

Doctor of Philosophy

of the

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July 1972

To my family

and

Andrée

Acknowledgement

I would like to express my sincere thanks to Professor G. Wilkinson F.R.S. for his interest and encouragement in this work, and for his useful advice during the past three years.

I would also like to thank all my colleagues at Imperial College, especially Dr. J. D. Ruddick and Dr. A. Spencer for useful discussion and advice and Mr. R. Shadwick and the late Mr. H. J. Smith for technical assistance.

I am also indebted to the Science Research Council for financial support during the past three years, and to Miss M. Clark and Miss T. E. Flint for typing this thesis.

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ABBREVIATIONS

g.l.c. gas-liquid chromatography
i.r. infra red
n.m.r. nuclear magnetic resonance
D.M.E. dropping mercury electrode
S.C.E. standard calomel electrode

Me - methyl; Et - ethyl; Pr - propyl;
nBu - n-butyl; Ph - phenyl.

Abstract

The new dirhodium ion Rh_2^{4+} has been characterised, and its use as a starting material for the synthesis of a number of rhodium(I) and rhodium(III) complexes is described.

In the presence of triphenylphosphine, the ion is exceedingly active as a homogeneous hydrogenation catalyst for the reduction of multiple carbon bonds in organic molecules. The dependence of the rate of catalysis on the concentration of catalyst, the concentration of substrate and the pressure of hydrogen has been studied, and a possible mechanism for catalysis suggested in the light of the kinetic results obtained.

The new monomeric rhodium carboxylates of the type $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$ have been synthesised, and a comparison with the chloride $\text{RhCl}(\text{PPh}_3)_3$ is made on the basis of their catalytic behaviour in benzene and acidified alcohols.

Carboxylato complexes of ruthenium are described and in particular, the electrochemical reduction of the new triphenylphosphine adduct of the acetate $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ has been studied. The reduced species in the presence of triphenylphosphine and a protonating acid give catalytically active solutions towards the hydrogenation of organic substrates. As well as mono-olefins, cyclic non-conjugated dienes are rapidly reduced, and an active intermediate of stoichiometry $[\text{Ru}(\text{PPh}_3)_2]^{2+}$ is suggested.

The same catalytic species is obtained by protonation of the hydridoacetate complex $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ in alcoholic solution, and a possible mechanism for the catalysis is suggested on the basis of the kinetic results obtained.

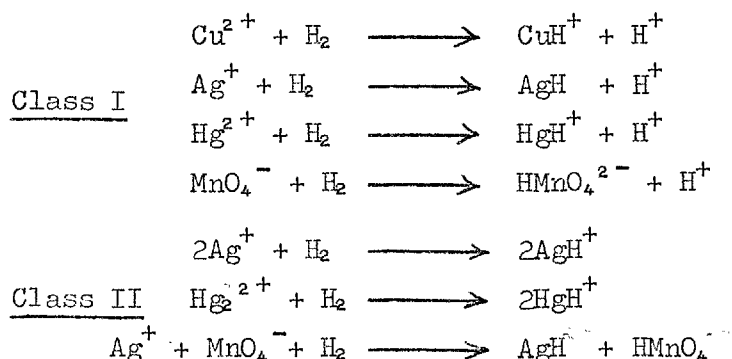
The new complexes $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$ and $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_2$ have been obtained, together with the longer chain carboxylates, and the electrochemical reduction and/or protonation with strong acid is described. The preparation of catalytically active species from these complexes is noted, and the rates of catalysis by such species is discussed.

Introduction

It is now well established that even under quite mild conditions, molecular hydrogen can undergo many reactions homogeneously in solution. This recognition is however of fairly recent origin and can be traced to Calvins discovery^{1,2} in 1938, that at temperatures of ca. 100°C, hydrogen reduces cupric acetate or benzoquinone homogeneously in quinoline solution in the presence of dissolved cuprous acetate. The latter functions as a true homogeneous catalyst for these, as well as for other reactions of hydrogen, e.g. parahydrogen conversion.

However since 1953 most of the homogeneous systems involving hydrogen have involved metal ions or complexes as reactants, or even catalysts. Among the species which can activate hydrogen in solution are a number of simple metal ions Cu^{2+} ,^{3,4} Ag^+ ,⁵ Hg^{2+} and Hg_2^{2+} ⁶ and the oxyanion MnO_4^- ⁷.

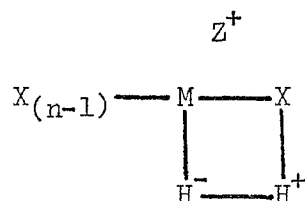
In aqueous solution these ions are reduced homogeneously by hydrogen at temperatures below 100°C, to compounds of lower valence, or to the metallic states. Cu^{2+} and Ag^+ can also catalyse exchange of hydrogen with water and hydrogenation of dissolved substrates such as oxygen or dichromate, which do not react with hydrogen in the absence of a catalyst. It has been shown that these reactions may be divided on the basis of their kinetics and mechanisms, into two classes depending on whether one or two metal ions participate together with hydrogen in the rate determining step. Some of the homogeneous hydrogenation reactions involving metal ions that have been observed in solution are summarised below, the equations relating to the rate determining stages.



It was proposed that the hydrogen undergoes heterolytic splitting in reactions of the first class and homolytic splitting in those of the second class.

The mechanisms proposed for the splitting of hydrogen by Cu^{2+} and Ag^+ have been adequately substantiated,⁸ although most of the reaction intermediates are unstable, and either undergo the reverse reaction to regenerate hydrogen or take part in some further reaction in which the metal ion itself or some other dissolved substrate is reduced.

However it has been shown that the rate of activation of molecular hydrogen by metal ions is greatly influenced by complexing,⁹ and in fact most of the early reactions studied with metal complexes, have involved the heterolytic cleavage of H_2 in the rate determining steps. A plausible representation of the transition state in such reactions, for a complex of the type MX_n^{2+} would be:-

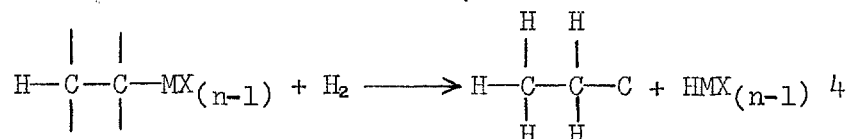
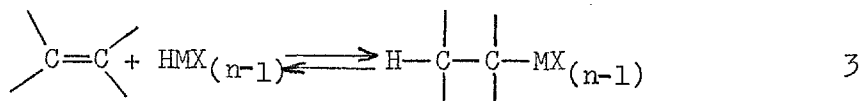
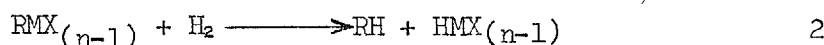
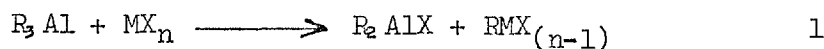


where X is a ligand molecule or ion (or a water molecule in the case of the aquo ion) originally coordinated to the metal. Formation of the transition state thus involves heterolytic stretching of the M-X and H-H bonds, and incipient formation of covalent M-H and X-H bonds. The reactions of the complex should then depend directly on the strength of the M-H and X-H bonds, all of which will vary with the nature of X. In complexes with relatively weak metal-ligand bonding (i.e. those with small formation constants), the main influence of the ligand on reactivity should be that arising from variation in the strength of the X-H bonds. This then implies that the reactivities of "weak" complexes should increase with the basicity of the ligands. The enhancement of the activity of the cupric ion by complexing with a number of ligands of different

basicity i.e. $\text{H}_2\text{O} < \text{Cl}^- < \text{SO}_4^{2-} < \text{acetate} < \text{propionate} < \text{butyrate}$ etc. is in accord with this. However the formation of stable complexes drastically reduces the activity of these ions, and the effect appears to be more pronounced in non-polar solvents than in aqueous solution.¹⁰

There has been considerable interest in soluble hydrogenation catalysts in recent years. From a theoretical viewpoint it has been felt that a study of soluble catalysts may shed some light on the mechanism of heterogeneous hydrogenations. Practically, soluble catalysts might show higher activity, be less susceptible to poisoning, and be also useful for the reduction of polymers.

Some of the early work on hydrogenation catalysts is covered in several review articles.¹¹ Recently hydrogenations catalysed by the pentacyanocobaltate(II) ion,¹² ruthenium(II) ion,¹³ boron alkyls¹⁴ and even t-butoxide ion¹⁵ have been reported. In 1963 it was shown that a number of transition metal compounds, combined with organometallic derivatives could act as soluble catalysts for the hydrogenation of alkenes. These metals, of groups IV - VIII, mostly as acetylacetonates or as alkoxides, were found to be active when combined with, preferably a trialkylaluminium compound. A postulated mechanism for hydrogenation with such soluble catalysts is as follows:-



Stage 1 represents the alkylation of the transition metal derivative. It is then considered that this step is followed by hydrogenolysis of the metal-alkyl bond formed to yield a metal hydride, 2, which then adds alkene 3, with the formation of a new

metal alkyl. Hydrogenolysis of the latter yields a saturated hydrocarbon with consequent regeneration of the metal hydride ⁴.

However up to 1966, only very few systems proved to be useful for the catalytic homogeneous hydrogenation of unsaturated organic compounds. One of the most versatile catalysts, but one which has the disadvantage of being only water soluble is the Co(III)-cyanide system. It allows the reduction of conjugated double bonds, as in buta-1,3-diene; α - β -unsaturated acids and aldehydes, but isolated ethylenic linkages are unaffected ¹⁶. There are quite a number of Ziegler-type catalysts, soluble in organic solvents which will allow hydrogenation of olefinic hydrocarbons, ¹⁷ while a chloroplatinate(II)-trichlorostannate(II) complex is effective for ethylenes and acetylenes. ¹⁸

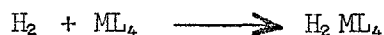
It has been known for quite some time that molecular hydrogen in the presence of soluble rhodium(III) amines could reduce quinone, ¹⁹ but unfortunately in this system, rapid deposition of metal occurs, a complication also encountered in the reduction of ferric ion by H₂ in the presence of a hexachlororhodate(III) ion. ²⁰

Mechanisms for Catalytic Hydrogenations.

The mechanism for the catalytic hydrogenation of unsaturated substrates can be conveniently regarded as one involving three stages, (a) H₂ activation, (b) substrate activation and (c) H₂ transfer.

Although many metal complexes have been shown to activate the hydrogen molecule, very few have been able to reduce alkenes and alkynes, either because the latter have not been activated by the metal complex, or because the transfer of activated hydrogen was kinetically or thermodynamically impossible.

For a d⁸ complex [as in Rh^(I)], or a d⁶ complex [as in Ru^(II)] to be oxidised by molecular hydrogen to give a d⁶ or d⁴ species respectively,



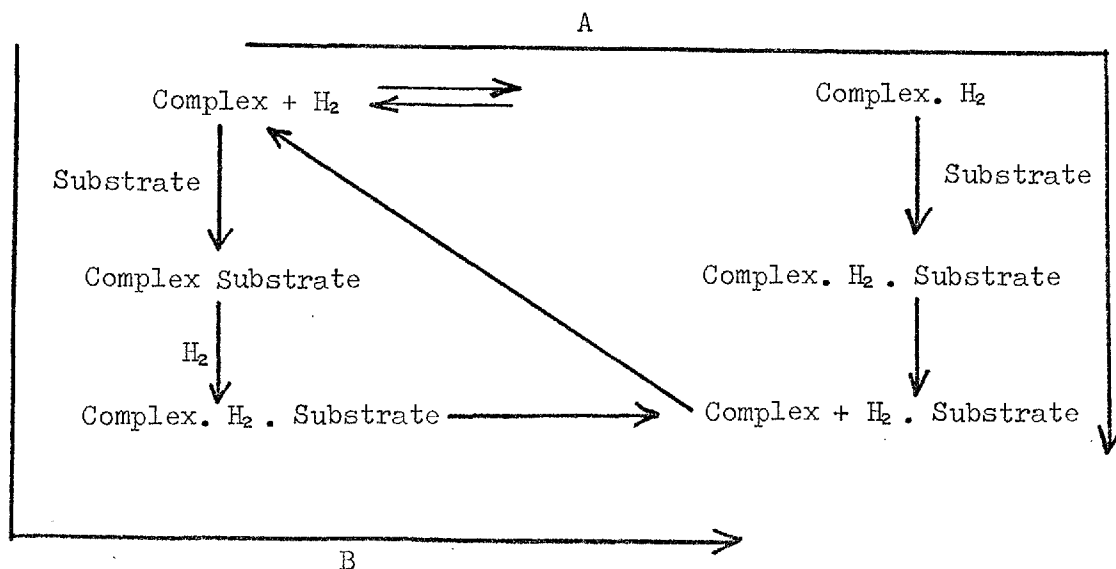
it would appear that $2E_{M-H} > E_{H-H} + A$, where E_{M-H} is the energy of formation of the metal-hydrogen bond, E_{H-H} is the bond strength for molecular hydrogen, and A is the promotional energy of the metal in the complex. It is evident that if hydrogen activation is to be reversible, then $2E_{M-H}$ must be approximately equal to $E_{H-H} + A$.

In general with a complex of the type ML_nX , any ligand X which withdraws electron density from the metal will increase the promotional energy and thus reduce the ability of the species to activate molecular hydrogen. It has been suggested that the primary interaction of molecular hydrogen with metal species, must involve the feeding-in of electron density in filled metal orbitals, to an acceptor orbital on one of the hydrogen atoms of the hydrogen molecule. Nyholm has made the suggestion²¹ that an antibonding orbital could be used as an acceptor, whereas it has been postulated, and not unreasonably by Halpern that the bonding electrons of H_2 could attack vacant metal orbitals. Since H_2 activators are generally electron rich systems, the proposal by Nyholm seems more likely.

It is now clear why certain species, even though they can activate molecular hydrogen quite rapidly and reversibly, e.g. $IrCl(CO)(PPh_3)_2$ or $RhCl(PPh_3)_3$, in pyridine or acetonitrile are either unable to catalytically hydrogenate alkenes at 25°C and 1 atm., or do so only very slowly. On the dihydrido species thus formed, there are no vacant sites for alkene coordination, i.e. they are coordinatively saturated. The fact that vacant sites are necessary for activity is shown by the slow hydrogenation of alkenes by the iridium species $Ir(H)_2Cl(CO)(PPh_3)_2$ at elevated temperatures, when it is assumed that thermal dissociation of a PPh_3 ligand, which would then competitively provide a coordination site, occurs. Thus once a vacant site has been established, substrate may coordinate at that point, and provided a suitable transfer of H_2 to the extremities of the reducible group of the substrate can arise, then reduction is likely.

In the case of $\text{RhCl}(\text{PPh}_3)_3$, it was originally suggested²² that a vacant site, essential for catalytic activity was provided by the initial dissociation of one of the phosphine groups in pure benzene. The bisphosphine species was then capable of activating hydrogen reversibly, and the dihydrido species could activate the multiple bond of the reducible substrate that was present in the homogeneous media. It was shown that a synchronous transfer of H_2 to the substrate occurs rapidly, and that there is no evidence for the formation of intermediate alkyls. However since 1966, other homogeneous catalysts have been studied, notably the hydridophosphine complexes of ruthenium, eg. $\text{RuH}(\text{Cl})(\text{PPh}_3)_3$,²³ and $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$,²⁴ and the carbonyl halide and carbonyl hydride of rhodium, $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ ²⁵ and $\text{RhH}(\text{CO})(\text{PPh}_3)_2$.²⁶ The formation of an intermediate alkyl by the hydridoacetate $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ in the homogeneous hydrogenation of alkenes has been shown to occur in pure benzene²⁴ (after initial PPh_3 dissociation has taken place), where the initial reaction is predominantly alkene addition followed by the activation of hydrogen.

Whether H_2 activation or alkene activation occurs first, it is essential to realise that either the hydrido complex or the alkene complex (whichever is formed first), has to be capable of activating alkene or hydrogen respectively. After this has been achieved, H_2 transfer either to the multiple bond of the coordinated alkene, or hydrogen transfer to the coordinated alkyl, must proceed efficiently, and the unsaturated species remaining (after the reduced group has been removed), must be capable of repeating the reaction cycle. Thus in general we have:-



For chlorotris(triphenylphosphine) rhodium I, ²² route A has been shown to be operative whereas for some of the hydrido complexes of ruthenium above, route B is predominant, where the intermediate "complex.substrate" is an alkyl.

The present work has been centred on the synthesis of new platinum metal complexes, notably of rhodium and ruthenium, bearing triphenylphosphine ligands, that may function as homogeneous hydrogenation catalysts for unsaturated substrates, with the emphasis being on coordinative unsaturation as a key factor in activity.

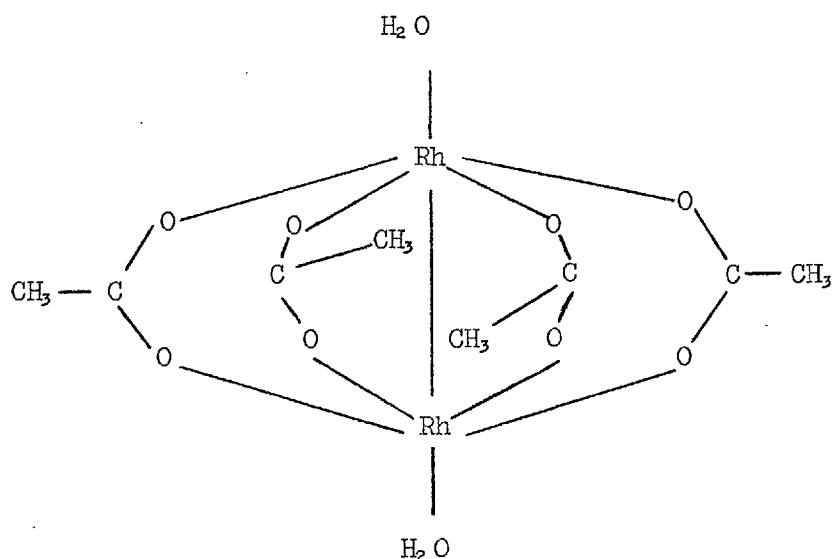
The work is described in four chapters, and deals with the synthesis, characterisation and catalytic studies of the complexes prepared, some of which are neutral, and some cationic. Protonation reactions have been of value in isolating cationic species of high unsaturation and activity, and most of the homogeneous hydrogenation reactions described have been carried out in the presence of strong, but non-complexing, non-oxidising acids.

Chapter 1 deals with the preparation and characterisation of an unsaturated cation of rhodium, Rh_2^{4+} , and its use as a starting material for the synthesis of a number of rhodium complexes, some of which are active catalysts in hydrogenations. Chapter 2 is concerned with the catalysis by rhodium complexes, where it is shown that the cation Rh_2^{4+} may be used as a base to which other groups, including hydrogen and a reducible substrate may be coordinated. Neutral Rh(I) complexes of stoichiometry $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$ (where R = alkyl, aryl or substituted alkyl) are described, and their kinetics as hydrogenation catalysts are compared to the chloride $\text{RhCl}(\text{PPh}_3)_3$. ²² Chapter 3 deals with the preparation, characterisation and chemical reactions of new ruthenium complexes. The electrochemical reduction of some of these complexes of high oxidation state, is also described, to give species of lower valence, that are then catalytically active. Chapter 4 is concerned with hydrogenation reactions of ruthenium cations, obtained by protonation of some of the complexes described in

Chapter 3. It is shown in this chapter how many of the complexes may be inter-related catalytically, after they have been reduced and/or protonated to give active cations in solution. In Chapters 2 and 4, the dependence of the rate of catalytic hydrogenation as a function of the concentration of catalyst, concentration of substrate, and the pressure of hydrogen is described, and a possible mechanism formulated on the basis of the results obtained.

Table I.1. Properties of the Dirhodium- μ_4 -acetate

Preparation	Hydrous rhodium(III) oxide or ammonium chlororhodate(III) is treated with acetic acid in ethanol to yield green crystals of the acetate. ²⁷ An improved preparative procedure ²⁸ is based on the method used to obtain the corresponding halogenocarboxylates $\text{CCl}_3\text{CO}_2^-$, CF_3CO_2^- , $\text{CH}_2\text{ClCO}_2^-$ etc., and involves the interaction of commercial rhodium trichloride with sodium acetate in ethanol. Recrystallisation from boiling methanol yields the methanol adduct $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{MeOH}]_2$.
Physical State	The methanol adduct forms dark blue green crystals, the pure anhydrous acetate being emerald green.
Structure ²⁹	An X-ray crystallographic analysis of $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}]_2$ has shown that the compound has the same dimeric structure as the hydrated copper(II) ³⁰ and chromium(II) ³¹ acetates. A Rh-Rh separation of 2.45 Å suggests significant metal-metal bonding.



- I.R. Spectrum The i.r. spectrum (in Nujol mull) is similar to that of anhydrous Cr(II) and Cu(II) acetates. The C-O stretching frequencies for $[\text{Rh}(\text{OCOCH}_3)_2]_2$ are $\nu_{\text{as}}\text{COO}$, 1588 cm^{-1} and $\nu_{\text{s}}\text{COO}$, 1433 cm^{-1} respectively.
- Solubility Insoluble in most non-polar organic solvents, and only slightly soluble in alcohols and ketones giving air-stable bluish green solutions.
- Electronic spectrum The electronic spectrum contains two main absorptions at 600 m μ and 450 m μ respectively. The band at 450 m μ is relatively insensitive to terminal ligands, while the one at 600 m μ is particularly sensitive, and its spectrochemical behaviour towards I^- , Br^- , Cl^- , H_2O , NCS^- , NH_3 and NO_2 has been noted by Johnson et al.³²

CHAPTER I

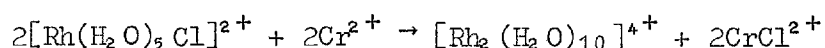
The Dirhodium Ion Rh_2^{4+} , and its use in the synthesis of new Rhodium Triphenylphosphine complexes.

Introduction

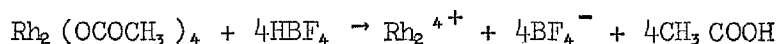
The displacement of acetic acid from the tetra-bridged molybdenum acetate $\text{Mo}_2(\text{OCOCH}_3)_4$ by hydrogen chloride³³ gives the dichloride MoCl_2 ; with concentrated hydrochloric acid, the ion $\text{Mo}_2\text{Cl}_8^{3-}$ is formed,³⁴ and similarly $\text{Re}_2(\text{OCOCH}_3)_4\text{Cl}_2$ gives $\text{Re}_2\text{Cl}_8^{2-}$.³⁵

The protonation of such bridged carboxylates having a strong metal-metal bond, by strong but non complexing, non oxidising acids should lead to the displacement of the carboxylate group, and provided the metal-metal bond remains intact, cationic binuclear species should be obtained. Such protonations have been achieved for molybdenum(II) and rhodium(II) acetates using a variety of acids, with consequent formation of cationic species of stoichiometry M_2^{4+} .

The hydrated ion Rh_2^{4+} has been obtained³⁶ and found to be a kinetically stable species. It was originally generated³⁷ by the reaction of aq. Cr^{2+} with $[\text{Rh}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$, a reaction which proceeds rapidly and essentially quantitatively according to the stoichiometry.



The cation Rh_2^{4+} has now been characterised in solution after it has been obtained by the protonation of rhodium(II) acetate using fluoroboric acid.³⁸



Its magnetic properties, behaviour on ion-exchange resins, and its reversibility with acetate ion, are consistent with a binuclear cationic species of stoichiometry Rh_2^{4+} .

The interaction of this cation with triphenylphosphine and carbon monoxide lead to the complexes $\text{Rh}(\text{PPh}_3)_3\text{BF}_4$ and $\text{Rh}(\text{CO})(\text{PPh}_3)_3\text{BF}_4$. With oxygen donors such as dimethylsulphoxide, hexamethylphosphoramide, alcohols, ketones and esters, the solutions of Rh_2^{4+} stay green and presumably these substances are merely solvating the ion.

Rhodium(I) carboxylates of stoichiometry $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$ (where R = alkyl, aryl or substituted alkyl) have been obtained by the interaction of the cation with triphenylphosphine and the lithium salt of the appropriate carboxylic acid. The chemical properties of these carboxylates are described, and include reactions with oxygen, carbon monoxide and straight chain aldehydes.

The interaction of Rh_2^{4+} with triphenylphosphine in the presence of sulphur containing ligands has also been studied, giving a collection of new rhodium(III) complexes, some neutral and some cationic.

A. The Preparation and Characterisation of Rh_2^{4+} .

Rhodium(II) acetate $[\text{Rh}(\text{OCOCH}_3)_2]_2$ or its methanol adduct $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{MeOH}]_2$ may be protonated in several ways, in either aqueous media or in organic solvents such as lower straight chain alcohols, to give a cationic species of stoichiometry Rh_2^{4+} . Despite numerous attempts to precipitate the cation with a wide variety of anions of various sizes and charges, and to obtain crystals by various cooling or evaporation techniques in different solvents, it has been impossible so far to isolate a simple salt. In the presence of good donor solvents (in which the protonation may be effected) such as acetonitrile, stabilisation of the cation through solvent coordination although possible, has not been of value in isolating a solid species.

After several treatments of the pure anhydrous acetate (or its methanol adduct) with pure trifluoromethylsulphonic acid at ca. 90°C , and vacuum evaporation of the mixture, an exceedingly deliquescent dark green solid, which appears to be the trifluoromethylsulphonate remains. However the protonation is most conveniently effected by the use of aqueous fluoroboric acid. With an excess of the acid (40% aqueous HBF_4), the methanol adduct suspended in methanol can be protonated

quite rapidly upon heating, but it is essential to keep the temperature below 100°C if metal formation is to be avoided. For the preparation of the cation with little or no excess free acid for catalytic studies (discussed in the next chapter), the methanol adduct is protonated in methanol as solvent using slightly greater than stoichiometric amounts of the acid. If fluoroboric acid is used as the protonating source, the solution is held at ca. 65°C for ca. 16-20h under N_2 .

The action of other acids upon rhodium(II) acetate:

- (a) With concentrated hydrochloric acid, the initial green solution at room temperature becomes yellow and eventually, within ca. 1h red, whereupon the electronic absorption spectrum is that of the ion $[\text{RhCl}_6]^{3-}$ ³⁷; the oxidation from rhodium(II) to rhodium(III) being accompanied by the evolution of hydrogen.
- (b) With perchloric acid, the solution in 60% aq. acid (9.2M) is dark green but, again some evolution of hydrogen occurs, and bands due to the yellow ion $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ appear in the electronic absorption spectrum.³⁶ However in 3M acid the spectrum is similar to that reported by Taube, and to that obtained in HBF_4 -MeOH solution (Table I.2). No variation with time is observed in either fluoroboric or 3M perchloric acid solutions.
- (c) Pure liquid fluorosulphonic acid, hydrogen fluoride or trifluoromethylsulphonic acid dissolve the acetate giving stable green solutions; the latter acid in methanol can be used in place of fluoroboric.

The evidence in support of the assumption that the green solutions contain the cation Rh_2^{4+} is as follows:

- (a) The green species in HBF_4 -MeOH solution is readily and completely absorbed on cation exchange resin columns (Dowex 50W-X8, 20-50 μm mesh in H^+ form). The cation can be subsequently eluted from the resin without change as shown by the electronic absorption spectrum, although with some difficulty, by use of aq. 2-3M-fluoroboric acid or 3M-perchloric acid.

Table I.2

Electronic absorption spectra of rhodium(II) solutions

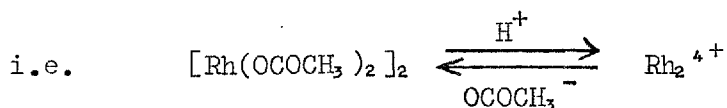
	Solvent	$\lambda_{\max}/\text{nm}(\epsilon)$
$[\text{Rh}(\text{OCOCH}_3)_2]_2$ ^a	H ₂ O	587(230), 447(94)
	EtOH	590(210), 446(98)
$\text{Rh}_2^{4+} \cdot (\text{BF}_4^-)_4$	MeOH	610(55.0), 423(61.8), 256(3.1 x 10 ³)
$\text{Rh}_2^{4+} \cdot (\text{ClO}_4^-)_4$ ^b	3M-HClO ₄	630(39.8), 412(59.1), 250(10.6 x 10 ³)

^a Ref 32 ^b Ref 36

(b) Acetic acid can be detected in the HBF₄-MeOH containing solutions before or after removal of the ions by exchange resins. Some methyl acetate is also obtained to the extent of 20-25% of the total acetic acid. The total acetate as acid and ester corresponds essentially quantitatively to that expected from complete protonation, and consequent removal of the acetate bridges of $[\text{Rh}(\text{OCOCH}_3)_2]_2$. However it appears that the ratio of acid to ester depends on the temperature and duration of the protonation.

(c) The aqueous methanolic solutions of the cation are diamagnetic by the n.m.r. method, and show no e.s.r. signal at either room temperature or at -19°C. No signal is given by rhodium(II) acetate in either frozen methanol or water.

(d) The solutions of Rh_2^{4+} in alcoholic solvents, notably methanol can be readily re-converted to the dimeric acetate by the addition of aqueous sodium acetate until the solution has a pH of 6-7, whereupon it precipitates as its methanol adduct.



Further evidence for the existence of a metal-metal bonded rhodium cation in the green methanolic solutions is provided by the reaction with lithium acetate and triphenylarsine, whereupon maroon microcrystals of a complex of stoichiometry $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{AsPh}_3]_2$ are obtained. It is analogous to the triphenylphosphine adduct of the acetate previously described.^{38b} The complex is diamagnetic by the Gouy method, and since the molecular weight in solution is consistent with a dimeric species, it seems reasonable to propose that the complex contains a metal-metal bond. The weakness of the binding of the triphenylarsine ligands is shown by the fact that the complex dissolves in donor solvents such as alcohols and ketones when warmed to give bluish green solutions, the electronic absorption spectra being identical to that of $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{L}]_2$ (where L = solvent), whereas in benzene or other non-polar solvents, the adduct dissolves giving purple coloured solutions containing the species $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{AsPh}_3]_2$.

Attempts to detect the presence of the metal-metal bond in the cation by laser Raman Spectroscopy have failed due to the colour of the solution interfering with or to decomposition by the excitation source.

It may be finally noted that solutions of Rh_2^{4+} in methanol that contain traces of unprotonated acetate, instantly react with a dilute solution of triphenylphosphine whereupon immediate precipitation of the orange adduct $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{PPh}_3]_2$ occurs.

B. (a) Interaction of the dirhodium ion with PPh_3

In view of the relevance to catalytic activity, it is of interest to discuss the reaction of Rh_2^{4+} with triphenylphosphine.

On addition of a saturated methanolic solution of PPh_3 to the green protonated solution of Rh_2^{4+} (obtained by protonation in methanolic fluoroboric acid), the colour changes immediately from green to red, and after standing for some hours, an orange semicrystalline solid A precipitates. The i.r. spectrum of A (in nujol mull) shows the presence of BF_4^- and of PPh_3 , and an elemental analysis of the complex is that of a species of

stoichiometry $\text{Rh}(\text{PPh}_3)_3\text{BF}_4$. The solid is moderately air stable, although exposure for several days results in the formation of a dark brown species, probably due to decomposition. The complex is insoluble in most non-polar solvents and is only slightly soluble in alcohols, ketones, acetonitrile and nitromethane. Conductivity measurements in nitromethane as solvent, using solutions varying in concentration from 10^{-2} to 10^{-4}M give a value for the slope of $\Lambda_o - \Lambda_e$ against $\sqrt{c}$ of 74, considerably less than that required for a fully dissociated 1:1 electrolyte.³⁹ It is not unreasonable to assume that this is due to ion-pair formation in solution, and that in the solid the fluoroborate ion is coordinated, through fluorine to the metal. Since the complex when treated with lithium chloride yields readily and quantitatively an authentic sample of $\text{RhCl}(\text{PPh}_3)_3$,²² A may be formulated as a monomeric $\text{Rh}^{(\text{I})}$ species with the fourth coordination position occupied by BF_4^- .



The nature of the reduction of $\text{Rh}(\text{II})$ is not fully understood. In view of the fact that triphenylphosphine is known to be a good reducing agent, it is possible that reduction from $\text{Rh}(\text{II})$ to $\text{Rh}(\text{I})$ by PPh_3 is occurring here. It is known, for example, that ethanolic solutions of rhodium trichloride even heated under reflux are not reduced unless PPh_3 is present, whereupon the rhodium(I) complex $\text{Rh}(\text{Cl})(\text{PPh}_3)_3$ is obtained. Since acetone-water mixtures can be used in place of ethanol as solvent in this reaction, the triphenylphosphine is without doubt the actual reducing agent.

An alternative formulation for A which would however preserve the oxidation state formally as $\text{Rh}^{(\text{II})}$, and which has considerable precedent⁴⁰ in rhodium chemistry, involves the loss of one of the α -H atoms of one of the phenyl rings of a triphenylphosphine group to give a Rh-C bond. However there is no i.r. evidence for the presence of a disubstituted phenyl ring and also no band in the

2000 cm^{-1} region expected for a metal hydride. Experiments in which solutions of the complex are exposed to D_2 give no evidence for exchange either in the i.r. of the complex or mass spectroscopic analysis of the gas. No high field resonance line is obtained by n.m.r. study of the red-phosphine-containing solution under an atmosphere of nitrogen or hydrogen, but the solution in methanol even when saturated may be too dilute for the detection of a metal hydride. (The phosphine complex rapidly precipitates from more concentrated solutions). However the fact that the red phosphine-containing-solution when stirred under H_2 turns pale yellow would seem to suggest that interaction with molecular hydrogen is taking place.

(b) Interaction of the dirhodium ion with PPh_3 and CO.

Although bubbling carbon monoxide through the protonated green methanolic solution of Rh_2^{4+} causes no visible colour change, the addition of excess triphenylphosphine to this solution while an atmosphere of CO is maintained produces an immediate orange colour, and orange crystals are obtained on cooling the solution. The crystals which have the stoichiometry $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$ are air stable indefinitely, and the i.r. spectrum shows the presence of a carbonyl group (ν_{CO} 2010 cm^{-1} in Nujol mull), PPh_3 and BF_4^- . The complex is soluble in most polar solvents such as alcohols and ketones etc., but virtually insoluble in non-polar solvents such as benzene or toluene. Conductivity measurements in nitromethane³⁹ indicate a 1:1 electrolyte [slope of $\Lambda_0 - \Lambda_c$ against $\sqrt{c} = 169$, molar conductivity (10^{-3}M) 79.0 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$], and hence it seems reasonable to formulate the species as a BF_4^- salt of the square $\text{Rh}^{(\text{I})}$ ion $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]^+$. This is confirmed by treatment of a methanolic solution of the carbonyl under hydrogen with sodium borohydride at 30°C whereupon a quantitative yield of a yellow solid, identical with an authentic sample of $\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3$ ⁴¹, is obtained.

The carbonyl cation may also be obtained as bright yellow crystals by treatment of $\text{Rh}(\text{CO})_2(\text{acac})$ in methanol with a

stoichiometric amount of 40% aq. HBF_4 (as a protonating acid for the acetylacetonato ligand) in the presence of a stoichiometric amount of triphenylphosphine. (see Experimental Section).

(c) Interaction of the dirhodium ion with PPh_3 and alkali metal carboxylates.

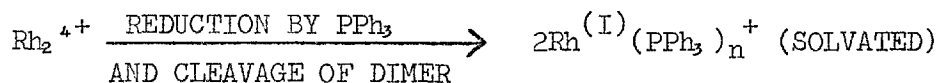
We have seen that treatment of the tris(triphenylphosphine)-rhodium(I) tetrafluoroborate salt, $\text{Rh}(\text{PPh}_3)_3^+ \text{BF}_4^-$, with lithium chloride gives chlorotris(triphenylphosphine)rhodium(I). This reaction can be readily extended using other lithium salts to give analogues of $\text{RhCl}(\text{PPh}_3)_3$ which are not otherwise readily synthesised. It is not necessary to isolate the tetrafluoroborate, and solutions of Rh_2^{4+} containing PPh_3 may be used.

The carboxylates of stoichiometry $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$ are of interest, in order to compare their properties with $\text{RhCl}(\text{PPh}_3)_3$ as hydrogenation catalysts as we shall see in Chapter 2.

Carboxylatotris(triphenylphosphine)rhodium(I) complexes.

When a solution of Rh_2^{4+} in methanol (prepared from rhodium(II) acetate by protonation with fluoroboric acid) containing triphenylphosphine ($\text{Rh}:\text{PPh}_3$, 1:4), and an excess of lithium acetate is heated, red crystals of the acetate, $\text{Rh}(\text{OCOCH}_3)(\text{PPh}_3)_3$ are obtained. Since the yield is over 80%, disproportionation of Rh_2^{4+} to $\text{Rh}^{(\text{I})}$ and $\text{Rh}^{(\text{III})}$ can be excluded, and since triphenylphosphine oxide is formed in the reaction, reduction by PPh_3 is clearly involved, as it is in the preparation of $\text{RhCl}(\text{PPh}_3)_3$.²²

Thus we may write:



(where n is probably 3)

Other carboxylates, either homologous or α -halogeno-substituted can be obtained similarly in high yield, although the butyrate and caproate are more soluble, and only ca. 50% yields are obtained by crystallisation from methanol at 25°C. There is increasing solubility in non-polar solvents with increasing chain length of the carboxylate grouping as is expected; the benzoate being fairly soluble in diethylether.

The i.r. spectrum of the carboxylates show characteristic asymmetric carboxylate stretches around 1600 cm^{-1} , and the symmetric stretches at lower frequencies, with the value of $\Delta\tilde{\nu}$ ($\nu_{\text{as}}\text{COO} - \nu_{\text{s}}\text{COO}$) being consistent with a unidentate carboxylate grouping (Table I.3).⁴² For the α -halogeno-substituted carboxylates, the energies of ν_{as} and ν_{s} are higher than those for the unsubstituted compounds.

The chemical properties of the rhodium(I) carboxylates are generally similar to those of the chloride $\text{RhCl}(\text{PPh}_3)_3$, and the compounds will undergo oxidative addition reactions, interaction with CO or aldehydes to give trans $\text{Rh}(\text{OCOR})(\text{CO})(\text{PPh}_3)_2$ complexes, and will act as homogeneous hydrogenation catalysts for alkenes and alkynes.

(d) Interaction of the dirhodium ion with PPh_3 and sulphur containing ligands.

By treatment of a methanolic solution of Rh_2^{4+} with a slight excess of triphenylphosphine, followed by a stoichiometric amount of the ligand in methanol, triphenylphosphine rhodium complex salts of the type $[\text{Rh}^{(\text{III})}(\text{L})_2(\text{PPh}_3)_2]\text{BF}_4$ where L is a bidentate anionic ligand (L^-) (eg. diethyldithiocarbamate), or a monodentate ligand (eg. SCN^- or $p\text{-CH}_3\text{C}_6\text{H}_4\text{S}^-$) have been obtained. In the absence of triphenylphosphine (i.e. direct interaction of the ligand with Rh_2^{4+} in methanol), brown insoluble and presumably polymeric solids are immediately precipitated from solution. The addition of excess triphenylphosphine to these brown suspensions produces clear red solutions from which salts of the above stoichiometry can be obtained. These complexes doubtless arise by the initial

Table I.3

Infrared spectra of Carboxylate complexes $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$
and $\text{Rh}(\text{OCOR})(\text{CO})(\text{PPh}_3)_2$ ^a

Compound	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$(\nu_{\text{as}} - \nu_{\text{s}})$	ν_{CO}
$\text{Rh}(\text{OCOCH}_3)(\text{PPh}_3)_3$	1601	1370	231	
$\text{Rh}(\text{OCOC}_2\text{H}_5)(\text{PPh}_3)_3$	1599	1379	220	
$\text{Rh}(\text{OCOC}_3\text{H}_7)(\text{PPh}_3)_3$	b	1383		
$\text{Rh}(\text{OCOC}_5\text{H}_{11})(\text{PPh}_3)_3$	b	1389		
$\text{Rh}(\text{OCOPh})(\text{PPh}_3)_3$	1590	1355	235	
$\text{Rh}(\text{OCOCH}_2\text{Cl})(\text{PPh}_3)_3$	1644	1405	239	
$\text{Rh}(\text{OCOCCLF}_2)(\text{PPh}_3)_3$	1673	b		
$\text{Rh}(\text{OCOCF}_3)(\text{PPh}_3)_3$	1673	1418	255	
$\text{Rh}(\text{OCOC}_2\text{F}_5)(\text{PPh}_3)_3$	1685	b		
$\text{Rh}(\text{OCOCH}_3)(\text{CO})(\text{PPh}_3)_2$	1608	1377	231	1976
$\text{Rh}(\text{OCOC}_2\text{H}_5)(\text{CO})(\text{PPh}_3)_2$	1607	1382	225	1980
$\text{Rh}(\text{OCOC}_3\text{H}_7)(\text{CO})(\text{PPh}_3)_2$	b	b		1981
$\text{Rh}(\text{OCOCH}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$	1600	1410	190	1979
$\text{Rh}(\text{OCOCCLF}_2)(\text{CO})(\text{PPh}_3)_2$	b	b		1980
$\text{Rh}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2$	1692	1410	282	1982
$\text{Rh}(\text{OCOC}_2\text{F}_5)(\text{CO})(\text{PPh}_3)_2$				1981
$\text{Rh}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2$				1982

^a Nujol or hexachlorobutadiene mulls, cm^{-1} .

^b Bands obscured.

reduction of $\text{Rh}^{(\text{II})}$ to $\text{Rh}^{(\text{I})}$ by PPh_3 . Since the reactions are accompanied by the formation of Ph_3PO , an extra 2 mole. proportions of PPh_3 per Rh_2^{4+} are required to complete the reduction; the oxygen presumably arising from the methanolic solvent, followed by oxidation to $\text{Rh}^{(\text{III})}$ in the presence of the anionic ligands.

Dithiocarbamato and other salts of stoichiometry $[\text{Rh}(\text{L})_2(\text{PPh}_3)_2]\text{BF}_4$.

On treatment of the cation Rh_2^{4+} with excess of triphenylphosphine and a stoichiometric quantity of sodium diethyldithiocarbamate in methanol at 25°C , a yellow crystalline solid is deposited from solution after several hours. The i.r. spectrum of this substance shows in addition to triphenylphosphine and tetrafluoroborate absorptions, a stretching vibration (ν_{CN}) at 1518 cm^{-1} characteristic of a bidentate dithiocarbamate grouping.⁴³ (Table I.4). The conductivity in nitromethane is consistent with a 1:1 electrolyte ($\Lambda_0 - \Lambda_e$ vs $\sqrt{c}$ gave a slope of 178), and the salt appears to be of stoichiometry $[\text{Rh}(\text{S}_2\text{CNet}_2)_2(\text{PPh}_3)_2]\text{BF}_4$ (I). (Fig. I.1). It is air stable indefinitely and is slightly soluble in the more polar solvents such as nitromethane, methanol and to a limited extent in acetone, but insoluble in non-polar solvents such as benzene or toluene.

It may be noted that by contrast to this reaction, treatment of the square cation $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$ in methanol with sodium diethyldithiocarbamate yields orange crystals of the complex $\text{Rh}(\text{S}_2\text{CNet}_2)_3(\text{PPh}_3)$, in which, by analogy with the dimethyldithiocarbamate complex,⁴³ two of the dithiocarbamate groups are chelated, and the other unidentate at 25°C , but are undergoing rapid interconversions at elevated temperatures.⁴⁴

Other complexes of stoichiometry $[\text{Rh}(\text{L})_2(\text{PPh}_3)_2]\text{BF}_4$ (where $\text{L} = 2\text{-mercaptopyridine, pyS; toluene-3-thiol, tt; or 2-mercaptobenzthiazole, mbt}$) have been obtained similarly.

For the bis(mercaptobenzthiazole) complex cation $[\text{Rh}(\text{mbt})_2(\text{PPh}_3)_2]^+$, the absence of a Rh-N stretching vibration, and the presence of the symmetric and assymmetric Rh-S vibrations in the i.r. spectrum

Table I.4

Infrared spectra of Rhodium(III) complexes^a

Compound	$\nu_{\text{Rh-S}}$		ν_{CN}	$\nu_{\text{P-S}}$	
	ν_{S}	ν_{as}		ν_{S}	ν_{as}
$[\text{Rh}(\text{S}_2\text{CNEt}_2)_2(\text{PPh}_3)_2]\text{BF}_4$	345	413	1518		
$[\text{Rh}(\text{mbt})_2(\text{PPh}_3)_2]\text{BF}_4$	319	408			
$[\text{Rh}(\text{pyS})_2(\text{PPh}_3)_2]\text{BF}_4$	344				
$[\text{Rh}(\text{tt})_2(\text{PPh}_3)_2]\text{BF}_4$	350				
$\text{Rh}(\text{S}_2\text{PPh}_2)_3(\text{PPh}_3)$	310	350		568	574
				562 ^b	
$\text{Rh}[\text{S}_2\text{P}(\text{EtO})_2]_3(\text{PPh}_3)_3$	290	413		638 ^b	
$\text{Rh}(\text{SCN})_3(\text{PPh}_3)_2$			2085		

^a Nujol or Vaseline mulls, cm^{-1} . mbt = 2-mercaptobenzthiazole;
 pyS = 2-mercaptopyridine; tt = toluene-3-thiol.

^b Bands due to P=S vibrations.

of the complex, suggests sulphur bonding of the ligand, and an octahedral ion as in (II) (Fig. I). The complex is air stable and slightly soluble in alcohols and ketones, but totally insoluble in non-polar solvents.

Both pyridine-2-thiol and toluene-3-thiol give complexes of stoichiometry similar to the above, and also show Rh-S stretching frequencies (Table I.4). The toluene-3-thiol complex clearly cannot have a chelated ligand, although the pyridine-2-thiol could be chelated as in the ruthenium complex $\text{Ru}(\text{pyS})_2(\text{PPh}_3)_2$ where the sulphur ligands are both bidentate.⁴⁵ Since the two complexes are very similar, and since square rhodium(III) complexes are so far unknown, it is conceivable that the reason why the thiolato-ligands act as unidentate groups bonding through only the sulphur atoms, is that there is some degree of additional coordination from the BF_4^- anion. This is the case with the previously described fluoroborate salt $\text{Rh}(\text{PPh}_3)_3\text{BF}_4$, and conductivities of the thiolates in nitromethane or nitrobenzene (10^{-2} to 10^{-4}M) suggests that both species are weak electrolytes. This implies ion-pair formation or some degree of coordination of BF_4^- .

Complexes of other stoichiometry.

Neutral rhodium(III) complexes of stoichiometry $\text{Rh}(\text{L})_3(\text{PPh}_3)_n$ (where $n = 1, 2$ or 3) have been obtained from Rh_2^{4+} , triphenylphosphine and an excess of the ligand L in methanol. When diphenylphosphorodithioic acid ($\text{Ph}_2\text{PS}_2\text{H}$) or its sodium salt is used, $n = 1$, and the octahedral complex $\text{Rh}(\text{S}_2\text{PPh}_2)_3(\text{PPh}_3)$ (III), (Fig. I) is obtained as bright maroon coloured crystals. It is clear that unless the normal octahedral coordination of $\text{Rh}^{(\text{III})}$ is not to be exceeded, at least one of the ligands must bond through only one sulphur atom [cf. $\text{Rh}(\text{S}_2\text{CNMe}_2)_3(\text{PPh}_3)$]. Both the symmetric and assymmetric P-S vibrations appear in the i.r. spectrum (Table I.4), and in addition, the P=S stretch of the unidentate group occurs at 642 cm^{-1} . The complex may be also obtained in almost quantitative yield by treatment of the salt $\text{Rh}(\text{CO})(\text{PPh}_3)_3\text{BF}_4$ with excess of the free acid ($\text{Ph}_2\text{PS}_2\text{H}$), the red complex separating from solution after

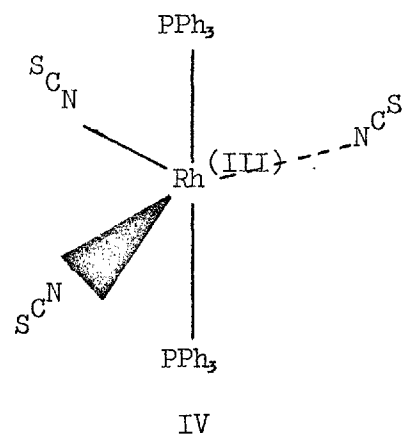
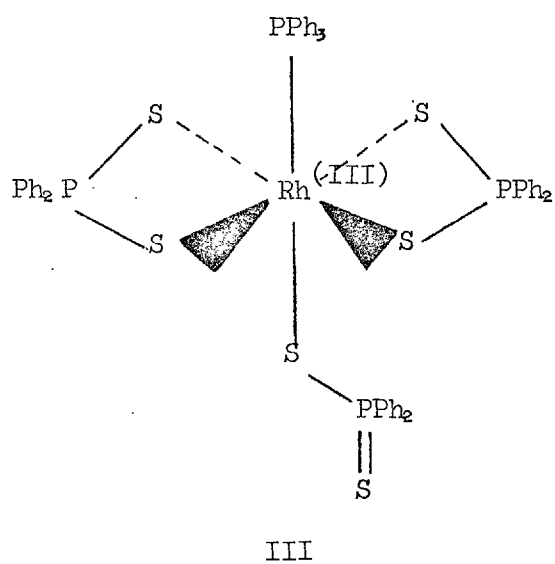
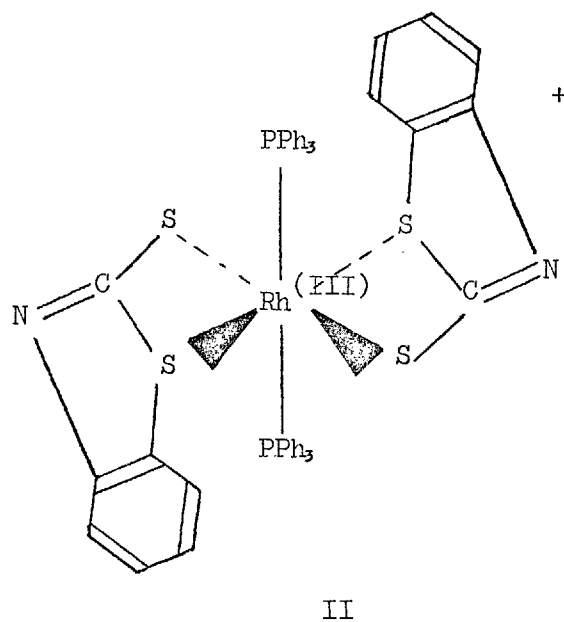
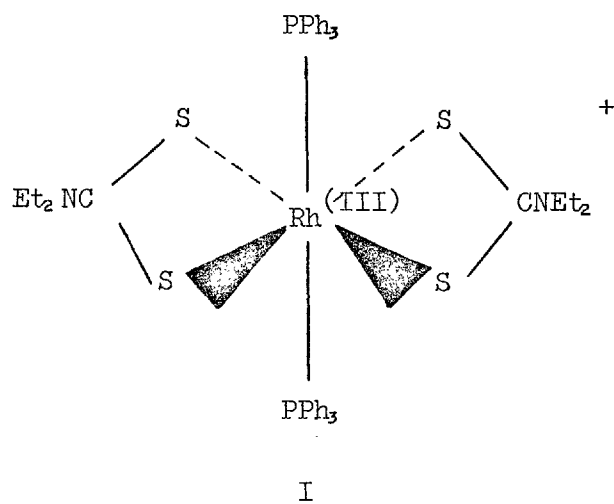


Fig. I.1

several hours. The complex is air stable indefinitely, and is only soluble in non-polar solvents such as toluene or benzene and chlorinated solvents such as chloroform or dichloromethane.

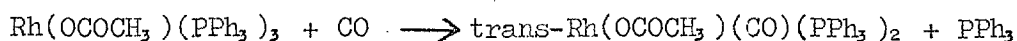
By contrast, presumably for steric and possibly electronic reasons, diethoxyphosphorodithioic acid $[(\text{EtO})_2\text{PS}_2\text{H}]$ (or its sodium salt), produces the octahedral complex $\text{Rh}[(\text{EtO})_2\text{PS}_2]_3(\text{PPh}_3)_3$, indicating that all three anionic sulphur ligands are unidentate ($\nu_{\text{PS}} 638 \text{ cm}^{-1}$).

Finally it is noted that methanolic Rh_2^{4+} , with triphenylphosphine and excess lithium thiocyanate gives the orange microcrystalline solid $\text{Rh}(\text{SCN})_3(\text{PPh}_3)_2$ (IV), (Fig. I). The SCN group appears to be N-bonded from its i.r. spectrum, and since the compound is monomeric in solution, it provides another example of five-co-ordinate $\text{Rh}^{(\text{III})}$, with two PPh_3 groups, which by analogy with $\text{Rh}(\text{CH}_3)(\text{I})_2(\text{PPh}_3)_2$ ⁴⁶ are probably trans. The complex is air stable, and very soluble in both polar and non-polar solvents giving stable yellow solutions.

C. Reactions of Rhodium Phosphine Complexes.

Relatively little work has been done on the chemistry of the rhodium(III) complexes, but the chemical reactions of the rhodium(I) carboxylates are worthy of mention in this chapter in view of their usefulness as homogeneous hydrogenation catalysts. Their reactions with carbon monoxide, straight chain aldehydes and molecular oxygen are described.

(a) With carbon monoxide: On bubbling carbon monoxide through a suspension of the acetate $\text{Rh}(\text{OCOCH}_3)_3(\text{PPh}_3)_3$ in benzene, the solid rapidly dissolves and a yellow solution is immediately obtained from which yellow crystals of the carbonyl complex $\text{Rh}(\text{OCOCH}_3)(\text{CO})(\text{PPh}_3)_2$ are obtained almost quantitatively. The i.r. spectrum shows the carbonyl band ν_{CO} at 1976 cm^{-1} (Table I.3), and the asymmetric and symmetric carboxylate frequencies occur at higher energy than in the parent acetate, consistent with a monodentate carboxylate grouping trans to CO

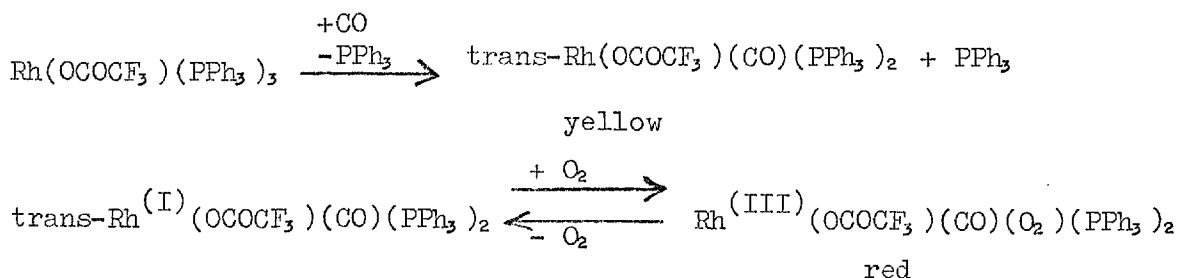


The strength of the binding of carbon monoxide is shown by the fact that the reaction is not reversed in solutions containing large quantities of triphenylphosphine, and even treatment of the carbonyl complex with molten PPh_3 shows no evolution of CO , the reaction being totally irreversible. The other carboxylates behave similarly giving stable yellow crystalline solids of general stoichiometry $\text{Rh}(\text{OCOR})(\text{CO})(\text{PPh}_3)_2$.

(b) With aldehydes: The carboxylates also abstract CO from aldehydes. Thus the acetate in benzene reacts quantitatively with n-heptaldehyde or valeraldehyde at 25°C , or extremely rapidly on warming to give the trans carbonyl derivative. This CO abstraction from aldehydes, or in effect the reverse of the hydroformylation reaction presumably follows the same reaction pathway as with $\text{RhCl}(\text{PPh}_3)_3$.⁴⁵

(c) With oxygen: The acetate and other carboxylates are unreactive towards oxygen in the solid state at atmospheric pressure and room temperature, but rapidly react when in solution. Thus a deoxygenated benzene solution of the acetate is yellow-orange but rapidly turns deep red in the presence of oxygen, and like the case of the chloride $\text{RhCl}(\text{PPh}_3)_3$, a red oxygen adduct may be isolated. However the exact stoichiometry and structure of the adduct is not at all certain, but an oxygen bridged dimeric species as was postulated⁴⁷ for the chloride seems feasible.

However the fluorocarboxylates are quite reactive towards oxygen, and unless thoroughly deoxygenated benzene solutions are used in the presence of CO , an oxygen adduct is formed reversibly:



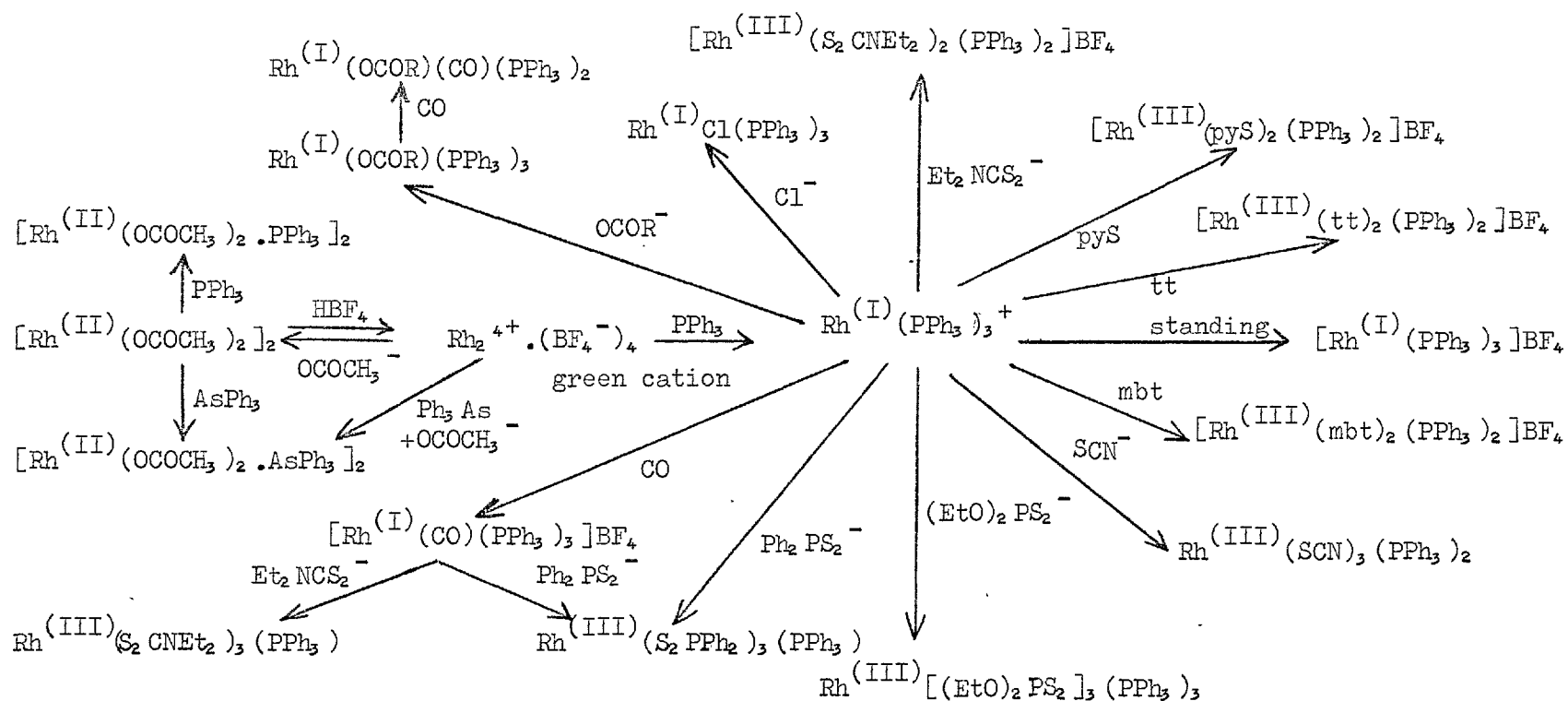
The orange-red adduct has a band at 833 cm^{-1} in the i.r. spectrum assignable as $\nu_{\text{O-O}}$, but there is no appreciable differences in the values of ν_{CO} of the yellow and red complexes (Table I.3). The weakness of the binding of O_2 is shown by the fact that on sweeping with CO, the oxygen is removed, and also by the fact that the oxygen adduct cannot be formed when more strongly coordinating solvents such as alcohols or ketones are used instead of benzene.

D. Conclusion

Reaction scheme I.1 indicates the usefulness of the dirhodium ion as a starting material for the synthesis of a range of rhodium(I), (II) and (III) complexes, some neutral and some cationic. It appears that in all cases, reduction by PPh_3 occurs first, and the rhodium(I) triphenylphosphine solvated cation is then capable of reacting in situ with the anionic ligand that may be present.

It has not been possible so far to isolate any rhodium(II) monomeric species from the green solution of Rh_2^{4+} , and presumably cleavage of the metal-metal bond with consequent reduction to rhodium(I) occurs in all cases after PPh_3 has been added. Only in the case of the addition of AsPh_3 and acetate ion is a rhodium(II) species formed, and this is dimeric, presumably arising from a reversal of the initial protonation reaction with acetate, followed by adduct formation with the AsPh_3 groups.

The fact that Rh_2^{4+} may be reduced by triphenylphosphine to give a coordinatively unsaturated rhodium(I) species makes it potentially useful as a starting material for catalytic and other reactions where vacant coordination sites are essential for activity. It will be shown in Chapter 2 how this cation may serve as a template to which groups such as phosphines, hydrogen and reducible organic substrates such as alkenes and alkynes may be coordinated.



Scheme I.1.

tt = toluene-3-thiol

pyS = 2-mercaptopyridine

mbt = 2-mercaptobenzthiazole

CHAPTER 2

The Catalytic Hydrogenation of Unsaturated Organic Substrates by Rhodium catalysts

Introduction

It now seems probable that rhodium complexes containing tertiary phosphine ligands, provided the metal is in a low oxidation state and coordinatively unsaturated, may function as homogeneous hydrogenation catalysts for the reduction of multiple bonds in organic molecules. Chapter 2 is concerned with the catalysis by rhodium triphenylphosphine complexes, either cationic of stoichiometry $\text{Rh}(\text{PPh}_3)_n^+$ (where $n = 1, 2, 3$ etc.), or neutral carboxylates of the general type $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$.

The cation $\text{Rh}(\text{PPh}_3)_n^+ \text{S}$, ($\text{S} = \text{solvent}$) resulting from the $\text{Rh}_2^{4+}/\text{PPh}_3$ system functions as a homogeneous hydrogenation catalyst in pure methanol, and the kinetics are identical to those obtained when $\text{RhCl}(\text{PPh}_3)_3$ is used in benzene.²²

The cation may be used heterogeneously also, on cation exchange resins, and is also active for the catalytic hydroformylation of hexene, and the carbonylation of methanol.

In benzene it is shown that pre-dissociation of $\text{RhX}(\text{PPh}_3)_3$ complexes (where $\text{X} = \text{Cl}^-, \text{OCOR}^-$ etc.) does not occur, but oxidative-addition of molecular hydrogen followed by dissociation of a PPh_3 group is the predominant reaction giving rise to unsaturated species of the type $\text{RhX}(\text{H})_2(\text{PPh}_3)_2$, which then proceed to follow a catalytic pathway similar to that previously described.²²

The carboxylates of stoichiometry $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$ as catalysts are very similar kinetically to the chloride, except that the electronic and steric effects of the carboxylate group affects the nature of the complexes.

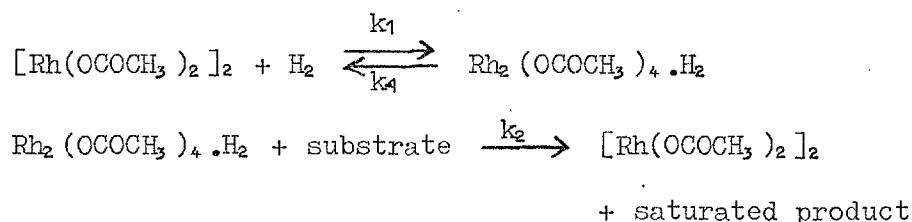
Although it has now been shown that alk-I-ene isomerisation takes place to a minute extent even when the chloride is used in pure benzene, the carboxylates will catalyse the isomerisation to such an extent that approximately equimolar quantities of alkane and isomer are produced.

Finally it is shown that the rates of hydrogenation of substrates by the carboxylates, and in fact the chloride, are greatly enhanced when polar solvents containing a non-oxidising, non-coordinating protonating acid is used.

A. The $\text{Rh}_2^{4+}/\text{PPh}_3$ System

The spectrochemical behaviour of rhodium(II) acetate $[\text{Rh}(\text{OCOCH}_3)_2]_2$ in a wide variety of solvents indicates rapid adduct formation, with the solvent occupying the terminal positions of the bridged complex.³² These coordinated solvent molecules appear to be extremely labile to substitution, being readily displaced upon the addition of ligands having a good donor strength.⁴⁸ It has now been shown that since rhodium(II) acetate may provide suitable vacant sites at the terminal positions of the metal-metal bond, it may function as a complex suitable for the activation of hydrogen and alkenes.⁴⁹

The following sequence of stages for the observed hydrogenation of simple alkenes and alkynes are consistent with the kinetic data and experimental observations.



Although the dimeric acetate is quite active for the catalytic hydrogenation of a number of unsaturated substrates in different solvents, it is not as active as the dimeric cation Rh_2^{4+} , resulting from the protonation of the acetate in methanol.

Catalytic Hydrogenation with Protonated solutions

The green solution of Rh_2^{4+} in methanol (obtained by protonation of rhodium(II) acetate with 40% aq. HBF_4 , (i.e. $\text{H}^+:\text{OAc}^-$ of ca. 1.2:1), in the absence of other ligands shows no activity as a hydrogenation catalyst, nor is there any evidence for the interaction with molecular hydrogen, except at elevated temperatures ($> \text{ca. } 50^\circ\text{C}$), when decomposition to rhodium metal occurs. However it was noted in Chapter 1 that triphenylphosphine cleaves the cation with reduction of the metal to rhodium(I), and a salt of stoichiometry $\text{Rh}(\text{PPh}_3)_3\text{BF}_4$ may be isolated. In solution, or prior to precipitation of the salt, there is little doubt that a solvated species, probably $\text{Rh}(\text{PPh}_3)_3^+\text{S}$ (S = solvent) exists, and in fact this species is extremely useful for the homogeneous hydrogenation of alkenes and alkynes.

It is not surprising that such a species should be catalytically active since most of the basic conditions for activity are fulfilled. These are: (a) low oxidation state of rhodium (oxidation state + 1), whereby oxidative addition of molecular hydrogen would give a $\text{Rh}^{(\text{III})}$ dihydrido species; (b) the species $\text{Rh}(\text{PPh}_3)_3^+$ is coordinatively unsaturated, that is, with only three phosphine ligands, the coordination sphere of rhodium may be expanded to six, giving a stable octahedral environment of the metal. Provided that the number of phosphines never exceeds three, then after oxidative addition of hydrogen has taken place, a vacant site (essential to catalytic activity) for substrate coordination, remains.

The catalyst solutions are made up as required from a stock solution of Rh_2^{4+} in methanol, and a methanolic solution of the phosphine is added via a syringe to the reaction vessel. The apparatus and general techniques are identical to those described previously. ²²

Table 2.1. gives some comparative data for the hydrogenation of different substrates under standard conditions using the $\text{Rh}_2^{4+}/\text{PPh}_3$ catalyst. However, the following points about the system ought to be noted.

Table 2.1

Relative rates of hydrogenation of substrates by the $\text{Rh}_2^{4+}/\text{PPh}_3$ catalyst. Metal concentration 2.5 mM; substrate concentration 1M; triphenylphosphine concentration 5 mM; temperature 25°C; solvent methanol.

Substrate	H_2 uptake/ml. min ⁻¹ at 450 mm.Hg
3-Methylbut-1-yne-3-ol	44.8
Hexa-1,5-diene	36.6
Hex-1-yne	34.2
Propargyl alcohol	17.6 ^a
Allyl phenyl ether	14.1
Hex-1-ene	10.9
Diethyl maleate	4.8
cis and trans-Hex-2-ene	3.3
cis-Hept-2-ene	2.2
Cyclohexene	1.1
Acetylenedicarboxylic acid	< 0.1 ^a
Cycloocta-1,5-diene	0.6 ^b

^a $[\text{PPh}_3] = 20 \text{ mM}$

^b $[\text{H}_2 \text{ pressure}] = 500 \text{ mm. Hg}$

- (a) The activity appears to be the highest with a Rh:PPh₃ ratio of 1:2. Since one PPh₃ is necessary for the initial reduction of rhodium(II) to rhodium(I), it seems that the active species is a cation of stoichiometry Rh^(I)(PPh₃)S⁺.
- (b) The catalytic activity is poisoned with O₂. Similar poisoning occurs with carbon monoxide.
- (c) The solution with Rh:PPh₃ ratios of 1:2 are normally red, but on addition of certain unsaturated substances, notably unsaturated carboxylic acids and alcohols, a colour change to greenish yellow occurs, presumably owing to the formation of complexes, possibly Rh^(II); no attempt has been made so far to study these interactions.
- (d) The stoichiometric protonation by HBF₄ in methanol of the benzoate complex [Rh(OBz)₂.PPh₃]₂ gives a brown-green solution which is also comparable in activity with the protonated acetate. Thus for hex-1-ene under the conditions of Table 2.1, but with [Rh] = 1.25 mM and with no added phosphine, the rate is 4.4 ml min⁻¹.

It can be seen from Table 2.1 that cyclic mono olefins and cyclic dienes are hydrogenated very slowly in contrast to the rapid rates for straight chain terminal olefins. Almost certainly this is attributed to difficulty of coordination of a cyclic ring to rhodium. Straight chain internal mono olefins such as cis-hept-2-ene and cis-pent-2-ene are reduced very slowly, and this again is attributed to difficulty in coordination.

Normally Rh:PPh₃ ratios of 1:2 are the most efficient, but for the hydrogenation of some substrates, notably propargyl alcohol, it was found that a ratio of 1:8 is necessary before any appreciable activity occurs, and presumably a cation of the type Rh(PPh₃)_n⁺ (where n = 2 or 3) is the active species involved.

Table 2.2 shows some hydrogenation data at 30°C for hex-1-ene, obtained using the Rh₂⁴⁺-PPh₃ catalyst under a range of catalytic conditions. These results indicate the dependence of the rate of hydrogenation as a function of [Rhodium], [hex-1-ene]

Table 2.2

Relative rates of hydrogenation of hex-1-ene at 30°C
with the $\text{Rh}_2^{4+}/\text{PPh}_3$ catalyst under a range of conditions.

[Rh]/mM	p(H ₂)/mm Hg	[Hex-1-ene]/M	[PPh ₃]/mM	10 ⁴ Rate/l.mol ⁻¹ s ⁻¹
1.0	400	1.0	2.0	1.10
2.0			4.0	2.19
3.0			6.0	2.96
4.0			8.0	3.48
2.0	400	0.5	4.0	1.23
		1.5		2.98
		2.0		3.38
		3.0		3.52
2.0	150	1.0	4.0	1.62
	200			1.66
	300			1.80
	350			1.88

The figures show how the rate of hydrogenation of hex-1-ene varies with (a) [Rh] concentration; (b) hexene concentration and (c) H₂ pressure. A ratio of Rh:PPh₃ of 1:2 is used throughout

and H_2 pressure.

(a) Dependence on the Catalyst concentration.

Fig. 2.1 shows the variation of the rate on the concentration of catalyst. The rate is linearly dependent on the concentration of rhodium up to values of ca. 3 mM, and the rate then levels off sharply at concentrations $>$ ca. 3.5 mM. Since the catalytic species is infinitely soluble in methanol, this break cannot be due to a maximum solubility limit. The apparent higher rates at low concentrations suggests a concentration dependent change from one active species to a less active one. Although there is no evidence to substantiate it, it is conceivable that at high rhodium concentrations, dimerisation or reassociation of the acetate ligands is occurring, which would account for a considerable reduction in the catalytic rate. However up to values of rhodium of 3 mM, the concentration dependence is consistent with a rate expression of the form

$$R = k[Rh(PPh_3)^+S] \text{ where } S = \text{solvent}$$

(b) Dependence on Hex-I-ene concentration

The rate is linearly dependent on the hex-I-ene concentration. A plot of the reciprocal of the rate ($l.mol.^{-1}S^{-1}$), against the reciprocal of the alkene concentration is linear with a positive intercept of the y axis. (Fig. 2.2).

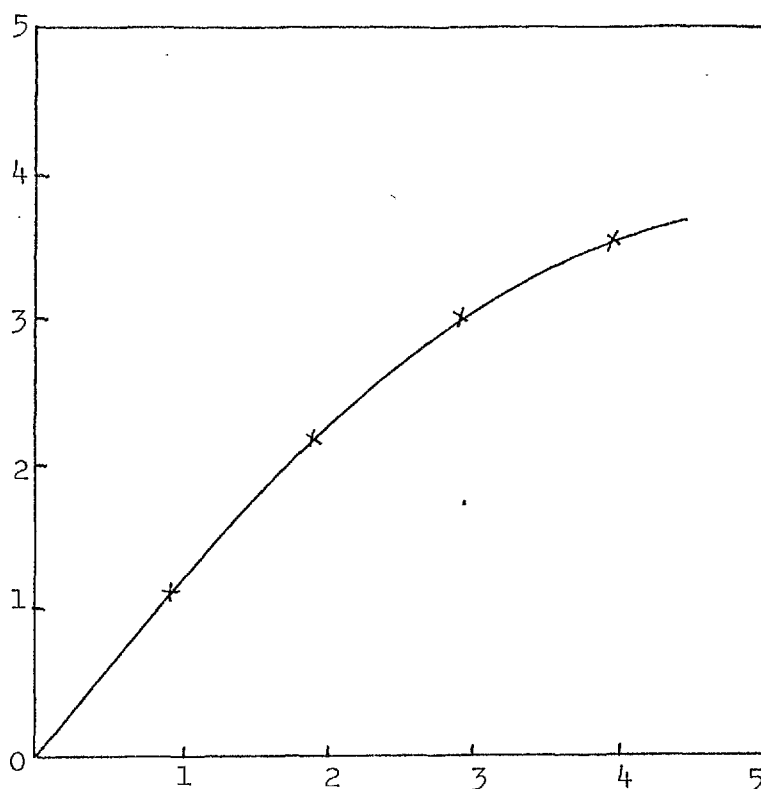
Hence $\frac{1}{R} = x (1/S) + y$ where x and y are constants. The reciprocal of the intercept gives the maximum possible rate of catalysis under the specified conditions.

(c) Dependence on the pressure of H_2

Fig. 2.3 (a and b) show how the rate of hydrogenation of hex-I-ene varies with the pressure of hydrogen. Assuming Henry's Law, then $R = \alpha p$ (the concentration of H_2 in the homogeneous media being proportional to the pressure). At low concentrations of catalyst and substrate, and at high pressures of H_2 (ca. $> 35 \text{ cm}^{-1}$), the rate appears to be approximately first order dependent in the pressure of H_2 , (a).

Fig. 2.1

$$-\frac{d[\text{Hex-I-ene}]}{dt} \quad (10^4 / \text{mol.}^{-1} \text{s}^{-1})$$

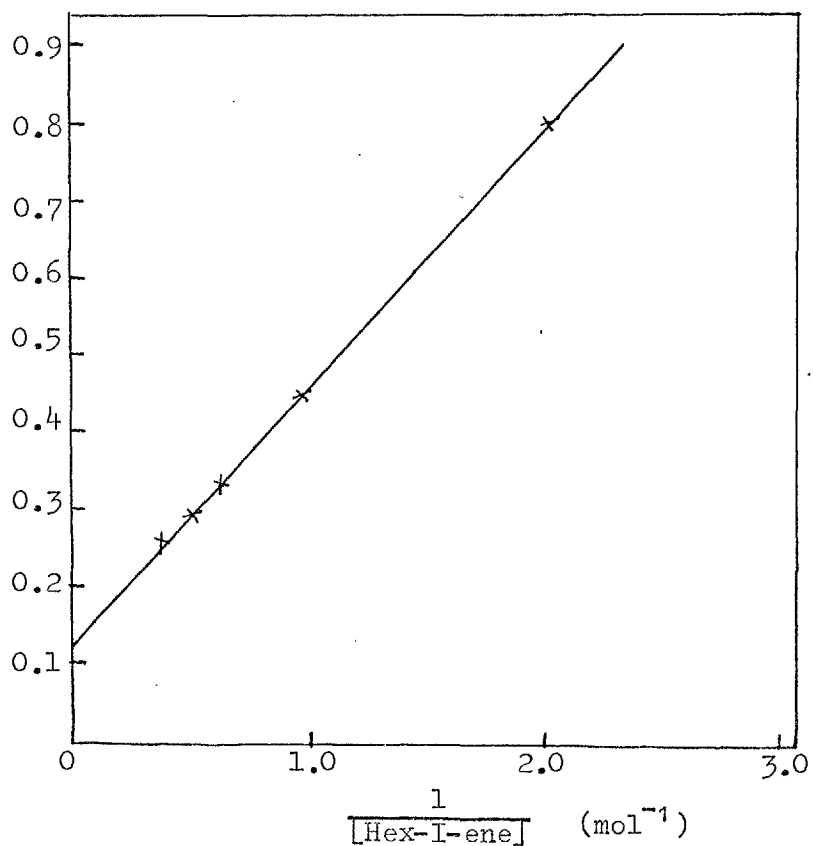


[Rhodium Concentration] (mM)

Rate of consumption of hex-I-ene as a function of the concentration of $\text{Rh}_2^{4+}/\text{PPh}_3$ catalyst.

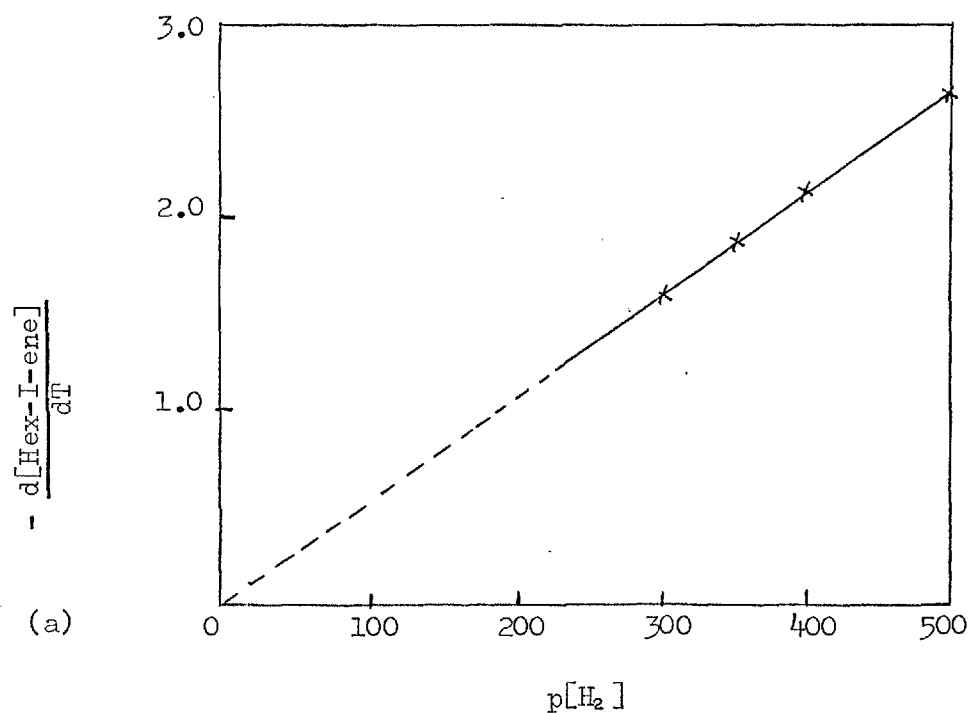
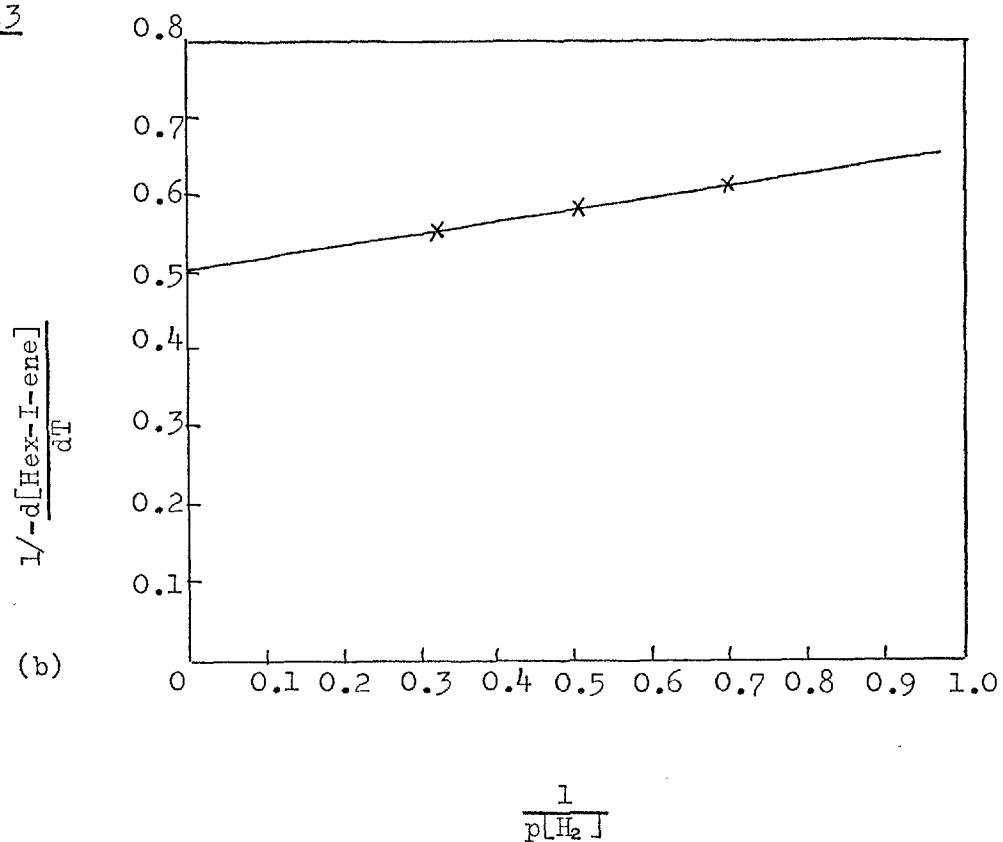
Fig. 2.2

$$1 / -\frac{d[\text{Hex-I-ene}]}{dt} \times 10^4 \quad (\text{mol.}^{-1} \text{s}^{-1})$$



Variation of rate with concentration of hex-I-ene, using the $\text{Rh}_2^{4+}/\text{PPh}_3$ catalyst.

Fig. 2.3



Variation of rate with the pressure of hydrogen:

(a) At high pressures (> 300 mm)

(b) At lower pressures (< 300 mm)

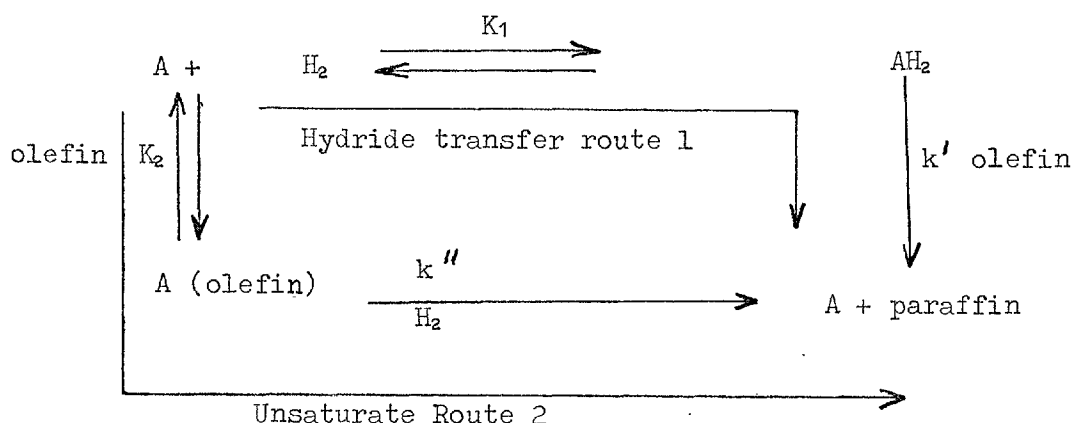
However at lower pressures, the plot of the reciprocal of the rate against the reciprocal of the gas pressure is linear, and a relationship of the type

$$\frac{1}{R} = \frac{1}{p} \alpha + \beta \text{ (where } \alpha \text{ and } \beta \text{ are constants) holds (b).}$$

Thus, depending on whether the pressure of H_2 is above or below ca. 35 cm^{-1} , the rate expression $R = \alpha p$ or $\frac{1}{R} = \frac{1}{p} \alpha + \beta$ becomes valid.

Although at very low concentrations of rhodium and hex-1-ene, the observed rates show approximately a first order dependence on each of these concentration variables, the rate dependence deviates markedly from linearity at the higher concentrations. This seems to suggest that there are a number of complex equilibria involved, with the possibility of dimeric species being formed as noted above.

The mechanism for the actual catalytic pathway doubtless follows an analogous route to that of $RhCl(PPh_3)_3$ (see later). Thus we have two possible routes, the Unsaturate (olefin activation) Route 2, or the Hydrogen Activation Route 1.



Since the red Rh_2^{4+}/PPh_3 solution reacts with molecular H_2 , but shows no activity with alkenes in the absence of H_2 (nor has it been possible so far to synthesize or characterise any olefin complexes), it seems reasonable to disregard the Unsaturate Route 2, and consider the Hydride Transfer Route 1.

If K_1 and K_2 are the equilibrium constants for the activation of hydrogen and alkene respectively, p is the concentration of H_2 in solution (assuming low pressures) and $[S]$ and $[A]$ are substrate and catalyst concentrations respectively, then:

$$\text{Rate} = - \frac{d[S]}{dt} = \frac{(K_1 k' + K_2 k'') p [S] [A]}{1 + K_1 p + K_2 [S]}$$

Assuming that the substrate is not activated until hydrogen addition to the complex has been achieved, then it may be assumed that $k'' = 0$, whereupon the rate expression reduces to:-

$$- \frac{dS}{dt} = \frac{K_1 k' p [S] [A]}{1 + K_1 p + K_2 [S]}$$

It is evident that the dependence of the rate of catalysis as a function of the concentration of catalyst, the concentration of substrate and the pressure of hydrogen, fits the rate expression satisfactorily.

The expression is valid for the linear first order relation between the rate and the catalyst concentration, except that for a small amount of dimerisation or reassociation of the catalyst, the rate expression approximates to

$$\text{Rate} = k[A] - k'[A]^2 \text{ where } k \gg k'$$

The rate equation may be rearranged to take the form

$$\frac{1}{R} = \frac{1 + K_2 [S]}{K_1 k' [S] [A]} \left(\frac{1}{p} \right) + \frac{1}{k' [S] [A]}, \text{ whereupon}$$

the plot of $\frac{1}{R}$ vs $\frac{1}{p}$ (where p is the hydrogen pressure) is shown to be linear, with the constants α and β being equal to

$$\frac{1 + K_2 [S]}{K_1 k' [S] [A]} \text{ and } \frac{1}{k' [S] [A]} \text{ respectively}$$

Finally, we have seen that the plot of $\frac{1}{R}$ vs $\frac{1}{S}$ (where S is the concentration of alkene) is linear, with a positive intercept on the y axis. Rearrangement of the rate expression to the

form $\frac{1}{R} = \frac{1}{[S]} \frac{1 + K_1 p}{K_1 k' p [A]} + \frac{K_2}{K_1 k' p [A]}$ gives the values

of the constants x and y to be $\frac{1 + K_1 p}{K_1 k' p [A]}$ and $\frac{K_2}{K_1 k' p [A]}$

respectively, whereupon the ratio $\frac{x}{y} = \frac{1 + K_1 p}{K_2}$

Other Catalytic Reactions by the Rh_2^{4+} - PPh_3 system

The red phosphine containing solutions of Rh_2^{4+} are readily and completely absorbed on cation exchange resins, and such a resin prepared by treating the green resin (containing Rh_2^{4+}) with a methanol solution of triphenylphosphine is also active as a heterogeneous catalyst. Under the conditions of Table 2.1 about 15 ml of resin, holding rhodium equivalent to a 10 mM solution gives a rate of hydrogenation for hex-1-ene of ca. 1 ml min⁻¹.

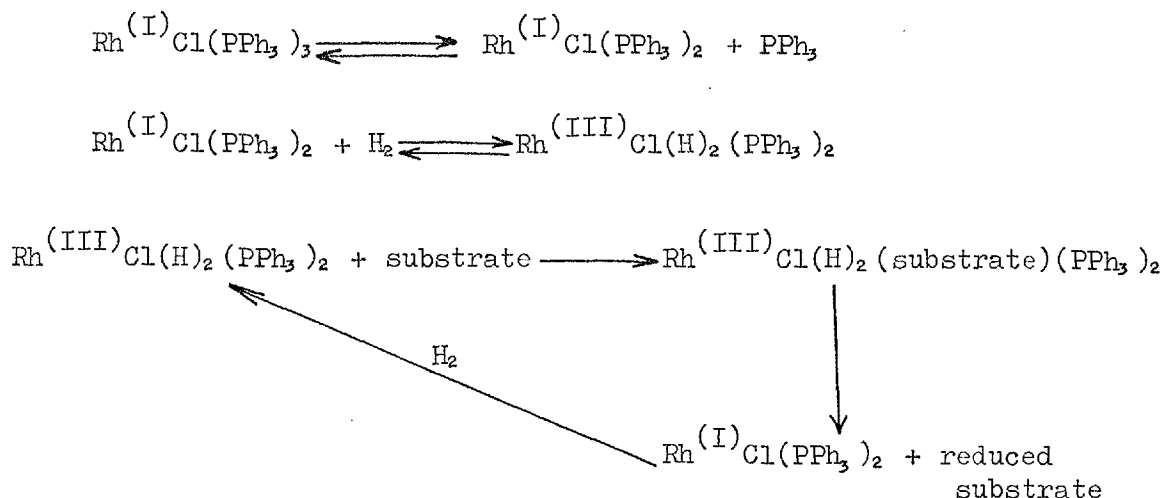
It may also be noted that the solutions with a ratio of Rh: PPh_3 of 1:2 are weakly active for the hydroformylation of hex-1-ene to heptanal at 35°C ($H_2:CO = 1:1$, at a total pressure of 450 mm Hg). A ratio of 1:2 is also effective for the carbonylation of methanol to acetic acid and methyl acetate; with 0.02M - Rh_2^{4+} solution (5.0 ml), and methanol (45.0 ml), the reaction occurs at 100°C and 25 atmos. CO pressure.

B. Carboxylatotris(triphenylphosphine)rhodium(I) complexes as catalysts

(a) Comparison with Chlorotris(triphenylphosphine)rhodium(I).

It has been previously noted ²² that square planar $Rh^{(I)}$ containing phosphine ligands may function as hydrogenation catalysts provided the coordinated phosphines may be displaced. It was originally suggested that $RhCl(PPh_3)_3$ dissociated a PPh_3 group in pure benzene and that the bisphosphine species $RhCl(PPh_3)_2$ had available sites for (i) activation of molecular hydrogen, and (ii) coordination of the unsaturated substrate.

The mechanism for catalytic hydrogenation of alkenes and alkynes was suggested to proceed according to the stoichiometry:



It seems reasonable to suppose therefore that the carboxylates of stoichiometry $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$ or indeed any species of the general type $\text{RhX}(\text{PPh}_3)_3$, may operate as homogeneous hydrogenation catalysts by an analogous pathway, although the activities would be largely dependent on the steric and electronic effects of the anionic ligand X^- .

Reaction with hydrogen. On exposure of an orange benzene solution of the acetate $\text{Rh}(\text{OCOCH}_3)(\text{PPh}_3)_3$ to H_2 , a colour change to yellow occurs rapidly and a hydride is formed reversibly in solution. However owing to the exceedingly low solubility of the carboxylates over the chloride, it has not been possible so far to obtain any good n.m.r. spectra to characterise any hydrides in the hydrogen saturated solutions (although a broad high field line at τ 29 is obtained), even using saturated solutions of the longer chain carboxylates (which are considerably more soluble) under a pressure of H_2 . The concentrated benzene solutions of the butyrate and caproate deposit dimeric species in minutes, thus making it impossible to obtain a high concentration of monomer in solution.

Molecular Weight measurements.

Osmometric molecular weight determinations, e.g. for the acetate in benzene under N_2 suggested that dissociation is

extensive. Since the values in dichloromethane were normal i.e. in the range 950-1050, this suggests that even using the best possible precautions to remove traces of oxygen, the use of benzene as solvent, in which O_2 is extremely soluble, is to be regarded with suspicion. During these studies, two other groups⁵⁰ stimulated by the apparent discrepancy between ^{31}P n.m.r. spectra, which suggested no dissociation of $RhCl(PPh_3)_3$, and osmometric data which did, have made cryoscopic studies under rigorous O_2 free conditions and confirm that there is indeed no dissociation.

These molecular weights have now been checked for the chloride and some of the carboxylates in benzene by a cryoscopic method using a slightly modified apparatus to that described by Shriver,⁵¹ which allows the total exclusion of air. The solid was weighed out into a side limb of the apparatus which may be rotated, and the solid thus tipped into the cell. Benzene was thoroughly deoxygenated under vacuum, cooled, melted and condensed into the cryoscopy cell attached to a high vacuum line. Determinations made on freshly prepared orange solutions of $RhCl(PPh_3)_3$ in benzene ranging from 2.35×10^{-3} to $2.80 \times 10^{-3} M$ under pure nitrogen gave molecular weights of 950 ± 10 (calculated 925). The solutions were found to be stable for several hours but, the slow formation of the halide bridged dimer $Rh_2Cl_2(PPh_3)_4$ ²² with loss of tri-phenylphosphine overnight, led to values of ca. 440 - 480.

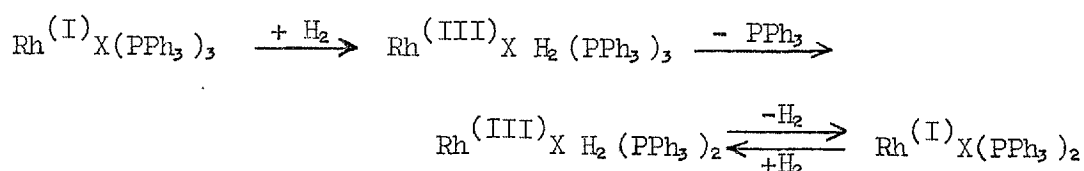
On evacuating a freshly prepared and measured solution and filling the cell with H_2 , the solution immediately turned pale yellow due to the formation of the dihydrido species,²² and the apparent molecular weight fell to 460 ± 10 . Removal of H_2 by evacuation reformed the orange solution, but this now had also molecular weight values of 460 ± 10 . Similar experiments by admission of oxygen to the benzene solution of the chloride were in agreement with previous findings,^{50b} and gave values of ca. 450.

Molecular weights for the acetate, propionate and α -halogeno-substituted carboxylato complexes under O_2 free conditions

are normal, but also show that pronounced dissociation is promoted by H_2 or O_2 . Since acetone or dimethylformamide solutions of the carboxylates (even in the presence of O_2) are non-conducting, it seems reasonable that dissociation of a PPh_3 group is occurring.

It may be concluded therefore that all molecular weights of air-sensitive compounds such as $RhX(PPh_3)_3$, determined by osmometers must be regarded with suspicion. Hence it follows that oxidative addition of molecular O_2 , and indeed of other molecules such as H_2 , HCl , CH_3I etc. promotes the dissociation. That is, the resulting octahedral tris(triphenylphosphine)-rhodium(III) species are evidently unstable, readily losing triphenylphosphine to give five coordinate complexes. This fact has already been confirmed for the addition of CH_3I to $RhCl(PPh_3)_3$, which gives a five coordinate complex whose structure has been determined.⁴⁶

It has been shown that if the added molecule can be readily removed like hydrogen, then at least in dilute solution, reassociation of triphenylphosphine does not occur and formally three coordinate solvated bisphosphine species are formed. Hence where $X = Cl, OCOR$ etc. we have:



It has been clearly shown⁵² that for the most effective hydrogenation, the ratio of $Rh:PPh_3$ is 1:2, and at high PPh_3 concentrations, the reaction is inhibited, evidently due to reassociation and consequent formation of the trisphosphine species. The fact that $RhX(PPh_3)_3$ compounds are not dissociated in solution as originally suggested²² does not alter the kinetic and mechanistic treatment, other than to require that dissociation is a property of the rhodium(III) species formed, after oxidative addition of hydrogen has taken place.

Alkene Hydrogenations

The carboxylates have been studied using the same procedure as before.^{22,52} However, in view of the known sensitivity to oxygen, some of the original catalytic experiments using $\text{RhCl}(\text{PPh}_3)_3$ in benzene were repeated with even more stringent precautions to remove traces of oxygen than those originally used, including for example distillation of benzene into the reaction flask in vacuo. No differences between current and previous runs were observed. In benzene at 25°C , 1 mmol l^{-1} catalyst concentration, 1 mol l^{-1} alkene concentration, the rate of H_2 uptake at 40 cm^{-1} H_2 pressure for hex-1-ene and cyclohexene, were 9.45 and 4.13 ml min^{-1} at s.t.p. compared to values of 9.47 and 4.20 ml min^{-1} obtained in an analogous way to that obtained previously.²²

It may be noted that both here and in previous studies, the catalyst solutions were stirred under hydrogen for several minutes before the addition of alkene, and that rates were measured after a short period of rapid stirring until steady state conditions were obtained. Under such conditions, complete oxidative dissociation has doubtless occurred, as shown by cryoscopy, so that it is unlikely that O_2 affects the maximum rate of catalysis for a given set of conditions as has been claimed.^{47,53}

It is perhaps of interest to note that numerous studies extending the original work²² have been made, but the precautions taken by other workers to purify the hydrogen or nitrogen used and to remove traces of O_2 or peroxides from solvents or substrates have not always been rigorous, nor have the reaction systems been high vacuum ones. Some of the results ought therefore to be regarded as suspect until repeated under stringent conditions.

The carboxylate system resembles that of the chloride in that the hydrogenated solutions are yellow-orange, and if stirring in of hydrogen is stopped in solutions containing large quantities of alkene, the colour becomes red. However the red colouration is formed more slowly than when the chloride is used, suggesting that formation of the alkene complex $\text{Rh}(\text{OCOR})(\text{alkene})(\text{PPh}_3)_2$

with loss of H_2 is much slower. Since there is no evidence that the carboxylates react with alkenes or alkynes in the absence of H_2 , it would appear that hydrogen activation followed by alkene addition is the predominant pathway for the catalytic mechanism. We have already seen that this hydride route is the predominant one for the $Rh_2^{4+} - PPh_3$ system and that initial alkene activation is minimal.

The kinetics for the chloride and carboxylates are similar; in dilute solution the rate of hydrogenation for straight chain terminal alkenes is approximately linearly first order dependent on the concentration of catalyst. A plot of rate vs rhodium concentration, and the reciprocal of the rate vs the reciprocal of alkene concentration are thus straight lines with zero and positive intercept on the y axis respectively.

Table 2.3 gives some representative data comparing the activity of the acetate and chloride in benzene for different organic substrates. It can be seen that the acetate is less than 25% as effective as the chloride for hex-1-ene and hex-1-yne, but is less than 2.5% as effective towards cyclohexene. Presumably the steric effect of the monodentate acetate is of importance here, and so evidently the steric or other factors involved allow some potentially useful selective reductions. Although most platinum metal homogeneous hydrogenation catalysts will not generally reduce internal alkenes and conjugated dienes effectively, it can be seen from the Table that cycloocta-1,3-diene is hydrogenated very rapidly in contrast to the negligible rate for the non-conjugated 1,5 isomer. On addition of cycloocta-1,5-diene to the catalyst solution under H_2 , an immediate yellow colouration is obtained, and no appreciable reduction is observed. Addition of hex-1-ene (a reducible substrate) to this diene containing solution shows no activity, and it therefore seems that a 1,5 diene complex has been formed in solution. This was also noted when $RhCl(PPh_3)_3$ was used as catalyst.

Table 2.3

Comparative rates of hydrogenation of substrates using acetato and chlorotris(triphenylphosphine)rhodium(I) complexes.^a

Substrate	Uptake of H ₂ in ml.min ⁻¹ at S.T.P.	
	Rh(OCOCH ₃)(PPh ₃) ₃	RhCl(PPh ₃) ₃
Hex-I-ene	4.5	21.2
Pent-I-ene	3.2	20.4
Hex-I-yne	9.5	21.2
Cyclooctene	< 0.1	
Cyclohexene	< 0.1	9.3
Cyclopentene	2.1	
Cycloocta-1,3-diene	3.1	< 0.1
Cycloocta-1,5-diene	< 0.1	< 0.1

^a Catalyst concentration 1 mM; substrate concentration 1 M in benzene. Temperature 25°C. Rates measured at 40 cm. H₂ pressure.

Table 2.4

Relative rates of hydrogenation of hex-I-ene at 25°C and 40°C using tris(triphenylphosphine)rhodium(I) complexes.^a

Compound	Rate of H ₂ uptake in ml.min ⁻¹ at S.T.P.	
	25°C	40°C
RhCl(PPh ₃) ₃	21.2	> 100
Rh(OCOCH ₃)(PPh ₃) ₃	4.5	16.8
Rh(OCOC ₂ H ₅)(PPh ₃) ₃	3.7	11.3
Rh(OCOCH ₂ Cl)(PPh ₃) ₃	< 0.1	16.1
Rh(OCOCCLF ₂)(PPh ₃) ₃	< 0.1	11.5
Rh(OCOCF ₃)(PPh ₃) ₃	< 0.1	11.7
Rh(OCOC ₂ F ₅)(PPh ₃) ₃	< 0.1	12.1
Rh(OCOPh)(PPh ₃) ₃	< 0.1	< 0.1

^a Catalyst concentration 1 mM in benzene; hex-I-ene concentration 1 M; H₂ pressure 40 cm⁻¹.

Although it has not been possible to isolate these olefin complexes from solution, it seems reasonable that since sterically cycloocta-1,3-diene cannot act as a chelate ligand to rhodium forming two synergic bonds, coordination of one double bond is occurring. G.l.c. analysis of the hydrocarbon mixture after 1h showed considerable quantities of cyclooctene, but virtually no cyclooctane. This is consistent with the data in Table 2.3, which shows that with the exception of cyclopentene, cyclic mono olefins are not hydrogenated by this catalyst.

The nature of the carboxylate group. Evidently this has no profound effect on the rate of hex-I-ene hydrogenation, but the rate for the more electron-withdrawing carboxylato complexes are negligible at 25° compared to 40°C. Table 2.4 shows some data for the hydrogenation of hex-I-ene at 25° and 40°C using different carboxylates. It is evident that at 40°C all the species are effective catalysts, but at 25° the complexes with α -halogeno substituted carboxylate groups are quite inert. Although it is difficult to measure the solution infrared spectrum of the carboxylates at 25°C, due to such a low solubility, it is conceivable that at this temperature some chelation of the carboxylato group is occurring, thus blocking the vacant site essential to catalytic activity. However the solution i.r. at 40° shows the carboxylates as monodentate groups (as in the solid) and as the Table shows, they are all effective catalysts.

Alkene Isomerisations Although negligible amounts of isomerised alkene was detected in early studies using $\text{RhCl}(\text{PPh}_3)_3$ as catalyst, the reaction times involved were only a few minutes and less than 1% of the total alkene was hydrogenated. Although some isomerisation has been shown to occur in ethanol-benzene solutions,⁵⁴ the present work confirms that in pure benzene, some isomerisation takes place. For a 1 mM catalyst concentration, 1M hex-I-ene at 25° and at ca. 1 atmos. H_2 , the hydrocarbon composition after 1h was approximately: hex-I-ene, 52.9%; n-hexane, 41.5%; cis + trans-hex-2-ene, 5-6%. Hence a two-step transfer of hydrogen,

involving an alkyl intermediate, evidently proceeds in pure benzene solution as suggested for the benzene-ethanol solution of Biemann and Jung.⁵⁴ Studies on the acetate $\text{Rh}(\text{OCOCH}_3)(\text{PPh}_3)_3$ have shown that considerable isomerisation of the alkene is occurring. Thus after 24h using the acetate 1 mM; hex-1-ene 1M at 25°C and ca. 1 atmos. H_2 , the composition of the product mixture was hex-1-ene, 23.5%; n-hexane, 38.2%; trans-hex-2-ene, 22.6% and cis-hex-2-ene, 15.7%. The trifluoroacetate under similar conditions but after ca. 1h gave a similar hydrocarbon mixture but with an additional 1-2% of hex-3-ene.

Although in the case of the chloride, the predominant reaction is reduction of the double bond of the substrate, with the carboxylates, the rates of hydrogenation and isomerisation are comparable. It therefore appears that the inefficiency of the carboxylates as hydrogenation catalysts over the chloride, lies in the fact that these complexes are capable of catalysing the migration of the double bond of an alk-1-ene to alk-2-ene almost as efficiently as catalysing its reduction.

We have seen that the fluorocarboxylates are more efficient isomerisation catalysts than the unsubstituted complexes and this is verified from the results in Table 2.4, which shows that at 40°C, the more electron withdrawing carboxylates are less efficient hydrogenation catalysts. The reason is quite clear if we assume that these species are isomerising the alk-1-ene to alk-2-ene or alk-3-ene (which is not hydrogenated) faster than it has time to catalyse its reduction to the corresponding alkane.

Effect of Co-solvents. The addition of polar solvents such as alcohols or ketones to the benzene solution of the carboxylates under H_2 enhances the rate of catalysis quite considerably, although there appears to be no correlation between the increased activity with the dielectric constant of the co-solvent. The solubility of hydrogen is not significantly different in the different solvent mixtures, and in fact using pure alcohols, the carboxylates dissolve under H_2 giving catalytic solutions, although slow

abstraction of CO occurs leading to deactivation of the catalyst. (It should be noted that the carboxylates are virtually insoluble in alcohols, although under H_2 they dissolve rapidly giving yellow solutions).

Thus in pure benzene at $40^\circ C$, the acetate 1 mM hydrogenates hex-I-ene 1 M at a rate of $16.8 \text{ ml. min}^{-1}$, compared to a rate of ca. $20.0 \text{ ml. min}^{-1}$ at S.T.P. in pure methanol. There is little doubt that in polar solvents such as alcohols, in the presence of H_2 some ionic dissociation is occurring (as shown by a slight increase in the solution conductivity with time). Thus in alcoholic media a small proportion of a cation of the type $Rh(PPh_3)_3^+$ may be present, which after oxidative addition of molecular hydrogen and dissociation, would lead to an extremely coordinatively unsaturated rhodium complex of higher activity. This may be the reason why such co-solvents like methanol, provided not too strongly coordinating, may enhance the rate of catalysis.

(b) Catalysis in the presence of acids

The carboxylates although quite active as hydrogenation catalysts in pure benzene are even more active when dispersed in alcoholic media in the presence of a protonating acid.

Thus the acetate 1 mM, at $25^\circ C$ and $40 \text{ cm}^{-1} H_2$ pressure will hydrogenate hex-I-ene 1 M at a rate of 4.5 ml. min^{-1} at S.T.P. compared to a rate of ca. $10.0 \text{ ml. min}^{-1}$ when in methanol containing 40% aq. HBF_4 (with a ratio of $H^+ : OCOCH_3^-$ of ca. 4:1). It may be noted that other acids beside fluoroboric may be used as the protonating source, and in fact using trifluoromethylsulphonic acid, rates of ca. $12-14 \text{ ml. min}^{-1}$ are obtained using the above conditions.

The acidity also affects the rate of activity of chlorotris-(triphenylphosphine)rhodium(I). Thus the chloride 1 mM in pure benzene with hex-I-ene 1 M at $25^\circ C$ and $40 \text{ cm}^{-1} H_2$ pressure gives a rate of H_2 uptake of ca. $21.0 \text{ ml. min}^{-1}$, compared to a

value of ca. 30.0 ml. min⁻¹ at S.T.P. in a fluoroboric acid - methanol solvent (with H⁺:Cl⁻ of ca. 4:1).

Although relatively little work has been done in this field, it does seem that protonation of the anionic ligand of these complexes is occurring, with the consequent formation of rhodium(I) cations. We shall see in Chapter 4 how catalytically active ruthenium complexes may be made exceedingly active by protonation and formation of active cations in solution.

C. Discussion

In this Chapter the Rh₂⁴⁺/PPh₃ system and the rhodium(I) carboxylates have been discussed as hydrogenation catalysts.

It should be finally noted that coordinative unsaturation is a vital factor for activity in these systems. It has been shown that protonation of the complexes of the type RhX(PPh₃)₃ with consequent displacement of the anionic ligand X⁻ into solution, together with PPh₃, provides further coordinative unsaturation, and as we saw, the rates of catalytic activity were enhanced considerably.

CHAPTER 3

Triphenylphosphine Carboxylato complexes of Ruthenium

Introduction

The first study of ruthenium carboxylate compounds was by Mond,⁵⁵ who obtained a series of complexes formulated as binuclear species, by refluxing a hydrated ruthenium(III, IV) oxide with the acid. However much of the early work has been questioned,⁵⁶ and has not proved reproducible.⁵⁷

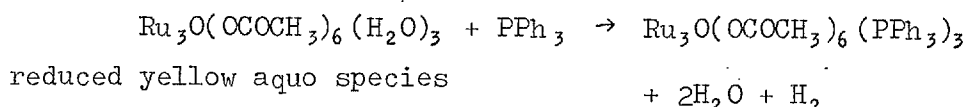
By the interaction of commercial hydrated ruthenium trichloride with acetic acid/acetic anhydride mixtures, the complex $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$ was obtained;⁵⁷ other carboxylates were similarly synthesised. The complex has equivalent ruthenium atoms in the mean oxidation state of +2.5, or as originally formulated, II, III.

The above reaction gives not only $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$ but in addition, a green solution that was originally considered^{38b} to contain a neutral dimeric species. By changing the reaction conditions somewhat, namely the interaction of ruthenium trichloride, acetic acid and sodium acetate in ethanol, a green impure material was isolated. This was shown to form adducts with triphenylphosphine and pyridine which were formulated as adducts of the dimer, by analogy with the well known adducts of the dimeric tetra-bridged acetates of Cr(II),³¹ Cu(II),³⁰ Mo(II) and Rh(II).²⁷ In further studies of these materials, especially electrochemical studies, it has been shown⁵⁸ that the green acetate could not be the dimer $\text{Ru}_2(\text{OCOCH}_3)_4$, but must be a ruthenium(III) complex of the acetate, oxo-centred type of stoichiometry $[\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{H}_2\text{O})_3]\text{OCOCH}_3$ and that the triphenylphosphine and pyridine adducts have the formulations $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ and $[\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{py})_3]\text{OCOCH}_3$ respectively.

It has been shown⁵⁸ that the oxo-centred trinuclear ruthenium carboxylates of the type $[\text{Ru}_3\text{O}(\text{OCOR})_6\text{L}_3]^+$, where $\text{L}=\text{H}_2\text{O}$ or py, undergo successive one and two-electron reductions to form the species $\text{Ru}_3\text{O}(\text{OCOR})_6\text{L}_3$ and $\text{Ru}_3(\text{OCOR})_6\text{L}_3$ respectively, and that the first reduction is electrochemically reversible.

It should be noted that additional proof of the preservation of the trinuclear structure in the reduced yellow aquo species, is the reaction under rigorously oxygen-free conditions or even under hydrogen, with triphenylphosphine to form the green adduct $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$.

It would appear that the reaction involves the reduction of one coordinated water molecule per complex, the oxygen atom being incorporated into the triangular structure, i.e.



where intermediates such as $\text{Ru}_3(\text{OCOCH}_3)_6(\text{H}_2\text{O})_2(\text{PPh}_3)$ must be presumed capable of reducing water.

The crystal structure of the green triphenylphosphine complex $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ confirms the oxo-centred formulation,⁵⁹ and this complex in which the ruthenium atoms are in the mean oxidation state $2\frac{2}{3}$ (or II, III, III), also undergoes a two electron reduction, but unlike the reduced aquo and pyridine species, the yellow solutions so obtained cannot be re-oxidised with molecular oxygen or pyridine-N-oxide back to the trimer. The two electron reduction gives a yellow species, probably $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)$, and the reduction in methanol containing fluoroboric acid gives a yellow solution also, which on addition of at least one extra mole of PPh_3 per Ru atom, acts as a homogeneous hydrogenation catalyst for alkenes and dienes. Such catalytic phenomena will be discussed in Chapter 4.

By protonation of the hydridoacetate $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ ²⁴ or the dihydride complex $\text{Ru}(\text{H})_2(\text{PPh}_3)_4$ ⁶⁰ with fluoroboric, trifluoromethylsulphonic or *p*-toluene-sulphonic acid in methanol, similar catalytically active solutions are obtained.

The reduced yellow active solution (obtained from the phosphine adduct above), or from the protonated hydridoacetate, are oxidised by air in the presence of acetate ion to a new type of oxo-bridged ruthenium(III) complex $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$, which is an intermediate in the preparation of $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ from commercial hydrated ruthenium trichloride.

The diacetate $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_2$ has been prepared and the reduction of the tetra- μ -acetato complex $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$ studied.

In Chapter 3, the electrochemical reduction of the adduct $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$, the protonation of the hydridoacetate $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ and the preparation and properties of the new complexes $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$ and $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_2$ are described. A number of analogues with other carboxylate groups are also described, and a detailed study of the preparation of catalytically active species for hydrogenation reactions is noted.

A. Reduction of Tris(triphenylphosphine)hexa- μ -acetato- μ_3 -oxotriruthenium(II, III, III.).

Although the complex $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ is not reduced in methanol by hydrogen at 2 atmos. pressure in the presence of a PtO_2 catalyst at 25°C , reduction does occur at 40°C after ca. 3h, and a yellow solution is obtained. The complex is also reduced in methanolic solution containing fluoroboric acid as previously reported.^{38b} However the reduction is most easily effected electrochemically as discussed below.

The polarogram of $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ in acetone with sodium perchlorate as a supporting electrolyte shows a reduction wave at -1.05v vs the aqueous S.C.E., and macrocoulometry at controlled potential gives n values of 2.01 and 1.88, the n -butyrate complex having a value of $n = 2.01$. It should be noted that the yellow solutions obtained by electrochemical reduction have electronic absorption spectra similar to those formed by hydrogen reduction in methanol (Table 3.1).

The polarogram of $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ in methanol containing fluoroboric acid shows only irregular reduction waves attributed to the catalytic reduction of hydrogen ions, thus making the coulometric determination of the reduction of ruthenium impossible. However the electrolysis of acid solutions at potential of -0.6v vs silver wire gives the yellow solution, and on addition of triphenylphosphine to give a ratio of $\text{Ru}:\text{PPh}_3$ of at least 1:2, the solutions (as we shall see later) are extremely active catalysts for the hydrogenation of unsaturated organic substrates. The extra triphenylphosphine was commonly added before the reduction, and reproducibility was obtained

Table 3.1

Electronic Spectra of Ruthenium Phosphine Carboxylato Complexes

Complex	$\lambda_{nm}(\epsilon)$
$Ru_3O(OCOCH_3)_6(PPh_3)_3$ ^a	974(6280); ca. 790sh; ca. 410sh; 347(11900)
$Ru_3O(OCOC_2H_5)_6(PPh_3)_3$	974(6630); ca. 790sh; ca. 410sh; 343(12000)
$Ru_3O(OCOnPr)_6(PPh_3)_3$	974(5060); ca. 790sh; ca. 410sh; 338(12200)
$Ru_2O(OCOCH_3)_4(PPh_3)_2$ ^a	559(5300); 372(4300); 313(12700)
$Ru_2O(OCOC_2H_5)_4(PPh_3)_2$	555(5780); 371(4990); 310(16100)
$Ru_2O(OCOnPr)_4(PPh_3)_2$	557(5840); 371(5240); 312(15900)
$Ru_2O(OCOPh)_4(PPh_3)_2$	563(5590); ca. 384sh(ca. 5900); 291(23300)
$Ru_2O(OCOCH_3)_4[(pFC_6H_4)_3P]_2$	560(5500); 396(4920); 310(13000)
Electrochemically reduced solutions: $(H^+/OCOCH_3^- = 4)$; $(PPh_3/Ru = 3)$	
$Ru_3O(OCOCH_3)_6(PPh_3)_3$	440(800); 353(3200)
$Ru_2O(OCOCH_3)_4(PPh_3)_2$	440(880); 353(3800)
Protonated solutions: ^b $(H^+/OCOCH_3^- = 4)$; $(PPh_3/Ru = 3)$ of $RuH(OCOCH_3)(PPh_3)_3$ orange-red solution yellow solution	543(1080); 460(1500); 341(11600) 560(340); ca. 460sh(ca. 1000)
Protonated solutions: ^b $(H^+/Ru = 4)$; $(PPh_3/Ru = 4)$ yellow forms of $RuH(OCOCH_3)(PPh_3)_3$ $Ru(H)_2(PPh_3)_4$	459(230); 353(1800) 459(270); 350(1800)

^a Spectra measured in chloroform. ^b Spectra measured in methanol.

when methanolic solutions of equal concentrations of $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$, PPh_3 and HBF_4 (42% aq.) were electrolysed at 40°C and at -0.6V as above, until the same quantity of electricity had passed in each case. The current-time curves so obtained were reproducible to within experimental error.

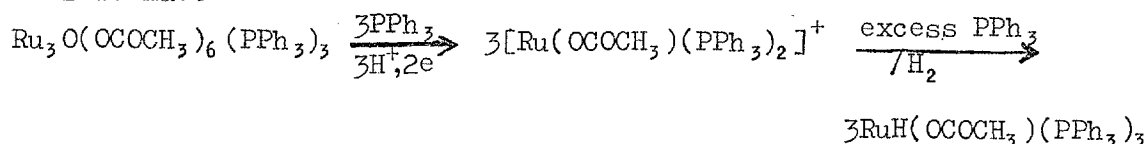
By contrast with the oxidation of the reduced yellow aquo and pyridine complexes,⁵⁸ no reoxidation to the initial starting material occurs when the air sensitive yellow solutions are exposed to air. The acidified solution are also air sensitive, rapidly turning green, then black and finally after ca. 2 days, purple. The purple colouration as we shall see later, is due to the formation of a new ruthenium(III) complex of formulation $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$.

It has not been possible so far to isolate any analysable solid from the air-sensitive yellow solutions but the n value clearly indicates reduction to ruthenium(II), and the failure to reoxidise indicates cleavage, to species probably of the type $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_x \cdot x\text{MeOH}$. There is no high field line in the n.m.r. spectrum to indicate a Ru-H bond.

The acid-containing solutions evidently contain cationic species, and the addition of at least one extra mole of excess triphenylphosphine is required to obtain catalytically active solutions. It therefor seems reasonable that the acid solutions probably contain the ions $[\text{Ru}(\text{PPh}_3)_n \cdot x\text{MeOH}]^{2+}$ where $n \geq 2$.

Evidence for the disruption of the trinuclear structure of the phosphine adduct upon reduction, and protonation with acid is provided by the fact that such yellow solutions upon treatment with excess triphenylphosphine under hydrogen gives the monomeric hydridoacetate $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$. It is important that the initial ratios of $\text{Ru}:\text{HBF}_4:\text{PPh}_3$ are 1:1:2 before the solution is reduced, since by using such concentrations there is only sufficient acid to protonate half of the acetate ligands, since the initial ratio of $\text{Ru}:\text{OCOCH}_3^-$ is 1:2.

Thus we have:-

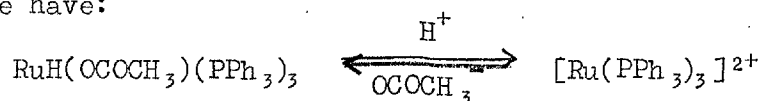


It should be noted that if excess fluoroboric acid is used, very low yields of the hydridoacetate are obtained, but cationic species of the type $[\text{Ru}(\text{PPh}_3)_n \cdot x\text{MeOH}]^{2+}$ are formed as noted above. Hence it would seem reasonable to propose that the cationic solutions ought to be obtained by directly protonating the hydridoacetate.

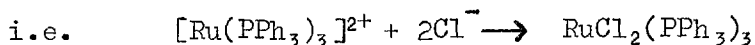
B. Protonation of Hydridoacetatotris(triphenylphosphine)ruthenium(II) and Dihydridotetrakis(triphenylphosphine)ruthenium(II).

Hydridoacetatotris(triphenylphosphine)ruthenium(II): The complex $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ was originally prepared²⁴ by the slow (24h) interaction of dichlorotris(triphenylphosphine)ruthenium(II) with two moles of sodium acetate in refluxing methanol under hydrogen. Using a large excess (10 moles) of acetate in refluxing methanol or ethanol under nitrogen, high yields (ca. 83%) of $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ are obtained in ca. 30 min., the hydride presumably arising from the alcoholic solvent. The complex may be obtained directly from ruthenium trichloride trihydrate by refluxing this with an excess of triphenylphosphine and sodium acetate in methanol for several hours under nitrogen, the purple ruthenium(III) complex noted above being an intermediate in this synthesis.

When the hydridoacetate in methanol is treated with fluoroboric acid (42% aq.) under N_2 , the solid rapidly dissolves on warming and a deep orange-red air-sensitive solution is obtained. N.m.r. study of the solution shows that the hydride is lost and acetic acid is formed, and solution electrophoresis shows that the red species is cationic, this being consistent with protonation of the hydride and acetate ligands of the complex giving a solvated cation of probable stoichiometry $[\text{Ru}(\text{PPh}_3)_3]^{2+}$, the solution being diamagnetic as expected. As we shall see in Chapter 4, the red cationic solutions obtained by protonation using fluoroboric, trifluoromethylsulphonic or p-toluene sulphonic acid are exceedingly active catalysts for the hydrogenation of alkenes and dienes. The fact that the above reaction is simply a protonation process is verified by addition of excess sodium acetate to the red cationic solution, whereupon precipitation of the hydridoacetate occurs after a few minutes refluxing. Thus we have:



Also treatment of the red solutions with excess chloride ion immediately gives the dichloride $\text{RuCl}_2(\text{PPh}_3)_3$, the solution turning deep maroon in colour.



However the isolation of pure red salts from the red cationic solutions have proved difficult due to the change to yellow noted below, but nevertheless orange red salts whose analysis indicates that they contain the cation $[\text{Ru}(\text{PPh}_3)_3]^{2+}$ have been isolated as fluoroborate or trifluoromethylsulphonate salts, when these acids respectively have been used as the protonating source.

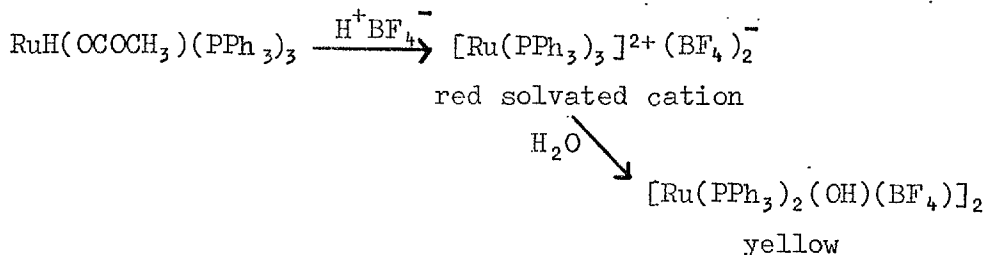
Unfortunately attempts to obtain ^{31}P n.m.r. spectra of the red solutions have failed due to the low concentrations. Using fluoroboric acid, the red species so obtained is stable for several hours under nitrogen but under hydrogen the decay is more rapid (ca. 15 min), the solution turning pale yellow in both cases. However with carbon monoxide or ethylene, the red solution immediately turns yellow but neither carbonyl nor ethylene complexes have been isolated, nor even characterised in solution. Instead, small amounts of formaldehyde and ethane were detected when the red solution, saturated with H_2 was exposed to the respective gases, and a crystalline fluoroborate salt isolated in both cases.

In all cases, when aq. HBF_4 has been used as the protonating acid in methanol, a yellow crystalline fluoroborate salt has been obtained from the yellow solutions, and the i.r. spectrum and elemental analysis supports a species of stoichiometry $[\text{Ru}(\text{PPh}_3)_2(\text{OH})(\text{BF}_4)]_2$, the dimeric complex being linked by hydroxy bridges. Conductivity measurements of the salt in nitromethane, using solutions varying in concentration from 10^{-2} to 10^{-4} M indicate that the species is a weak electrolyte,³⁹ implying some degree of covalence or association of the fluoroborate anions.

It is worthy of note that no such yellow species has been obtained so far when trifluoromethylsulphonic or p-toluene sulphonic acid has been used in methanol under identical conditions. The hydridoacetate under H_2 or N_2 very rapidly dissolves in both cases to give the red species, but only very slow conversion to the yellow species occurs, even under H_2 . This is presumably due to the lack of formation of hydroxy bridges in the anhydrous alcoholic

media.

Hence, when fluoroboric acid is used, we have:-



It may finally be noted that such a tris(triphenylphosphine) ruthenium cation $[\text{Ru}(\text{PPh}_3)_3]^+$ may be obtained by treatment of the dichloride $\text{RuCl}_2(\text{PPh}_3)_3$ with silver tetrafluoroborate in methanol, whereupon immediate precipitation of AgCl occurs, leaving an orange-red cationic solution whose electronic absorption spectra and catalytic activity are identical to those of the red solution obtained by protonation of the hydridoacetate above.

Dihydridotetrakis(triphenylphosphine)ruthenium(II): This complex has been known for some time,⁶⁰ and like the hydridoacetate above, is susceptible to protonation by acid in alcoholic solvents. The complex is only slightly soluble in methanol, but when dilute aqueous fluoroboric acid is added, the yellow solid rapidly dissolves giving an orange-red cationic solution as above. For a direct comparison with the protonation of the hydridoacetate, the dihydride with one mole of acetate added, and the hydridoacetate containing one extra mole of PPh_3 , is treated with aq. HBF_4 in methanol so the ratio $\text{H}^+:\text{OCOCH}_3^-$ is 4:1. Both solutions become red, and the cationic species have similar electronic absorption spectra (Table 3.1) and catalytic properties (see later) in both cases. Under such conditions the solutions (a) react with excess acetate ion to give $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$, (b) react with chloride ion to give $\text{RuCl}_2(\text{PPh}_3)_3$ and (c) decay to the yellow hydroxy bridged dimeric fluoroborate species with time.

Whether the cationic species obtained from $\text{Ru}(\text{H})_2(\text{PPh}_3)_4$ contains four triphenylphosphine groups, or whether PPh_3 dissociation is occurring, is difficult to ascertain, although as we shall see in Chapter 4, there is good reason to suppose that in the absence of added triphenylphosphine, the cationic species is one of stoichiometry $[\text{Ru}(\text{PPh}_3)_3]^{2+}$.

C. μ -oxobis[(triphenylphosphine)diacetatoruthenium(III)]

It has been noted earlier that reduced solutions of the phosphine adduct $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ on prolonged exposure to air turn purple. Similarly the orange-red solutions obtained by dissolving $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ in acidified methanol give on addition of excess acetate ion followed by air oxidation purple species, and in fact treatment of the hydridoacetate (in the absence of acid) with excess acetate in air also gives purple species. It may also be mentioned that when commercial ruthenium trichloride trihydrate is refluxed in methanol containing triphenylphosphine and sodium acetate trihydrate, purple solutions are quite rapidly (ca. 5 min) obtained. Prolonged heating of the mixture produces the hydridoacetate as noted earlier, the formation of which is further enhanced by increasing the proportions of triphenylphosphine.

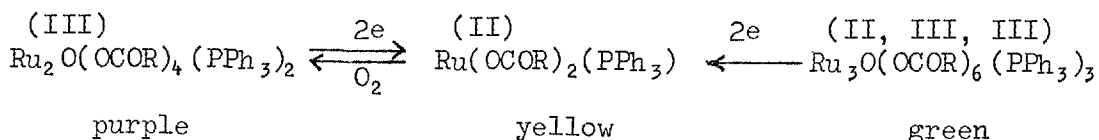
In all cases purple acicula crystals of the acetate and other carboxylates may be obtained on slow evaporation of the methanolic purple solutions and analyse for the solvates $\text{Ru}_2\text{O}(\text{OCOR})_4(\text{PPh}_3)_2 \cdot \text{CH}_3\text{OH}$, the methanol being readily detected in the i.r. or n.m.r. spectra. The n-butyrate may be obtained solvent free on crystallisation from benzene.

The complexes are quite soluble in most organic solvents and the n-butyrate in methanol and benzene has a molecular weight corresponding to the unit $\text{Ru}_2\text{O}(\text{OCOnBu})_4(\text{PPh}_3)_2$. All the complexes are insoluble in alkanes and water; the solutions in alcoholic solvents are stable indefinitely to oxygen, but in aromatic solvents, decomposition to brown unidentified species occurs slowly. Analogous triphenylphosphine complexes of the propionate, trifluoroacetate, benzoate, and the acetatotris(*p*-fluorophenyl)phosphine complex were also prepared (Table 3.1) and all except the trifluoroacetate were isolated in crystalline form.

Confirmation of the oxidation state as Ru(III) comes from polarographic reduction of the triphenylphosphine acetate in acetone using sodium perchlorate as a supporting electrolyte. There is a well defined reduction wave at -0.99v vs S.C.E. and coulometric reduction at -1.3v gives an n value of 1.99 per Ru_2O unit. The reduced solutions are yellow and appear to be identical with those

of the yellow solutions formed by reduction of $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ discussed earlier.

Thus we have:-



The electrochemical reduction of the purple acetate species in methanol containing fluoroboric acid and triphenylphosphine also gives a yellow solution whose electronic absorption spectra, polarogram and behaviour as a hydrogenation catalyst for hex-1-ene is similar to the solution obtained from $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$.

The complex $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$ is diamagnetic both in the solid state (Gouy Method) and in solution (Evans Method), and shows no e.s.r. signal in the solid or in solution. The infra-red spectrum of the purple complexes shows no band in the region $800\text{--}940\text{cm}^{-1}$ characteristic of a linear M-O-M system, since known ruthenium complexes with a linear Ru-O-Ru grouping, all of which contain $\text{Ru}^{(\text{IV})}$ however, absorb at $860\text{--}870\text{cm}^{-1}$.

It is not unreasonable therefor to propose that the Ru-O-Ru group is bent. However it has been said that spin interaction is possible only in linear systems,⁶¹ but since spin-pairing occurs in the oxo-centred systems with $\text{Ru}^{(\text{II, III, III})}$, (6e per Ru), there seems no reason why it should not occur in a bent $\text{Ru}^{(\text{II})}\text{-O}_2\text{-Ru}^{(\text{II})}$ bridge (6e per Ru).

Whether the complex also has bridging carboxylate groups as in Fig 3.1, or whether both groups are chelated is not certain, as neither i.r. nor n.m.r. criteria can readily distinguish between these possibilities.

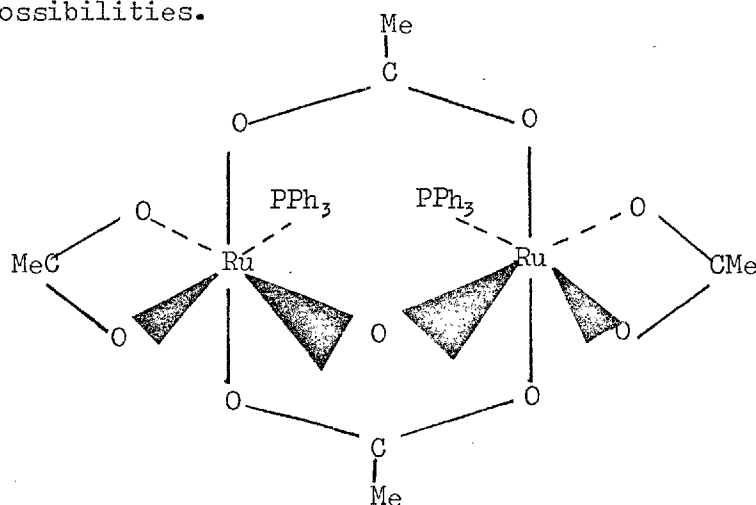


Fig 3.1

However, the n.m.r. spectrum of the acetate complex shows two methyl resonances (ratio 1:1) and this would be consistent with a structure as in Fig 3.1; the methanol of solvation commonly formed could occupy the fourth bridge position.

The n.m.r. spectrum of the propionate, n-butyrate and tris(*p*-fluorophenyl)phosphine complexes also show similar inequivalence of the carboxylates, the spectra at 60 and 100MHz indicating that this is a chemical shift effect and not due to long range coupling to the phosphorus nuclei.

D. Diacetatobis(triphenylphosphine)ruthenium(II).

It has been noted earlier that the hydridoacetate complex $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ is obtained via hydride abstraction from the solvent when the dichloride $\text{RuCl}_2(\text{PPh}_3)_3$ is refluxed with sodium acetate under N_2 . Since bistriphenylphosphine species appear to be involved in the chemistry above, it was of interest to attempt the synthesis of a monomeric bistriphenylphosphine ruthenium species.

The orange yellow diacetate complex $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_2$ is obtained by the interaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with sodium acetate in refluxing *t*-butanol (to prevent hydride abstraction) under N_2 .

The molecular weight is normal, and the n.m.r. spectrum shows only a single methyl resonance, and the structure is presumably as shown in Fig 3.2, where the acetate groups are chelated as in $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$.

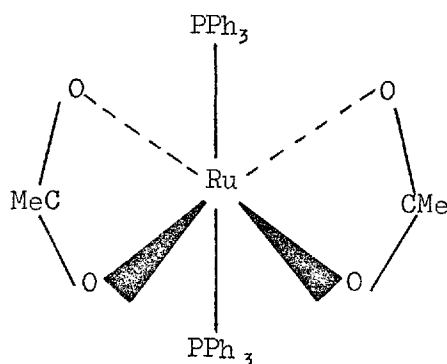
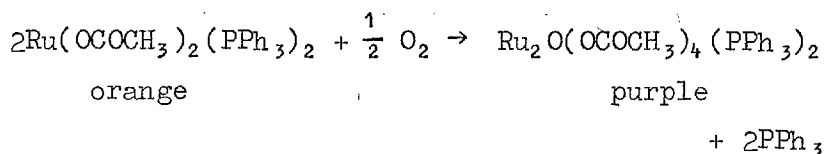


Fig 3.2

The complex is also susceptible to protonation by trifluoromethylsulphonic or fluoroboric acids to give catalytically active yellow-orange solutions in methanol. The methanolic solutions of the complex are stable for weeks under nitrogen but in air, oxidation to the μ -oxo species occurs slowly, i.e.



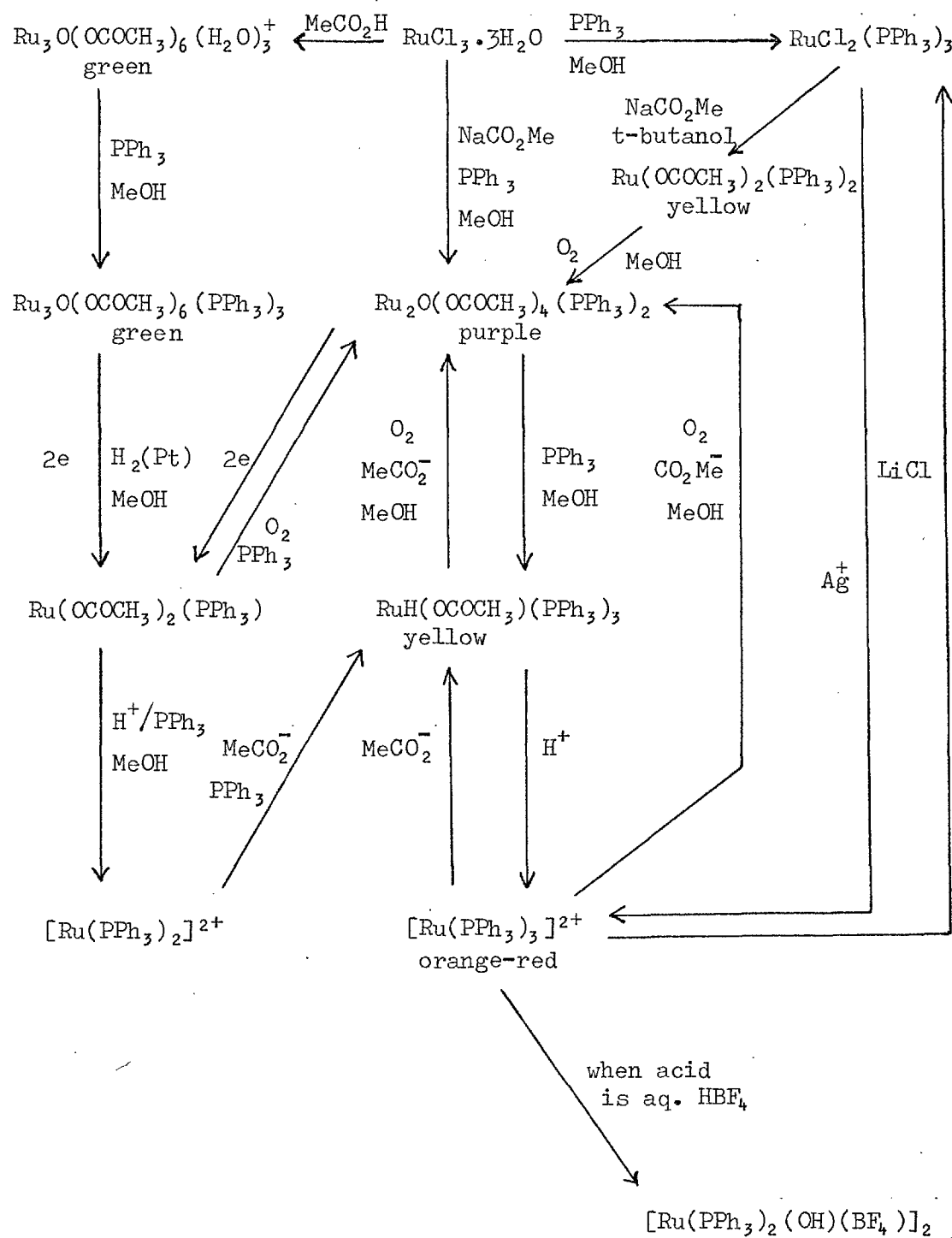
Scheme 3.1 sets out the relationship of the complexes and intermediate species discussed in sections A, B and C of this chapter.

E. Tetra- μ -acetatobis(triphenylphosphine)diruthenium(II).

On treatment of the paramagnetic complex $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$ ⁵⁷ for which the proposed tetra- μ -acetato structure has been confirmed⁶² by X-ray diffraction, with triphenylphosphine in methanol under nitrogen, a light brown precipitate is formed (ca. 24h). This may be separated into buff and yellow components. The latter has the stoichiometry $\text{Ru}(\text{OCOCH}_3)_2\text{PPh}_3$, but the solubility is too low for molecular weight determinations, as is also that of the corresponding n-butyrate.

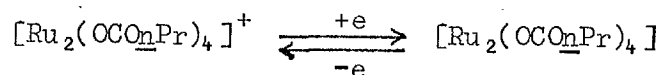
The polarograms of the complexes $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$, $[\text{Ru}_2(\text{OCOC}_2\text{H}_5)_4]\text{Cl}$ and $[\text{Ru}_2(\text{OCO}n\text{Pr})_4]\text{Cl}$ in methanol containing sodium perchlorate as a supporting electrolyte, all show oxidation and reduction waves of approximately equal height. For the n-butyrate, the reduction wave has $E_{1/2} = 0.09\text{v}$, and the oxidation wave has $E_{1/2} = +0.12\text{v}$ vs the aqueous S.C.E. The reduction waves of the acetate and propionate are obscured by maxima of the first kind, which are not suppressed by the addition of a surfactant (Triton X-100), but are at roughly the same potential as the n-butyrate. The oxidation waves are at $+0.14\text{v}$ (acetate) and $+0.08\text{v}$ (propionate) and coulometric reduction at the mercury pool at -0.5v gave n values of 0.99 (acetate), 1.03 (propionate) and 0.92 (n-butyrate).

Attempts to obtain the yellow species $[\text{Ru}(\text{OCOR})_2(\text{PPh}_3)]_n$ by reaction of the reduced solutions with triphenylphosphine were not successful.



Scheme 3.1

The polarogram of the electrochemically reduced solution of $[\text{Ru}_2(\text{OCO}\underline{n}\text{Pr})_4]\text{Cl}$ shows an oxidation wave at exactly the same half-wave potential as the original reduction wave, indicating a thermodynamically reversible reduction. This is clearly:



in which both species are expected to have coordinated methanol in the axial positions. The occurrence of maxima with the other two complexes prevent a similar comparison of potentials (in methanol) to be made. The oxidation waves at +0.08 to 0.12v undoubtedly arise from oxidation to ruthenium(III), but the waves are irregular and the oxidation appears to involve more than a simple electron transfer. The original preparation of the complex $[\text{Ru}_2(\text{OCOR})_4]\text{Cl}$ ⁵⁷ leads to appreciable formation of the trinuclear oxygen centred complex $[\text{Ru}_3\text{O}(\text{OCOR})_6\text{L}_3]^+$, the yield of the desired chloro-species frequently being less than 10%. It should be noted that the addition of anhydrous lithium chloride to the reaction mixture completely suppresses formation of the trinuclear species, the yield of $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$ being then ca. 80%. The yield of this complex is not affected by carrying out the reaction under oxygen, air or nitrogen. A similar yield was obtained with the propionate (under oxygen), but with the n-butyrate however it was necessary to use a nitrogen atmosphere, the yield then being ca. 38%.

F. Conclusion

Scheme 3.1 inter-relates the complexes that have been described in this Chapter. No matter what the starting material, air oxidation in the presence of excess triphenylphosphine and/or acetate ion gives the purple μ -oxo species $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$, which is shown to be an intermediate in the synthesis of the hydridoacetate complex $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ from ruthenium trichloride. The solvated cations $[\text{Ru}(\text{PPh}_3)_2]^{2+}$ and $[\text{Ru}(\text{PPh}_3)_3]^{2+}$ have been obtained by electrochemical reduction and/or protonation reactions of some of the complexes shown, and as we shall now see in Chapter 4, such cationic species may function as useful homogeneous hydrogenation catalysts for some unsaturated organic molecules.

CHAPTER 4

The Catalytic Hydrogenation of Unsaturated Organic Substrates by Cationic complexes of Ruthenium

Introduction

Neutral ruthenium triphenylphosphine complexes have been used in homogeneous hydrogenation reactions for quite some time, but relatively little work appears to have been done concerning cationic complexes.

Some early work³⁸ concerned protonation reactions of ruthenium complexes, especially the chloro species $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$ in methanol using aq. fluoroboric acid. Under such conditions, the chloroacetate is readily protonated to give a blue air-sensitive solution, turning first green and finally yellow-brown on exposure to air. The blue solution is readily and completely absorbed on cation-exchange resins, and the eluate can be shown to contain acetic acid. The electronic absorption spectrum of the aqueous protonated solution, $\lambda_{\text{max}} (\epsilon) 437(460), 537\text{sh}(180)$, is different from that of the aqueous solution of $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$, $423(750)$, although the nature of the blue cationic solution is not certain at present.

Although the blue solutions are not catalytically active under mild conditions, the addition of triphenylphosphine gives immediately a very active catalyst for the hydrogenation of alkenes and alkynes, (Table 4.1) without causing any initial colour change. Under hydrogen the blue solution becomes a more greenish blue and as hydrogenation proceeds, the solution becomes mauve.

However on treatment of $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$ in methanol with a stoichiometric amount of AgBF_4 , silver chloride is precipitated. After removal of silver chloride, the solution is bright red and on subsequent addition of a stoichiometric amount of HBF_4 , a deep red-brown solution is obtained. This solution is also catalytically active on addition of triphenylphosphine (Table 4.1). If silver nitrate however is used initially to remove Cl^- , the final red protonated phosphine-containing solution is not active; although not yet proved, the inactivation through formation of a nitrosyl complex

Table 4.1

Relative rates of hydrogenation of substrates by the ruthenium catalyst, obtained by protonation of $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$ under hydrogen. Metal concentration 2.5mM; substrate concentration 1M; triphenylphosphine concentration 5mM; temperature 25°C; solvent methanol.

Substrate	H_2 uptake/ml. min ⁻¹ at 450 mm. Hg.
3-Methylbut-1yn-3-ol	14.1
Hexa-1,5-diene	46.2
Allyl phenyl ether	1.3
Hex-1-ene	30.5 ^a
cis- and trans-Hex-2-ene	0.5

^a Red-brown chloride free solution with hex-1-ene gives a rate of ca. 30 ml. min⁻¹.

seems likely.

Since the catalytically active solutions appear to contain a cationic ruthenium-triphenylphosphine species, it was of interest to look at protonation reactions of other ruthenium complexes containing easily protonating ligands such as carboxylate groups.

In Chapter 4, the catalytically active species $[\text{Ru}(\text{PPh}_3)_n \cdot x\text{MeOH}]^{2+}$ where $n \geq 2$ is described, having been obtained from reduction and/or protonation of the complexes $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$, $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$, $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_2$, $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$ and $\text{Ru}(\text{H})_2(\text{PPh}_3)_4$, that have been already described in Chapter 3. The rates of hydrogenation for different organic substrates are noted, and a mechanism formulated on the basis of the results obtained.

A. Catalytic species obtained from:

- (a) Tris(triphenylphosphine)hexa- μ -acetato- μ_3 -oxotriruthenium (II, III, III).

We saw earlier that this complex in the presence of excess triphenylphosphine and fluoroboric acid, may be reduced by 2e to give a ruthenium(II) cation of stoichiometry $[\text{Ru}(\text{PPh}_3)_n \cdot x\text{MeOH}]^{2+}$.

Kinetic studies and gas uptake measurements on the homogeneous hydrogenation of hex-1-ene at 40°C using such cationic solutions suggests that the rate of catalysis is dependent on the acidity of the solution, as can be seen from the data given in Table 4.2. In view of the fact that the complex is only active when (a) reduced electrochemically, or under H_2 , or in the presence of a chemical reducing agent such as NaBH_4 , (b) treated with triphenylphosphine so the ratio of $\text{Ru}:\text{PPh}_3$ is at least 1:2 and (c) treated with fluoroboric acid so the ratio of $\text{H}^+:\text{OCOCH}_3^-$ is at least 1:1, suggests that the catalytically active species has the stoichiometry to that above, where $n \geq 2$.

Table 4.2 shows that the activity rises to a maximum when ratios of $\text{H}^+:\text{OCOCH}_3^-$ of 4:1 are used, but the rates are considerably lower when the acid concentration is increased. At high acid ratios, the protonation of Ru-H bonds does occur and presumably any activation of molecular hydrogen by such cationic species would be nullified by the presence of excess acid, thus decreasing the

catalytic rates.

G.l.c. analysis of the hydrocarbon mixture from hex-1-ene (using the catalyst with an acid:acetate ratio of 1:1) gave after 1h, unchanged hex-1-ene, 43%; n hexane, 55% and trans hex-2-ene, 2%. The hydrogenating mixture is yellow and shows no decay in activity with time. However admission of O₂ to the mixture turns the solution green and inhibits the reduction completely, but on deoxygenating and flushing with hydrogen several times, the yellow solution is restored and hydrogenation proceeds at a comparable rate of 8.6 ml min at 40cm⁻¹ pressure as before (Table 4.2). However after 3h, the final mixture contained unchanged hex-1-ene, 4%; n hexane, 93% and trans hex-2-ene, 3%.

Table 4.2. clearly indicates that provided the solutions are not too acidic, there is competition between the rate of hydrogenation of hex-1-ene and the rate of double bond isomerisation, as we saw was the case with the rhodium(I) carboxylates in Chapter 2.

(b) Hyridoacetatotris(triphenylphosphine)ruthenium(II).

This complex has been used as a hydrogenation catalyst in pure benzene and the kinetics previously discussed.²⁴ However it was noted²⁴ that the addition of alcohols to the benzene solution of the complex, could accelerate the rate of catalysis, and it will be shown here that in alcohols in the presence of a protonating acid, a totally different catalyst is obtained.

When the hydridoacetate $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ is dissolved in methanol under H₂ at 40°C, the final yellow solution is very sluggish towards the catalytic hydrogenation of alkenes, and the activity is completely inhibited on addition of acetic acid or sodium acetate. However if a trace of fluoroboric acid is added, the solution turns red and hydrogen uptake is observed with virtually no induction period, the red species being due to the formation of the solvated cation $[\text{Ru}(\text{PPh}_3)_3]^{2+}$ as we saw in Chapter 3.

In the presence of alkenes such as hex-1-ene, the orange-red protonated solutions turn yellow under H₂ and reduction of the double bond occurs with rates of H₂ uptake remarkably rapid for such dilute solutions used. The hydrogenating mixture, as in the previous case, is poisoned by admission of O₂, the solution turning pale green.

Table 4.2.

The effect of acidity on the rates of hydrogenation and isomerisation of hex-1-ene using species formed by the reduction of $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ as catalyst.

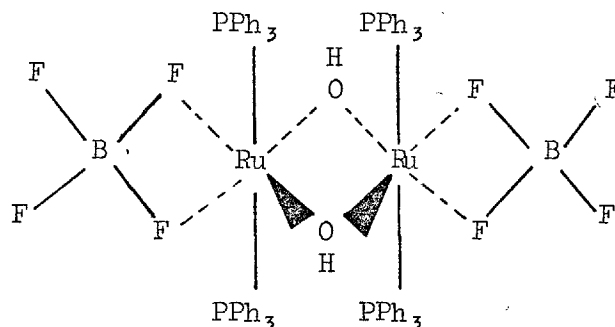
Concentration, 7.5×10^{-4} mol. ℓ^{-1} in $[\text{Ru}]$; hex-1-ene concentration 1 mol. ℓ^{-1} ; temperature 40°C ; H_2 pressure 40cm^{-1} ; solvent media, fluoroboric acid in methanol;

$\text{Ru}:\text{PPh}_3$ ratio, 1:2.

Ratio of $\text{H}^+:\text{OCOCH}_3^-$	Uptake of H_2 in ml. min^{-1} at S.T.P.	% of unchanged hex-1-ene	% of <u>n</u> hexane	% of <u>trans</u> hex-2-ene
1:1	8.6	43.0	55.0	2.0
2:1	17.0	31.0	68.0	<0.5
3:1	26.8	28.0	71.5	0.5
4:1	36.0	0.7	99.0	0.3
5:1	27.4	14.0	85.0	1.0
6:1	25.0			
8:1	22.1	23.0	75.0	2.0

However deoxygenation and re-saturation with H_2 restores the yellow solution and the activity to that prior to admission of O_2 .

It may be noted here that although the red species $[Ru(PPh_3)_3]^{2+}$ in the presence of fluoroboric acid appears to be catalytically active, prolonged stirring under H_2 in the absence of substrate gives the yellow species (as noted earlier), that shows no activity. Similarly the yellow solution obtained by treatment of the red cation with CO or C_2H_4 , on degassing and stirring under H_2 does not give catalytically active red solutions again. The yellow solutions as we saw earlier contain a hydroxy bridged dimer, with tetrafluoroborate coordinated to the metal. A probable structure is as shown below, where the ruthenium atoms are in an octahedral environment. The antisymmetric and symmetric



stretching vibrations of the metal-OH grouping occur at 845 and 540cm^{-1} in the i.r. spectrum, consistent with a chelating bridging arrangement as shown.⁶³ The metal thus appears to be coordinatively saturated and this is probably why such yellow solutions are catalytically inactive.

Other acids besides fluoroboric may be used as protonating agents, and p-toluene-sulphonic acid (monohydrate) for example gives catalytic species of almost identical activity and selectivity (Table 4.3). Sulphuric acid in methanol or acetone gives a species that is ca. 30% and 10% respectively as active as that when fluoroboric acid in methanol is used, suggesting that the rate of activity is strongly dependent on (a) the nature of the solvent and (b) the nature of the protonating acid, i.e. to its coordinating ability.

Table 4.3

Relative rates of hydrogenation of substrates by protonated ruthenium catalysts. Ruthenium concentration 7.5×10^{-4} M; substrate concentration 1M; solvent methanol; H_2 pressure 40cm^{-1} ; temperature 40°C ; protonating acid HBF_4 (ratio of $H^+ : OCOCH_3^- = 4:1$).

Uptake of H_2 in ml min^{-1} at S.T.P.

Substrate	Catalyst obtained from $RuH(OCOCH_3)(PPh_3)_3$ in		Catalyst obtained from $Ru_3O(OCOCH_3)_6(PPh_3)_3$ ^a
	$H^+ - CH_3OH$	Benzene	
Hex-1-ene	48.0, 49.1 ^b	15.1	36.0
Pent-1-ene	37.0, 38.8 ^b		30.7
<u>cis</u> -Hex-2-ene	<0.1, <0.1 ^b	<0.1	<0.1
<u>cis</u> -Pent-2-ene	<0.1, <0.1 ^b	<0.1	<0.1
Cyclooctene	31.9, 30.6 ^b	<0.1	28.0
Cycloocta-1,3-diene	<0.1	<0.1	<0.1
Cycloocta-1,5-diene	58.8	<0.1	51.5
Bicyclo[2.2.1]hepta-2,4-diene	1.0	<0.1	0.7

^a Ratio of $Ru:PPh_3 = 1:2$, and reduced electrochemically.

^b p-toluene sulphonic acid was used as the protonating acid in methanol.

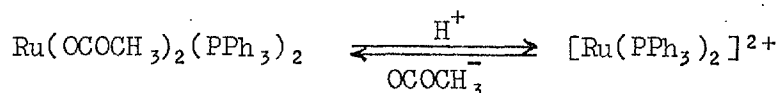
A comparison between the active species obtained from $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ and $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$:- Table 4.3 gives some data for the rates of hydrogenation of various substrates using the cationic species obtained from the hydridoacetate and that from the trinuclear complex. Since it has been shown earlier that the complex $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ can be converted to the monomeric hydridoacetate in high yield, provided the solution is not too acid, and since we now know that the hydridoacetate itself is susceptible to protonation by acid, it is conceivable that the active species in both systems could be similar. This is substantiated by the results given in Table 4.3, which show that, although the rates of H_2 uptake for different substrates are lower when the trinuclear species has been used, the selectivity towards different substrates is remarkably similar in both cases. The lower rates for the latter are due to a poisoning agent that appears to be produced in small quantity during the electrochemical reduction process, the proportion of which depends on the time of electrolysis. The exact nature of the poisoning agent is not at all certain however, but solutions that have been electrolysed for several hours gives brown species that are totally inactive.

From Table 4.3 it can be seen that internal mono-alkenes are not reduced, and g.l.c. analysis of the hydrocarbon mixture from cis hex-2-ene gave considerable quantities of the trans isomer. Although, like $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ in pure benzene,²⁴ there is high selectivity for alk-1 vs alk-2-enes, the cationic species by contrast will hydrogenate cycloalkenes and cycloocta-1,5-diene. For the latter only traces of the expected cyclooctene could be detected by g.l.c., and it would appear that reduction proceeds directly to cyclooctane, the proportion of which was ca. 98% after 1h. reduction.

Although it has not been possible so far to isolate any π -bonded olefin complexes or characterise any by n.m.r. spectroscopy (owing to the low solubilities), it does seem reasonable that in the diene reduction above, both double bonds are coordinated to ruthenium in which a coordinatively saturated species would be obtained (see later).

(c) Diacetatobis(triphenylphosphine)ruthenium(II).

The orange crystalline complex when dissolved in methanol containing fluoroboric acid gives a cationic yellow-orange solution that is catalytically active for the hydrogenation of hex-I-ene (Table 4.4). Comparative rates for hex-I-ene shows that using an acid:acetate ratio of 8:1 for trifluoromethylsulphonic acid, a rate of $41.2 \text{ ml. min}^{-1} \text{ H}_2$ uptake is obtained, compared to $36.1 \text{ ml. min}^{-1}$ when fluoroboric acid is used. Like the previous cases, the addition of acetate ion to the hydrogenating solution suppresses catalysis, the activity being regenerated by the addition of excess acid. This is consistent with the formulations:-



However even in the absence of added acetate, the solution is soon poisoned, probably due to partial reassociation of the displaced acetates in solution. Such poisoned solutions are yellow and rapidly turn orange on addition of excess triphenylphosphine whereupon the activity is regenerated with rates comparable to those initially obtained. As we shall see shortly, the presence of excess phosphine prevents the reassociation of acetate ion, with consequent stabilisation of the triphosphine cation $[\text{Ru}(\text{PPh}_3)_3]^{2+}$.

(d) μ -oxobis[(triphenylphosphine)diacetatoruthenium(II)].

We have seen that this complex behaves similarly to the trinuclear complex $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ on reduction.

However, it can itself act as a catalyst in acidified methanol. Thus under hydrogen at 60°C , a blue solution is obtained after ca. 1h, and on addition of triphenylphosphine and fluoroboric acid to give $\text{Ru}:\text{PPh}_3$ and $\text{H}^+:\text{OCOCH}_3^-$ ratios of 1:2 and 1:1 respectively, the solution becomes mauve, and reduces hex-I-ene with essentially no accompanying isomerisation. However the initial rate is slow and increases with time, when the solution begins to turn yellow. Thus it appears that reduction of the complex by hydrogen is occurring, to give the same species as obtained by reduction of the trinuclear complex $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$, which in the presence of excess PPh_3 and acid gives the originally formulated cation $[\text{Ru}(\text{PPh}_3)_3]^{2+}$.

Table 4.4

Relative rates of H_2 uptake for the hydrogenation of hex-1-ene using the different catalytic species.

Temperature $40^\circ C$; substrate concentration 1 mol. l^{-1} ; solvent methanol; H_2 pressure 40 cm^{-1} ; ruthenium concentration $7.5 \times 10^{-4} \text{ mol. l}^{-1}$; protonating acid HBF_4 , unless otherwise stated.

Catalyst source	Ratio Ru:PPh ₃	Ratio H ⁺ :OCOCH ₃ ⁻	H ₂ uptake in ml. min ⁻¹ at S.T.P.
RuH(OCOCH ₃)(PPh ₃) ₃	1:3	4:1	48.0
	1:3	8:1 ^a	56.8
	1:3	16:1 ^b	17.2
	1:4	4:1	56.8
	1:10	4:1	56.8
	1:3 ^c	4:1	25.8
Ru ₃ O(OCOCH ₃) ₆ (PPh ₃) ₃ ^d	1:2	4:1	36.0
	1:3	4:1	38.0
Ru ₂ O(OCOCH ₃) ₄ (PPh ₃) ₂ ^d	1:2	4:1	53.2
	1:3	4:1	50.1
Ru(OCOCH ₃) ₂ (PPh ₃) ₂	1:2	8:1	36.1
	1:2 ^a	8:1	41.2
	1:3	8:1	31.0

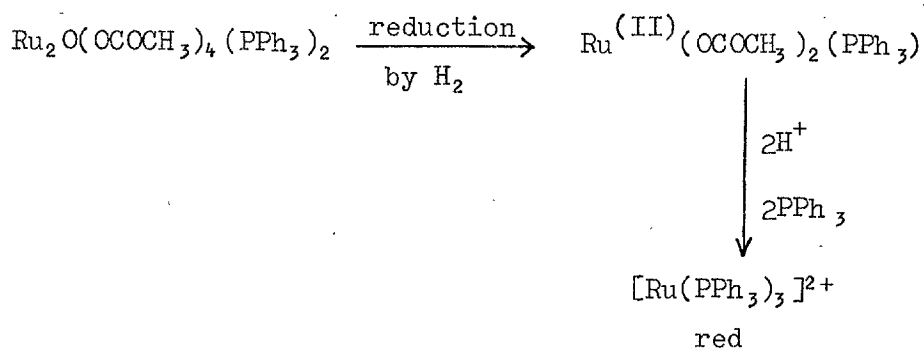
^a CF₃SO₃H used as protonating acid in methanol.

^b CF₃SO₃H used as the protonating acid in t-butanol.

^c Excess acetate ion added to catalyst solution.

^d Species reduced electrochemically prior to use.

i.e.



This is confirmed by the addition to the initial Ru(III)-acid-phosphine containing solution, of a little powdered zinc, when reduction to the yellow solution is immediate, the solution then having similar rates to those made electrochemically. (Table 4.4). As before, the hydrogenating solutions are yellow and are susceptible to poisoning by O_2 , but are regenerated when degassed and stirred under H_2 .

(e) Dihydridotetrakis(triphenylphosphine)ruthenium(II).

Although this complex has been known for some time,⁶⁰ its properties as a hydrogenation catalyst do not appear to have been studied, although it is possible that if alkenes other than alk-1-enes [for which $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ in benzene is very selective, cf. ref 24] were used, this property could well have been overlooked.

In methanol, Ru concentration 7.5×10^{-4} M, hex-1-ene 1M, at 40°C and at 40cm^{-1} H_2 pressure, the rate of H_2 uptake is $45.4 \text{ ml. min}^{-1}$, which can be directly compared to the data given in Tables 4.3 and 4.4.

Dissolution of the dihydride in acidified methanol gives an orange-red cationic solution as noted before, the catalytic properties of which are very similar to those obtained, e.g. from $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ upon protonation. There is of course an extra phosphine present, so that it is necessary to compare $\text{Ru}(\text{H})_2(\text{PPh}_3)_4$ plus HBF_4 with the hydridoacetate containing an extra mole of phosphine, using the same acid concentration in both cases; the rates under standard conditions (Table 4.4) were 57.6 and 56.8 ml. min^{-1} respectively.

B. Discussion

The following general points can be made about the catalytic systems.

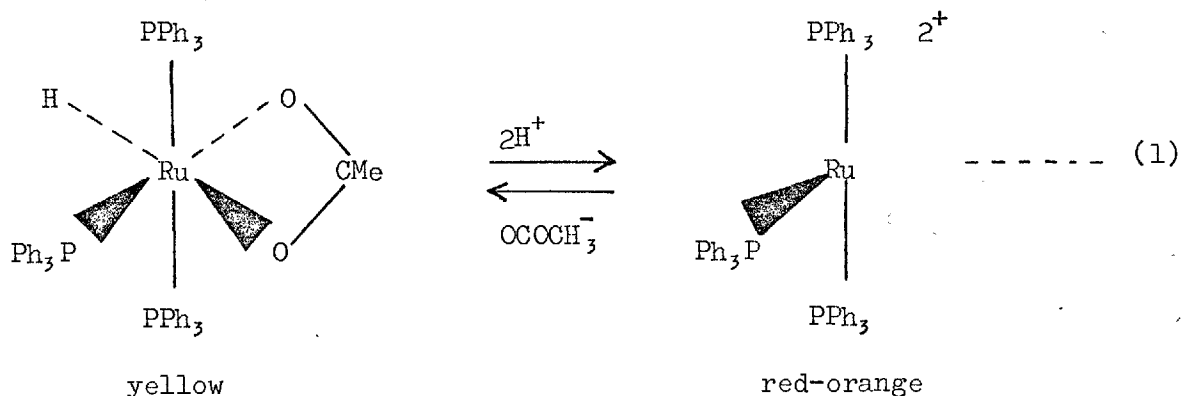
(a) Essentially identical catalytic solutions can be made by (i) reduction in acidified methanol of the complexes $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ or $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$ in the presence of excess PPh_3 ; (ii) protonation of the complexes $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$, $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_2$ or $\text{Ru}(\text{H})_2(\text{PPh}_3)_4$ with strong, but non-complexing acids, or (iii) removal of Cl^- from $\text{RuCl}_2(\text{PPh}_3)_3$ by silver ions. It should be noted that in this particular case, the removal of Cl^- from the complex using a stoichiometric amount of AgBF_4 gives the red cation $[\text{Ru}(\text{PPh}_3)_3]^{2+}$, but excess use of silver ion gives a stable green solution, probably containing the species $\text{Ag}[\text{Ru}(\text{PPh}_3)_3(\text{BF}_4)_3]$.

(b) Where the $\text{Ru}:\text{PPh}_3$ ratio is less than 1:2, as in the reduction of $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ or $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$, the solutions are inactive, and are only made active when the ratio is at least 1:2, and increases in the ratio up to 1:8 produce virtually no appreciable changes in the rate of hydrogenation.

(c) All the systems are poisoned by O_2 , but are rendered catalytically active again after deoxygenating and stirring under H_2 .

It therefore seems that the active species is a bis(triphenylphosphine)ruthenium(II) cation, the properties being closely similar regardless of the method of production, the most straightforward way being the interaction of acid with $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_2$.

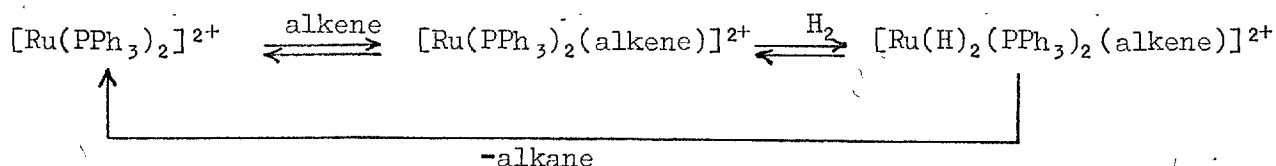
In the hydridoacetate $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$, X-ray study confirms the approximately meridinal configuration of the PPh_3 groups, and it may be reasonably assumed that the initial orange-red species formed by protonation, which removes the hydrido and acetato ligands (equ 1) has the same mer. configuration. The quantitative reversal of the reaction under hydrogen with acetate ion is good evidence for this, and additional evidence that the red species is a tris(triphenylphosphine) one, is the quantitative reaction with lithium chloride to give $\text{RuCl}_2(\text{PPh}_3)_3$.



It is reasonable to accept that such a cation could dissociate one of the trans PPh_3 groups to leave a bis(triphenylphosphine) species with PPh_3 groups in the cis positions. It is reasonable that in the presence of alkene under hydrogen (hydrogen appears to be required since there is no visible colour change with alkene under nitrogen), promoted dissociation of the trans PPh_3 group occurs, to give the bisphosphine species, similar to those obtained in other ways directly.

Since there is no spectroscopic or other evidence to indicate that the red cation activates molecular hydrogen in the absence of alkene, the catalytic cycle may then proceed by steps commonly accepted for other homogeneous systems.^{22, 24} This would be oxidative addition of molecular hydrogen to the cationic alkene complex, followed by simultaneous hydride transfer to the extremities of the coordinated multiple bond, or hydride transfer to give an intermediate alkyl followed by a second hydride transfer and alkane elimination.

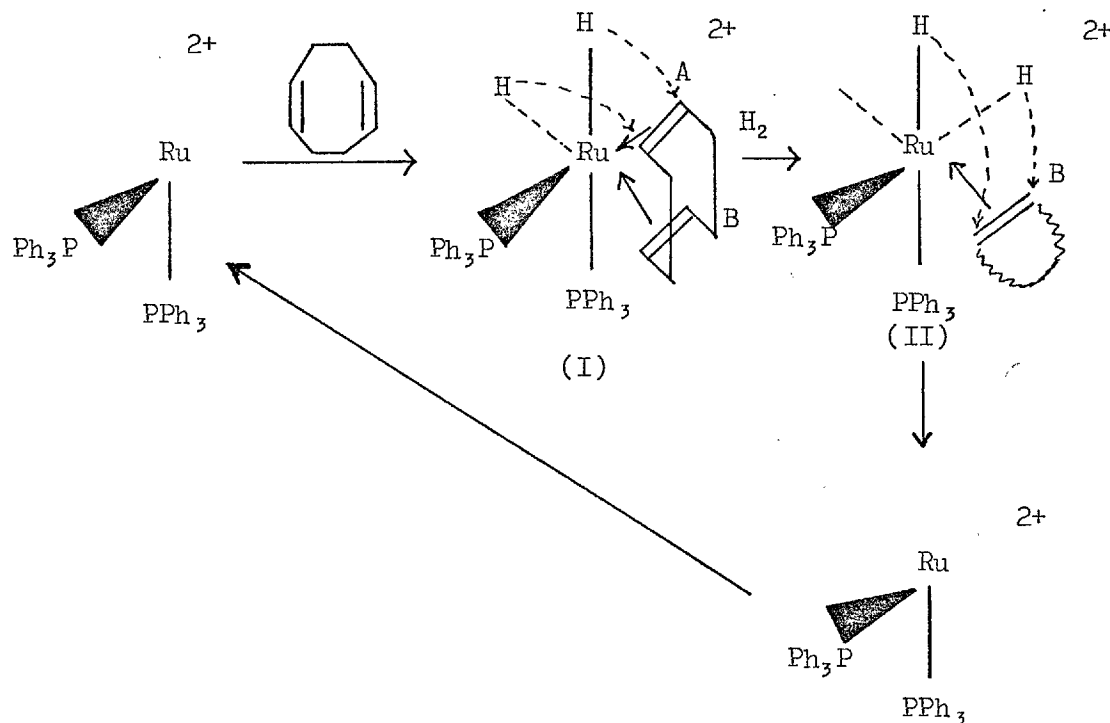
i.e.



It is possible that more than one alkene molecule is coordinated, in view of the rapid hydrogenation of cyclooctadiene (see below). The other vacant coordination site if not occupied by a second molecule of alkene is almost certainly solvated. Since the addition of excess phosphine has little effect on the catalytic rate, the alkene complexes must be fairly resistant to substitution,

although it should be realised that the alkene concentration is vastly greater than either the Ru or PPh_3 concentration.

The fact that cycloocta-1,5-diene is rapidly hydrogenated to cyclooctane would suggest that the formation of an alkyl complex which would be sterically unfavourable here, is not occurring. In this case, a more reasonable representation of the reaction pathway, with no intermediate cyclooctene would be as follows:-



Double bond A would first be susceptible to reduction as in (I), followed by reduction of the second double bond B as in (II). It should be noted that if a synchronous H_2 transfer is to occur in (II), then reactivation of hydrogen by complex (I) must place the hydrogen atoms in new cis positions as shown, otherwise a hydrogen atom trans to the second double bond B would have to be involved in the transfer, which would be sterically unfavourable. The failure to reduce conjugated dienes may be due to the formation of stronger, possibly allylic complexes.

Dependence of rate on hydrogen pressure and substrate concentration

For hex-1-ene as substrate, the rate of hydrogenation is first order dependent on the H_2 pressure, and at low concentrations, is dependent on the concentration of substrate. This is consistent with the mechanism above, where the alkene is initially coordinated to the metal followed by hydrogen activation, which would be

considered the rate determining step.

It is worthy of note that in the presence of liquid alkenes, there is no poisoning of the red cationic species, as shown by the lack of any fall off in the rate of hydrogenation with time. This implies formation of alkene complexes which are sufficiently strong to resist substitution by the displaced phosphine in solution. In all cases, the hydrogenating solutions contain the cation $[\text{Ru}(\text{PPh}_3)_2]^{2+}$, together with displaced PPh_3 , and except in the case of the protonated dihydride $\text{Ru}(\text{H})_2(\text{PPh}_3)_4$, acetate ion. Addition of excess acetate ion suppresses the activity in all cases, and solutions that have been rendered inactive by this method, are restored by the addition of excess acid. It is not inconceivable that hydrogen transfer reactions involving α -hydrogen atoms of the triphenylphosphine groups are occurring also, as is well known in other similar complexes, although this aspect has not been studied. Excess triphenylphosphine restores the activity of the artificially decayed solutions obtained from the protonation of $\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_2$, and in this particular case, it appears that provided there is excess PPh_3 in the homogeneous media, the assumed reassociation of acetate ion is suppressed.

Finally it should be noted that although the nature of the yellow crystalline product which separates from the aqueous fluoroboric acid-methanol solution seems reasonably certain, the exact nature of the inactive yellow solutions, especially when little or no water is present, are not. It is possible that isomerisation of the red cation occurs to give a fac-tris(triphenylphosphine) species, the latter would then be less likely to readily dissociate a phosphine molecule to provide the necessary coordinative unsaturation.

Experimental

A. General

Microanalyses were by the Microanalytical Laboratory, Imperial College, and Alfred Bernhardt Laboratories, West Germany. These are tabulated in Tables E.1., E.2., and E.4.

Molecular weights were determined using an Hitachi-Perkin Elmer Model 115 osmometer at 38°C under N₂, and melting points were obtained using an Electrothermal Melting Point apparatus or a Küfler hot-stage microscope.

Instruments

Infrared spectra were recorded on Perkin Elmer Model 257 and 457 spectrophotometers. The spectra of solids were obtained in nujol, hexachlorobutadiene or vaseline mulls, and solution spectra was measured with compensation, in 0.1, 0.5 and 1.0 mm path length liquid cells. Variable temperature infrared measurements on solutions were obtained using a Beckman (Research and Industrial Instrument Company) variable temperature cell VLT-2.

N.m.r. spectra at 35° were obtained using a Perkin Elmer R 14 spectrometer at 100 MHz for protons. A Varian HA 100 instrument (100 MHz: by Mr. P.N. Jenkins, Imperial College) was used for high pressure n.m.r. studies.

G.l.c. measurements were made using Perkin Elmer Model F 11 chromatographs with flame ionisation and hot wire detectors for liquid and gases respectively; the peak areas were obtained using a Kent Cromalogue integrator. For acetic acid and methyl acetate detection, a 2M columb of Chromosorb 102 (80-100 mesh) at 150°C was used.

U.v. - visible spectra were obtained on Perkin Elmer 350 and Cary 14 recording spectrophotometers.

Electrochemical Measurements

A Beckman Electroscan TM 30 was used for polarography at controlled potential. This instrument or a Chemical Electronics

TR 70/2A Potentiostat was used for controlled potential reductions.

Materials

Rhodium trichloride trihydrate and hydrated ruthenium trichloride were from Johnson Matthey Limited and triphenylphosphine was from Albright and Wilson Limited. Reagent grade solvents were used throughout and thoroughly deoxygenated before use. All reactions and other operations were carried out under nitrogen unless stated otherwise.

For catalytic studies, alkenes and other unsaturated substrates were purified as before,²² and distilled over sodium under nitrogen prior to use. Hydrogen from British Oxygen Company was passed through an Engelhardt "Deoxo" catalyst and a silica gel drying tower before admission to the vacuum system.

All gases for rigorous oxygen free work were purified by passed through a series of chromium(II) solutions, after which the issuing gases were dried by concentrated sulphuric acid and a silica gel drying tower.

Samples of rhodium(II) acetate and chlorotris(triphenylphosphine)-rhodium(I) were prepared by the late Mr. H.J. Smith.

B. Chapter 1

Preparations

Rhodium(II) Acetate. A solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (5 g) and sodium acetate trihydrate (10 g) in glacial acetic acid (100 ml) and absolute ethanol (100 ml) was refluxed under nitrogen for ca. 1 h. The red solution rapidly became green and a green solid was deposited. After cooling to room temperature the latter was collected, dissolved in boiling methanol (ca. 600 ml), and filtered. After concentration to about 400 ml the solution was chilled overnight in the refrigerator to produce dark green crystals of the methanol adduct. After collection of the crystals, the mother-liquor was concentrated and chilled to yield a further crop of the blue-green methanol adduct $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{MeOH}]_2$. When the adduct was heated at 45°C in vacuo

for 20h, methanol was removed to leave emerald-green crystals of the acetate, (3.2 g, 76% based on $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$).

Dirhodium(II)- μ_4 -benzoate Bis(triphenylphosphine) and Bis(pyridine)

A solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1 g), in methanol (125 ml), benzoic acid (12 g), and sodium benzoate (5 g) was heated to ca. 60°C whereupon it rapidly became green. On concentration of a portion of the solution, only benzoic acid and sodium benzoate was obtained. The addition of a cold saturated solution of triphenylphosphine in methanol to the green solution at room temperature gave light brown crystals of the adduct. The complex was recrystallised from benzene-methanol essentially quantitatively.

In a similar way, addition of pyridine to the green solution gave a corresponding adduct as raspberry-red crystals.

Protonation of Rhodium(II) Acetate.

In a typical experiment the methanol adduct of rhodium(II) acetate (0.55 g) in methanol (60 ml) was treated with 40% aqueous fluoroboric acid (1 ml), and the solution held at 65°C for ca. 20h. The protonation was normally complete, but on cooling a portion at ca. -15°C for a few hours, any unchanged acetate precipitated as the methanol adduct; a more rapid test for the presence of unprotonated acetate was to add triphenylphosphine in methanol whereupon immediate precipitation of the red crystalline solid $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{PPh}_3]_2$ indicated incomplete protonation.

Interaction of Methanolic Rh_2^{4+} with Triphenylarsine and Lithium Acetate.

A methanolic solution of Rh_2^{4+} (15 ml) was refluxed for 20 min with triphenylarsine (1.2 g) in methanol (ca. 20 ml) and an excess of lithium acetate to give maroon crystals. The spectroscopic data and elemental analysis indicates a triphenylarsine adduct of rhodium(II) acetate $[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{AsPh}_3]_2$. The adduct was also obtained quantitatively by treating rhodium(II) acetate (or the methanol adduct), (0.5 g) in boiling methanol (100 ml) with excess methanolic triphenylarsine.

The propionato-, chloroacetato-, and trifluoroacetato-complexes were obtained similarly.

Rhodium(I) Complexes

Interaction of Rh_2^{4+} with Triphenylphosphine.

To a methanol solution of Rh_2^{4+} (20 ml of the solution made above), was added a saturated solution of triphenylphosphine (0.8 g) in methanol. There was an immediate colour change to red, and on standing, an orange precipitate of the complex $\text{Rh}(\text{PPh}_3)_3\text{BF}_4$ was obtained essentially quantitatively.

Interaction of $\text{Rh}(\text{PPh}_3)_3\text{BF}_4$ and LiCl.

The orange rhodium complex (0.3 g) was treated with excess of LiCl (ca. 0.8 g) in 2-methoxyethanol (20 ml), and the mixture was gently refluxed under nitrogen for 15 min. On cooling, red crystals were obtained; these were washed with methanol and dried under vacuum. The m.p. and i.r. spectrum of the crystals were identical to that of an authentic sample of $\text{RhCl}(\text{PPh}_3)_3$.²²

Interaction of Rh_2^{4+} with Triphenylphosphine and CO.

Carbon monoxide was bubbled through a methanol solution of Rh_2^{4+} (ca. 40 ml of the standard solution) which was subsequently treated with an excess of triphenylphosphine (ca. 1.5 g) in methanol. The solution changed from green to orange-red on addition of the phosphine, and after gentle refluxing for a few hours under carbon monoxide, became bright yellow. After concentration to ca. half volume, the solution made under CO was chilled to ca. 5°C overnight to give orange crystals of the complex, which was washed with diethyl ether and dried under vacuum.

An improved procedure for the preparation of this carbonyl complex is to treat $\text{Rh}(\text{CO})_2(\text{acac})$ in methanol, with a stoichiometric amount of 40% aqueous HBF_4 in the presence of a stoichiometric amount of PPh_3 . The solution is refluxed for 30 min and on cooling, the complex is obtained quantitatively.

Carboxylatotris(triphenylphosphine)rhodium(I).

Complexes of the type $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$ were prepared by the following procedure. To the green solution of Rh_2^{4+} (20 ml) was added a solution of triphenylphosphine (1.0 g) in methanol, followed by an excess of a methanolic solution of the lithium carboxylate. In all cases, except for the butyrate, caproate and benzoate, the red mixture was refluxed for 20 min. filtered hot, and the crystalline product washed with methanol and vacuum dried. The butyrate, caproate and benzoate complexes were precipitated from the red mixture at 25°C after standing for several hours.

Carboxylato(carbonyl)Bis(triphenylphosphine)rhodium(I).

Complexes of the type $\text{Rh}(\text{OCOR})(\text{CO})(\text{PPh}_3)_2$ were prepared as follows. Carbon monoxide was passed through a suspension of the carboxylate $\text{Rh}(\text{OCOR})(\text{PPh}_3)_3$, (0.5 g) in benzene (10 ml), to give a bright yellow solution, which was then concentrated to ca. 1 ml. Addition of diethyl ether gave the product. The oxygen adduct of the trifluoroacetate $\text{Rh}(\text{OCOCF}_3)(\text{CO})(\text{O}_2)(\text{PPh}_3)_2$ was obtained quantitatively by bubbling oxygen into the carbon monoxide-saturated yellow solution above. The solution was evaporated to small volume under oxygen, and crystallised from ether. λ_{max} ($\epsilon \cdot 10^{-3}$) in benzene for $\text{Rh}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2$: 389 nm (13.5); for $\text{Rh}(\text{OCOCF}_3)(\text{CO})(\text{O}_2)(\text{PPh}_3)_2$: 389, (12.9), 424, (7.7).

Rhodium(III) Complexes

Bis(NN-diethyldithiocarbamato)Bis(triphenylphosphine)rhodium(III) tetrafluoroborate.

To a methanolic solution of Rh_2^{4+} (20 ml) was added a saturated methanolic solution of triphenylphosphine (15 ml). To this red solution was added a solution of sodium diethyldithiocarbamate (0.8 g) in methanol (10 ml). The complex which was precipitated on standing at 25°C , was filtered, washed with methanol and dried in vacuo.

Bis(2-mercaptobenzthiazolato)Bis(triphenylphosphine)rhodium(III)-tetrafluoroborate.

As above, using 2-mercaptobenzthiazole (0.4 g). The crystals were collected and dried in vacuo.

Bis(2-mercaptopyridinato)Bis(triphenylphosphine)rhodium(III)-tetrafluoroborate.

Similarly, using 2-mercaptopyridine (0.2 g) in methanol, to give after ca. 24h the complex, which was washed with light petroleum and vacuum dried.

Bis(toluene-3-thiolato)Bis(triphenylphosphine)rhodium(III)-tetrafluoroborate.

Similarly, using toluene-3-thiol (0.4 g) in the minimum of methanol to give after standing for some time, orange crystals of the complex, which were washed in a little methanol and dried in a stream of nitrogen.

Tris(diphenylphosphorodithioato)triphenylphosphinerhodium(III).

Similarly, using diphenylphosphorodithioic acid (0.8 g) in methanol. The red solution slowly deposited the complex which was recrystallised from benzene-methanol.

This complex can also be obtained by the action of excess diphenylphosphorodithioic acid ($\text{Ph}_2\text{PS}_2\text{H}$) in methanol on $\text{Rh}(\text{CO})(\text{PPh}_3)_3\text{BF}_4$ in methanol.

Tris(diethoxyphosphorodithioato)Tris(triphenylphosphine)rhodium(III).

Similarly, using the sodium salt of the free acid $[(\text{EtO})_2\text{PS}_2\text{H}]$ (0.75 g), in methanol, to give after several hours, orange crystals of the complex, which was washed with methanol and vacuum dried.

Tris(thiocyanato)Bis(triphenylphosphine)rhodium(III).

Similarly, using excess lithium thiocyanate. The crystals were washed with a few ml of light petroleum and vacuum dried.

Table E.I.

Analytical and other data for Rhodium(I) complexes

Compound	Yield (%)	Colour	m.p. (°C)	Analysis: found(calc) (%)		
				C	H	
$\text{Rh}(\text{PPh}_3)_3 \text{BF}_4$	95	Orange	92-93	66.4(66.4)	5.0(4.6)	9.2(9.5) ^a
$\text{Rh}(\text{CO})(\text{PPh}_3)_3 \text{BF}_4$	65	Yellow	190-191	65.9(65.8)	4.9(4.5)	
$\text{Rh}(\text{OCOCH}_3)(\text{PPh}_3)_3$	80	Orange	134-136	71.0(70.9)	5.1(5.1)	
$\text{Rh}(\text{OCOC}_2\text{H}_5)(\text{PPh}_3)_3$	75	Orange	134-135	71.1(71.2)	5.4(5.2)	
$\text{Rh}(\text{OCOC}_3\text{H}_7)(\text{PPh}_3)_3$	55	Orange	130-132	71.4(71.3)	5.6(5.3)	
$\text{Rh}(\text{OCOCH}_2\text{Cl})(\text{PPh}_3)_3$	75	Orange	135-137	68.1(68.4)	5.6(4.8)	
$\text{Rh}(\text{OCOCClF}_2)(\text{PPh}_3)_3$	72	Orange	136-138	65.7(66.0)	4.4(4.4)	
$\text{Rh}(\text{OCOCF}_3)(\text{PPh}_3)_3$	70	Orange	138-139	67.2(67.1)	4.6(4.5)	
$\text{Rh}(\text{OCOC}_2\text{F}_5)(\text{PPh}_3)_3$	70	Orange	136-139	65.0(65.2)	4.1(4.3)	
$\text{Rh}(\text{OCOCH}_3)(\text{CO})(\text{PPh}_3)_2$	95	Yellow	171-173	65.8(65.6)	4.8(4.6)	
$\text{Rh}(\text{OCOC}_2\text{H}_5)(\text{CO})(\text{PPh}_3)_2$	90	Yellow	147-148	65.8(65.9)	5.2(4.8)	
$\text{Rh}(\text{OCOCH}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$	95	Yellow	172-174	62.3(62.6)	4.6(4.3)	
$\text{Rh}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2$	95	Yellow	175-177	61.0(60.9)	4.0(3.9)	
$\text{Rh}(\text{OCOCF}_3)(\text{CO})(\text{O}_2)(\text{PPh}_3)_2$	95	Orange	176-178	59.0(58.5)	4.0(3.8)	

^a Phosphorus analysis

Table E.2.

Analytical and other data for Rhodium(II) and Rhodium(III) Complexes

Compound	Yield (%)	Colour	M.p. (°C)	Analysis: found(calc.) (%)		
				C	H	Other Elements
$[\text{Rh}(\text{OCOPh})_2 \cdot \text{PPh}_3]_2$	95	light brown	172-173	63.1(63.2)	4.1(4.1)	P, 5.4(5.1)
$[\text{Rh}(\text{OCOPh})_2 \cdot \text{py}]_2$	95	Red	> 230	53.6(53.8)	3.5(3.5)	N, 3.3(3.3)
$[\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{AsPh}_3]_2$	30	Maroon	267-268	49.8(50.0)	4.1(4.0)	
$[\text{Rh}(\text{OCOC}_2\text{H}_5)_2 \cdot \text{AsPh}_3]_2$	30	Maroon	228-229	52.4(52.0)	4.4(4.5)	
$[\text{Rh}(\text{S}_2\text{CNEt}_2)_2 (\text{PPh}_3)_2] \text{BF}_4$	45	Yellow	252-253	54.3(54.5)	5.3(5.0)	N, 2.4(2.7); P, 6.1(6.1)
$[\text{Rh}(\text{mbt})_2 (\text{PPh}_3)_2] \text{BF}_4$	35-40	Orange	220-222	58.8(58.2)	3.6(3.8)	N, 2.6(2.7); P, 5.0(5.9)
$[\text{Rh}(\text{pyS})_2 (\text{PPh}_3)_2] \text{BF}_4$	ca. 40	Yellow	> 260	57.9(58.9)	4.1(4.3)	N, 2.8(3.0)
$[\text{Rh}(\text{tt})_2 (\text{PPh}_3)_2] \text{BF}_4$ ^a	ca. 30	Orange-Brown	125-127	62.7(62.6)	5.0(4.6)	
$\text{Rh}(\text{S}_2\text{PPh}_2)_3 (\text{PPh}_3)$ ^b	40	Maroon	112-114	58.7(58.3)	4.2(4.1)	P, 10.5(11.1); S, 18.2(17.3)
$\text{Rh}[\text{S}_2\text{P}(\text{EtO})_2]_3 (\text{PPh}_3)_3$	40	Red		55.2(54.9)	5.1(5.2)	
$\text{Rh}(\text{SCN})_3 (\text{PPh}_3)_2$ ^c	45	Yellow-Orange	159-160	58.4(58.5)	4.9(3.8)	N, 4.7(5.2)

^a M (in MeOH by osmometer) 465 (required 962).^b M (in benzene by osmometer) 1140 (required 1120)^c M (benzene by osmometer) 845 (required 801).

Interaction of $\text{Rh}(\text{OCOCH}_3)(\text{PPh}_3)_3$ with Aldehydes.

A solution of the acetate complex (0.5 g) in deoxygenated benzene was heated to 40°C under nitrogen, and n-heptaldehyde (ca. 2 ml) was added dropwise. After 10 min. a bright yellow solution was obtained. Vacuum evaporation and crystallisation of the product from methanol-ether gave yellow crystals identical with an authentic sample of $\text{Rh}(\text{OCOCH}_3)(\text{CO})(\text{PPh}_3)_2$. Similar results were obtained using the propionate or the substituted carboxylates, or using valeraldehyde as the CO source.

Deuterium Exchange Studies

5 ml of the green solution of Rh_2^{4+} were evaporated to dryness under reduced pressure, and the residue dissolved in CH_3OD (5 ml). A solution of PPh_3 (0.15 g) in CH_3OD (5 ml) was added and deuterium (ca. 1 l) circulated through the mixture for 5h. Nitrogen was then passed through the yellow solution, and the resultant precipitate was isolated and found to have an i.r. spectrum ($4000\text{--}625\text{ cm}^{-1}$) identical with that of $\text{Rh}(\text{PPh}_3)_3\text{BF}_4$; there was no band characteristic of ortho-deuterated triphenylphosphine.

C. Chapter 2.

Molecular Weight Studies

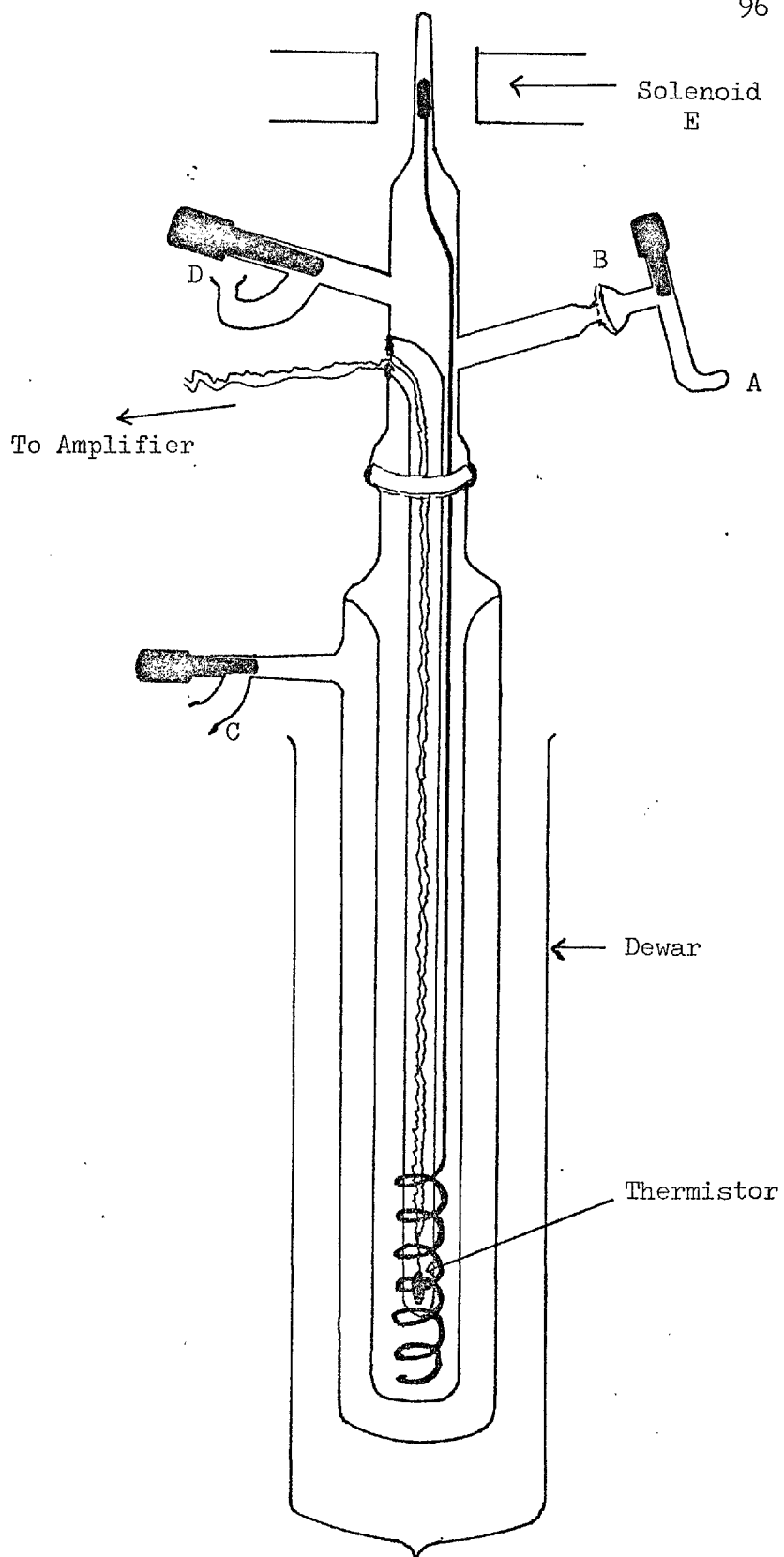
The determination of molecular weights of $\text{RhX}(\text{PPh}_3)_3$ compounds in benzene by the method of "freezing point depression" was carried out using a standard freezing point apparatus fitted with an inert gas source. However owing to the necessity to rigorously remove all traces of oxygen from benzene, it was necessary to use a cryoscopy cell as illustrated in Fig. E.1. The cell is so designed to allow automatic recording of cooling curves, high sensitivity and complete exclusion of air and other contaminants such as stopcock grease.

The sidearm of the cell at D permits vacuum and nitrogen, (or hydrogen) purge cycles, and allows the cell to be flushed when it is attached to an apparatus which contains the solvent to be added. The sample to be studied is weighed into the side limb

at A and may then be tipped into the body of the cell by rotation at the ball-joint B. This allows pure solvent to be introduced into the cell, the freezing point measured and then the solution made up internally, without the necessity of opening the cell to the atmosphere. Supercooling is minimised by rapidly stirring the solution using a spiral metal stirrer as shown, this being operated by a "make-and-break" circuit attached to the solenoid at E.

Procedure: Since the complexes to be studied were only slightly soluble in benzene, the solids were powdered first, and then accurately weighed into the side limb of the cryoscopy cell. The cell was then attached to a high vacuum line at D and the apparatus evacuated and filled with pure nitrogen several times. Dry benzene was purified externally by evacuating, flushing with nitrogen and re-evacuating several times. It was then frozen, pumped, melted and flushed with nitrogen at least three times before it was vacuum distilled into the cell. (The volume of solvent could readily be ascertained from the calibrated scale on the wall of the cell). The apparatus was then filled with nitrogen and the tap at D closed, and the cell removed from the vacuum line and transferred to an amplifier circuit for recording the freezing points.

A slow rate of cooling was achieved by evacuating the outer jacket at C and surrounding the cell by a coolant of CO₂/acetone, whereupon rapid stirring of the solvent allowed reproducible cooling curves to be obtained. After the freezing point curve of pure benzene had been obtained, the vacuum was released at C, the coolant removed and the solvent subsequently melted. The solid was then tipped into the cell and the apparatus vigorously shaken until a homogeneous solution was obtained. The freezing point of the solution was then recorded in an analogous way. Determinations were made on the chloride RhCl(PPh₃)₃ and the carboxylates Rh(OCOR)(PPh₃)₃ in benzene using solutions varying in concentration from 2.35×10^{-3}

Fig. E.1.Cryoscopy cell:

- A Sample compartment
- B Rotating ball joint by which sample may be tipped into the main cell
- C Exit to vacuum
- D Opening where solvent is vacuum distilled into cell

to $2.80 \times 10^{-3} \text{ M}$ under pure nitrogen. (Nitrogen was rigorously deoxygenated and dried by passage through three chromous bubblers and several wash bottles of concentrated sulphuric acid and two silica-gel drying towers). After a determination had been made under nitrogen, the cell was reattached to the vacuum line, evacuated, filled with hydrogen several times, and the yellow hydride solution re-measured in an analogous way. The molecular weights of the chloride and some of the carboxylates are given in Table E.3.

Hydrogenation Studies.

The apparatus and general techniques were those described previously.²² Studies using the $\text{Rh}_2^{4+}/\text{PPh}_3$ catalyst were made on freshly prepared solutions of Rh_2^{4+} (in methanol), and the requisite amount of methanolic triphenylphosphine was added via a syringe to the green solution in the thermostatically controlled jacketed flask. The red mixture at 30°C was then degassed and flushed with hydrogen three times to remove all traces of oxygen. The pressure of hydrogen was then adjusted to 40 cm^{-1} and the homogeneous mixture rapidly stirred until no noticeable pressure change on the manometer could be detected. A known volume of freshly prepared substrate (to be studied) was then added from a burette attached directly to the reaction flask, and when steady state conditions had been achieved, gas uptake measurements were recorded on the manometer. The total volume of solution was 50 ml.

22

As before, the rate of uptake of hydrogen was taken at the standard gas pressure from the tangent of the plot of pressure vs time.

The carboxylates in benzene were studied in an analogous way to that described for the chloride $\text{RhCl}(\text{PPh}_3)_3$; previously, the catalyst being introduced to the pre-deoxygenated benzene solution in a small teflon bucket. The mixture was then stirred under hydrogen until homogeneous, and the solution was then treated as described above.

Table E.3.

Molecular Weights of Tris(triphenylphosphine)rhodium(I) complexes
in benzene

Compound	$M(N_2) \pm 10$	$M(H_2) \pm 10$		M(calc.)
$RhCl(PPh_3)_3$	950	460	460 ^a	925
$Rh(OCOCH_3)(PPh_3)_3$	925	498	491 ^a	948
$Rh(OCOCH_2Cl)(PPh_3)_3$	979	513	513 ^a	983
$Rh(OCOCF_3)(PPh_3)_3$	1090	600	491 ^a	1002
$Rh(OCOPh)(PPh_3)_3$	987	489	491 ^a	1010

^a Molecular weights measured after removal
of hydrogen and resaturation with nitrogen.

D. Chapter 3.

Preparations

Hydridoacetatotris(triphenylphosphine)ruthenium(II)

(a) From Dichlorotris(triphenylphosphine)ruthenium(II):-
The dichloride $RuCl_2(PPh_3)_3$ (1.0g) and sodium acetate trihydrate (1.42g) were heated in ethanol (250 ml) under reflux in a nitrogen atmosphere for $\frac{1}{2}$ h. The reaction mixture was then allowed to cool to 25°C under nitrogen and the yellow crystalline complex was collected (in air), washed with ethanol, water, ethanol again and dried in vacuo over silica gel. Yield 0.85g (ca. 85%).

(b) From Ruthenium trichloride trihydrate:-
The trichloride (0.3g), triphenylphosphine (1.8g) and sodium acetate

trihydrate (1.56g) were heated in methanol for 4h. The product separates from the purple solution as a yellow crystalline deposit. The complex was collected by filtration of the hot solution, washed with methanol and ether, and dried in vacuo over silica gel. Yield 0.64g (59%).

(c) From a reduced solution of tris(triphenylphosphine) hexa- μ -acetato- μ_3 -oxotriruthenium(II, III, III):-

A methanol solution (100 ml) of $\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{PPh}_3)_3$ (36.6g), triphenylphosphine (19.8g), and fluoroboric acid (20 ml. of a solution containing 0.42g of 42% aqueous HBF_4 in 500 ml. methanol) was reduced under nitrogen at -0.6v vs silver wire electrode for ca. 2h. The yellow air-sensitive solution was transferred under hydrogen to methanol (50 ml) containing PPh_3 (ca. 1g), and the mixture was refluxed under hydrogen for 12h. The precipitated hydridoacetate was collected and washed and dried as above. Yield 80% based on Ru.

Yellow salt from the protonated solution of $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$

To thoroughly deoxygenated methanol (250 ml) containing fluoroboric acid (0.8 ml. of a 42% aq. soln.) was added the hydridoacetate (0.25g) under N_2 , and the mixture was heated to 65°C. The solid slowly dissolves to give a deep red solution which after ca. $\frac{1}{2}$ h turned yellow. The yellow solution was evaporated to small volume under N_2 (ca. 10 ml) and the complex $[\text{Ru}(\text{PPh}_3)_2(\text{OH})(\text{BF}_4)]_2$ crystallised by the addition of diethyl ether. The solid was filtered, washed with a little methanol and ether and dried under N_2 .

Conductivity measurements were made in nitromethane using solutions varying in concentration from 10^{-2} to 10^{-4} M. A straight line plot of Λ_c against $\sqrt{c}$ was extrapolated to give Λ_0 , and a further plot of $\Lambda_0 - \Lambda_c$ vs $\sqrt{c}$ gave a straight line passing through the origin. A slope of 112.0 which is slightly greater than expected of a fully dissociated 1:1 species, but less than that for a 2:1 electrolyte suggests significant ion pairing, or some degree of coordination of the BF_4^- ion in the solid.

Red species: A saturated solution of the hydridoacetate in deoxygenated methanol (100 ml) containing fluoroboric acid (1-2 ml. of a 42% aq. soln.) was heated to 65° until the solution was deep red.

The solution was then filtered under N_2 from any

unreacted hydridoacetate, and excess degassed hot water was added to the hot filtrate. The complex of approximate stoichiometry $\text{Ru}(\text{PPh}_3)_3(\text{BF}_4)_2$ was precipitated immediately as a pink solid. In an analogous way using trifluoromethylsulphonic acid, the complex $\text{Ru}(\text{PPh}_3)_3(\text{SO}_3\text{CF}_3)_2$ was obtained.

μ -oxobis[diacetatotriphenylphosphineruthenium(III)]methanolate

(a) From Ruthenium trichloride trihydrate:-

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (4.0g) and sodium acetate trihydrate (4.2g) in methanol (200 ml) was heated under reflux for 15 min in a nitrogen atmosphere to prevent oxidation of triphenylphosphine. The reaction mixture was cooled to room temperature under nitrogen and then filtered into water (200 ml), which was rapidly stirred. The purple precipitate was removed by centrifugation and washed by stirring and centrifugation with water until the supernatant liquid was colourless. The crude product was dried in vacuo over silica gel, and then dissolved in hot methanol (ca. 70 ml) and filtered. The filtrate was cooled at -40°C for 1 day, and the dark residue which separated was filtered. The filtrate was then allowed to evaporate at 25°C to give purple needle crystals of the complex after 4-5 days. These were collected, washed with a little methanol (ca. 10 ml) then with light petroleum and finally dried in vacuo over silica gel. The complex crystallises with one methanol of crystallisation per molecule.

(b) From $[\text{Ru}_2(\text{OCOCH}_3)_4]\text{Cl}$:-

Tetraacetatodiruthenium(II, III) chloride (0.2g) and PPh_3 (0.22g) were stirred in methanol (30 ml) in air for 24h. The resulting purple solution was cooled to -40°C for ca. 6h and filtered. Addition of water to the solution precipitated the complex, which was collected, washed with water, and a little diethyl ether and vacuum dried. Yield, essentially quantitative.

μ -oxobis[dipropionatotriphenylphosphineruthenium(III)]methanolate

Sodium hydroxide (0.31g) was dissolved in methanol (50 ml) by warming. To the cooled solution was added propionic acid (0.57g), triphenylphosphine (1.0g) and ruthenium trichloride trihydrate (0.5g). The mixture was heated under reflux for 15 min, and then treated as for the acetate above.

μ -oxobis[di-n-butyratotriphenylphosphineruthenium(III)]

Sodium hydroxide (0.31g) was dissolved in hot methanol (50 ml). To the cooled solution was added n-butyric acid (0.67g), triphenylphosphine (1.0g), and ruthenium trichloride trihydrate (0.5g). The mixture was heated for 15 min, cooled, filtered into water and finally the product was washed and dried as for the acetate.

The crude product was dissolved in benzene (ca. 50 ml) and the filtered solution was allowed to evaporate. The dark residue which first separates was filtered, and further slow evaporation of the filtrate at room temperature gave the crystalline complex. This was collected, washed with methanol and dried in vacuo over silica gel.

μ -oxobis[dibenzoatotriphenylphosphineruthenium(III)]methanolate

Ruthenium trichloride trihydrate (0.5g), triphenylphosphine (1.0g) and sodium benzoate (1.1g) in methanol (50 ml) was heated under reflux in a nitrogen atmosphere for 30 min. The solution was cooled to 25°C under nitrogen and filtered. The filtrate was cooled at -40°C overnight to yield the complex which separated almost quantitatively as a dark purple, almost black precipitate. This was filtered and dissolved in hot methanol, and the filtered hot methanolic solution was allowed to evaporate at room temperature. The complex separated in crystalline form after ca. 2 days. It was collected, washed with methanol and vacuum dried over silica gel.

μ -oxobis[diacetatotriss(p-fluorophenyl)phosphineruthenium(III)]
methanolate

This complex was obtained from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.5g), tris(p-fluorophenyl)phosphine (1.21g) and sodium acetate trihydrate (1.03g) in methanol (50 ml) as for the acetatetriphenylphosphine complex above.

Diacetatobis(triphenylphosphine)ruthenium(II)

$\text{RuCl}_2(\text{PPh}_3)_3$ (2.0g) and sodium acetate trihydrate (2.84g) both finely ground in t-butanol (100 ml) were heated under reflux for 1h, and the mixture then cooled to near room temperature. The orange crystalline product was removed by centrifugation, transferred to a sintered glass funnel with ether, and finally washed well with water, methanol and ether. It was then dried in vacuo over silica gel.

Table E.4

Analytical and other data for Ruthenium Complexes.

Compound	Yield (%)	Colour	Analysis : found (calc.) (%)			
			C	H	P	other elements
$[\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2]\cdot\text{MeOH}$	41	purple	53.2(53.4);	4.6(4.6);	6.6(6.1);	O, 14.6(15.0)
$[\text{Ru}_2\text{O}(\text{OCOC}_2\text{H}_5)_4(\text{PPh}_3)_2]\cdot\text{MeOH}$	48	purple	55.0(55.1);	5.0(5.1);	5.8(5.8)	
$[\text{Ru}_2\text{O}(\text{OCO}_n\text{Pr})_4(\text{PPh}_3)_2]\cdot\text{MeOH}^{\text{a},\text{b}}$	50	purple	56.9(57.0);	5.5(5.1);	5.7(5.8)	
$[\text{Ru}_2\text{O}(\text{OCOPh})_4(\text{PPh}_3)_2]\cdot\text{MeOH}$	54	purple	61.9(62.0);	4.3(4.3);	5.3(4.9)	
$[\text{Ru}_2\text{O}(\text{OCOCH}_3)_4\{(\text{pFC}_6\text{H}_4)_3\text{P}\}_2]\cdot\text{MeOH}$	36	purple	47.9(48.3);	3.3(3.6);	5.0(5.5)	
$\text{Ru}(\text{OCOCH}_3)_2(\text{PPh}_3)_2^{\text{c}}$	71	orange	64.7(64.6);	5.1(4.9);	8.5(8.3)	
$[\text{Ru}(\text{PPh}_3)_2(\text{OH})(\text{BF}_4)]_2$	57	yellow	59.0(59.2);	4.7(4.3);	9.1(8.5);	F, 10.4(10.4); B, 1.6(1.5)

^a M (in benzene) 990 (required) 1106. ^b M (in methanol) 1180. ^c M (in chloroform) 740 (required). 743.

Conversion of carbon monoxide to formaldehyde and ethylene to ethane using $\text{RuH}(\text{OCOCH}_3)(\text{PPh}_3)_3$ in acid.

The red solution of the hydridoacetate in fluoroboric acid/methanol (250 ml solution containing ca. 1.0g of complex) at 60°C was transferred under H_2 into a 500 ml flask containing carbon monoxide or ethylene. An immediate yellow solution was obtained in both cases, with the isolation of the yellow complex $[\text{Ru}(\text{PPh}_3)_2(\text{OH})(\text{BF}_4)]_2$. G.l.c. analysis of the gas mixture above the solution after 1h shaking showed traces of formaldehyde (ca. 0.5%) and ethane (ca. 7-8%) respectively.

Electrochemistry

Polarography and controlled potential electrolysis were carried out in conventional H-cells. All solutions were deoxygenated with pure nitrogen. A conventional D.M.E. was used for polarographic studies, and all controlled potential electrolysis were performed at a mercury pool. The anode was of platinum foil in a 0.1M aqueous solution of the supporting electrolyte separated from the ruthenium solutions by a 3% agar bridge. The reference electrodes are described below.

Polarography and Coulometry in Acetone

AnalaR sodium perchlorate was dried at 80°C under vacuum (48h) for use as supporting electrolyte and AnalaR acetone was used without further purification.

An aqueous S.C.E., in contact with a 0.1M aqueous NaClO_4 solution, separated from the acetone solution by an agar bridge was used as reference electrode. Concentrations in the range $5 \times 10^{-3} - 10^{-4}$ M were used. The half-wave potentials for reduction of the trinuclear species $\text{Ru}_3\text{O}(\text{OCOR})_6(\text{PPh}_3)_3$ have been quoted elsewhere.⁵⁸ For the acetate, n values of 2.01 and 1.88, and for the n -butyrate, 2.10 were obtained by reduction at -1.3v. The binuclear complex $\text{Ru}_2\text{O}(\text{OCOCH}_3)_4(\text{PPh}_3)_2$ showed a half wave potential of -0.99v for the reduction to ruthenium(II), and an n value of 1.99 being obtained on reduction at -1.3v.

E. Chapter 4.Preparation of Catalyst solutions by Controlled Potential Electrolysis

(a) From Tris(triphenylphosphine) hexa- μ -acetato- μ_3 -oxotriruthenium(II, III, III):-

The complex (0.0366g) and triphenylphosphine (0.0198g) were dissolved in ca. 70 ml. of warm methanol and the solution was cooled to room temperature. To this solution was added a fluoro-boric acid solution (20 ml. of a solution containing 0.825g of 42% aqueous HBF_4 /500 ml. MeOH), and the volume was made up to 100 ml. with methanol giving an $\text{H}^+:\text{OCOCH}_3^-$ ratio of 1:1.

This solution was reduced at -0.6v vs an internal silver wire electrode at 40°C for 1h. The greenish-yellow reduced solution was transferred under pure hydrogen to a 100 ml. burette attached to the hydrogenation line, and after thoroughly deoxygenating the thermostatically controlled jacketed hydrogenation flask containing 10 ml. of methanol, 50 ml. of this solution, under a pressure of H_2 was admitted. Measurements that were made at different phosphine and acid concentrations were performed by deoxygenating a 10 ml. methanol solution containing the excess acid or phosphine in the hydrogenation flask before admission of the reduced solution. The solution was then allowed to stir under H_2 until steady state conditions had been achieved, whereupon it was then treated as described in section C of the Experimental.

The silver wire reference was preferred to an S.C.E., as the latter electrode led to poor reproducibility of the current-time curves. However, it should be noted that if the solutions were electrolysed until complete reduction to the yellow species occurred (ca. 2-3h), no catalytic activity was observed. This is assumed to be due to the slow generation of a poisoning agent, but the exact nature of this process is not known at present.

(b) From μ -oxobis[diacetatotriphenylphosphineruthenium(III)]:- The complex (0.038g) and triphenylphosphine (0.0198g) were dissolved in ca. 70 ml. of warm methanol, the fluoro-boric acid solution (20 ml. of the solution above) was added to the cooled solution, and the volume was made up to 100 ml. as before.

This solution was electrolysed exactly as above, the yellow reduced species being obtained after ca. 1h. No inhibition of the catalytic activity occurs here on complete reduction to the yellow species. The catalyst solution under H_2 was transferred to the hydrogenation apparatus and treated as above.

Preparation of Catalyst solutions by Protonation

The methanol solution containing the required amount of acid and, if necessary triphenylphosphine, was deoxygenated in the hydrogenation apparatus, and the ruthenium complex $RuH(OCOCH_3)(PPh_3)_3$, $Ru(OCOCH_3)_2(PPh_3)_2$ or $Ru(H)_2(PPh_3)_4$ was added from a polythene bucket. After dissolution under H_2 , substrate was run in and gas uptake measurements recorded.

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