

HOMOGENEOUS CATALYSIS USING INORGANIC
COMPLEXES

A Thesis submitted

by

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To Janet

Abbreviations.

Me	methyl
Et	ethyl
Ph	phenyl

All temperatures are in Centigrade.

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I should like to thank all my colleagues especially Dr. J. A. Osborn, Dr. J. F. Young and Dr. L. Pratt for their unfailing advice.

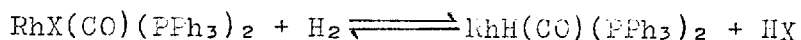
I should also like to thank my wife for typing this manuscript for the price of a new dress.

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ABSTRACT.

A simple and quick method of preparing trans-chlorocarbonyl-bis(triarylphosphine)rhodium(I) complexes and trans-chlorocarbonylbis(triphenylarsine)rhodium(I), from rhodium trichloride trihydrate is described.

The hydroformylation of olefins using compounds of general formulae $\text{RhX}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$ or I ; $\text{R} = \text{alkyl}, \text{aryl}$ or mixed alkyl-aryl) is described. The dependence of hydroformylation on the equilibrium



has been demonstrated by using alkyl amines as co-catalysts when the aminehydrohalide can be recovered from the reaction mixture. This hydrido species is only one of several complexes in equilibrium in the reaction solution, but it appears that the active catalytic species is $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$. This species is formed by addition of carbonmonoxide to $\text{RhH}(\text{CO})(\text{PPh}_3)_2$, the latter complex is also formed by dissociationwhen $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is dissolved in organic solvents. An improved method of preparing $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is described and its reaction with carbonmonoxide has been investigated. The preparation of the new rhodium complexes $(\text{Rh}(\text{CO})_2(\text{PPh}_3)_2)_2$ and $(\text{Rh}(\text{CO})\text{S}(\text{PPh}_3)_2)_2$ ((where $\text{S} = \text{ethanol}$ or $\text{methylene chloride}$) and their reactions with carbonmonoxide, hydrogen and iodine are described.

Hydroformylation of olefins under very mild conditions,

25° and 1 atm. has been demonstrated using $\text{RhH(CO)(PPh}_3)_3$, and ratios of straight- to branch-chain aldehyde as high as 20 have been obtained.

$\text{RhH(CO)(PPh}_3)_3$ has been shown to catalyse double bond migration in olefins, and hydrogen atom exchange between olefins and $\text{RhH(CO)(PPh}_3)_3$ are described. ~~These~~ experiments clearly demonstrate the involvement of the metal hydride in olefin isomerisation.

Some possible mechanisms for the hydroformylation of olefins by $\text{RhH(CO)(PPh}_3)_3$ are discussed.

The increased effectiveness of pentacarbonyl iron as an hydroformylation catalyst, when in the presence of triphenylphosphine is demonstrated, also hydroformylation with several ruthenium and iridium complexes as catalysts is described and their effectiveness compared with rhodium catalysts is discussed.

INTRODUCTION

Although the Fischer-Tropsch process for the conversion of water gas into hydrocarbons has been known since 1925, it was not until much later that its dependence on the in situ formation of metal carbonyls was recognized. The first work in the application of metal carbonyls as catalysts was not carried out until the Second World War, when Reppe and his co-workers pioneered the use of metal carbonyls in organic synthesis. Reppe (1) used iron, cobalt and nickel carbonyls to catalyse the carboxylation of acetylene to acrylic acid (2), olefins to carboxylic acids (3), alcohols to carboxylic acids (4), and cyclic ethers to dicarboxylic acids (5). In each case the esters, thioesters, amides and anhydrides were also obtained by conducting the reaction in the presence of the appropriate alcohol, mercaptan, amine or carboxylic acid.

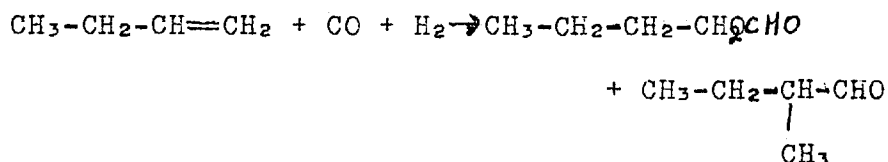
Organic synthesis by catalytic carboxylation with metal carbonyls has since been greatly extended, and is reviewed to the end of 1960 by Bird (6).

Although Reppe postulated that in the formation of propanol and higher alcohols by the carboxylation of ethylene in an aqueous alkaline solution of iron pentacarbonyl, that the reaction proceeds through the intermediate formation of propionaldehyde, which is either hydrogenated to propanol or undergoes condensation followed by hydrogenation in the case of higher alcohols, he did not prepare aldehydes.

Latter workers have shown that the reaction conditions employed would hydrogenate aldehydes to yield alcohols (8), and by using less alkaline media aldehydes can be obtained by this reactio (9).

Roelen was the first to prepare aldehydes by the reaction of synthesis gas with olefins (10), during 1938, in the course of an investigation into the Fischer-Tropsch reaction, using a cobalt-thorium catalyst. This reaction of an olefin with synthesis gas, a mixture of carbonmonoxide and hydrogen, to form an aldehyde is often referred to as the "Oxo" synthesis. However, as the reaction may be visualised as the addition of formaldehyde (H - CHO) across the olefin double bond, it is also referred to as the "hydroformylation" reaction.

As usually performed a cobalt catalyst is employed, other metals have been indicated in the patent literature as catalysts for the hydroformylation reaction, but have generally required higher temperatures and pressures than cobalt (see Page 25). The products of hydroformylation, of a terminal olefin is usually a mixture of straight chain aldehyde containing one carbon atom more than the olefin used, and its α -methyl isomer

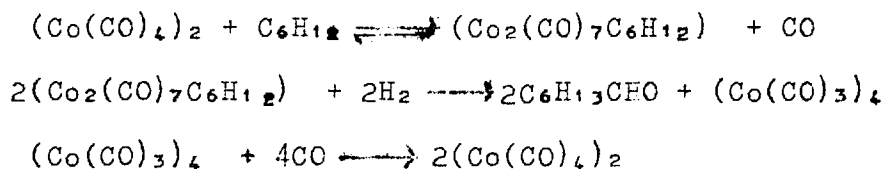


The percentage of the aldehyde formed being straight chain, depends on temperature, pressure and catalyst concentration, but usually varies between 40% and 80%. The hydroformylation of alk-2-enes yields a mixture of aldehydes containing about 50% as straight chain aldehyde.

Most of the early work on hydroformylation was not unnaturally, because of its great industrial importance, carried out by industrial chemists. Much of the work, recorded in the patent literatures, was concerned with improving yields, recovering the cobalt used and continuous flow methods rather than attempts to discover the mechanism of the catalysis.

Roelen had apparently not realised that homogeneous catalysis was involved. It was not until 1948 that it was shown to be homogeneous catalysis (12) when it was observed that when hydroformylating with reduced cobalt on kieselguhr as catalyst, hydroformylation was always accompanied by a coloured reaction mixture at the end of the reaction, also an initiation period was always observed. The same workers demonstrated, however, that there was no initiation period if, instead of metallic cobalt, cobalt octacarbonyl was used. They also proposed a mechanism for the reaction involving cobalthydrotetracarbonyl, no evidence for this was given. Natta (13) also showed that when Raney cobalt is used as catalyst in the hydroformylation of hex-1-ene the rate of

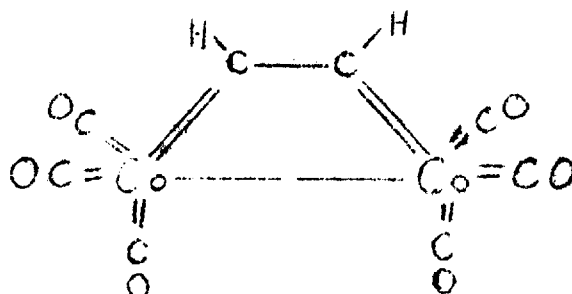
of reaction increased with time, as also happens when soluble cobalt salts are used, when the rate approaches that observed for dicobalt octacarbonyl. The reaction velocity was found to be proportional to the concentration of cobalt octacarbonyl. Highest rates were observed when using a mixture of cobalt octacarbonyl and Raney cobalt, from this it was concluded that the active catalyst was cobalt hydrotetracarbonyl. The rate of reaction was found to increase at constant carbonmonoxide pressure with increasing hydrogen pressure and also to increase at constant hydrogen partial pressure with increasing partial pressure of carbonmonoxide up to 10 atm. but decrease with higher partial pressures of carbonmonoxide (14). Natta tentatively suggested, because of the absence of firm evidence for the presence of cobalt hydrotetracarbonyl, the following reaction sequence to explain these observations:



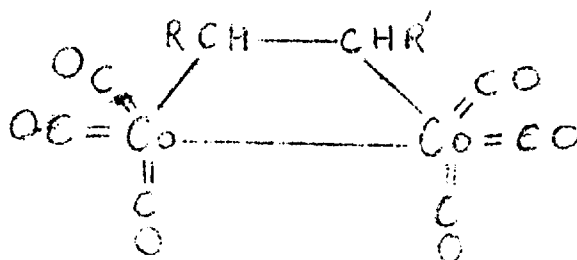
Martin (15) confirmed the above observation and extended them to show that although the rate of reaction increases with increase in the ratio of hydrogen to carbonmonoxide partial pressures, it does so at a diminishing rate of increase as the ratio increases, to explain this he suggested that an equilibrium was not maintained between dicobalt octacarbonyl

and olefin on the one hand and complex and carbonmonoxide on the other, as suggested in Natta's scheme.

By comparison with acetylene dicobalthexacarbonyl (16), assigned the structure



it was assumed that the olefin intermediate in hydroformylation reaction was (17)



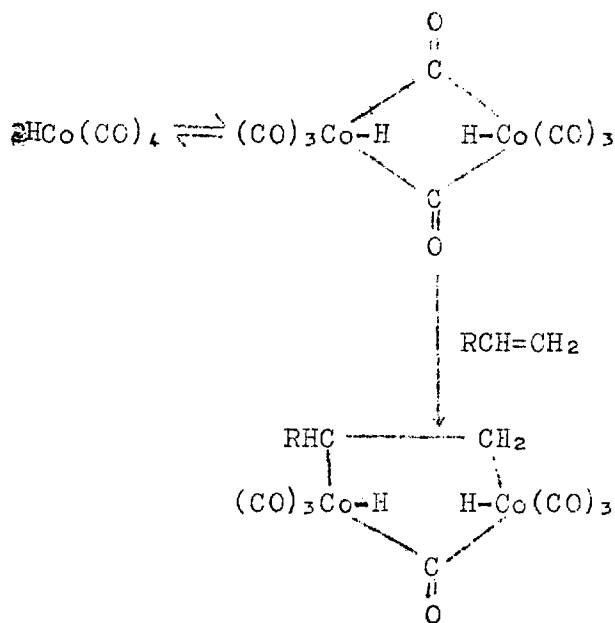
As the ease of formation of this compound, and hence the rate of hydroformylation, will depend on the configuration of the olefin about the double bond, the results in Table I were considered as further evidence for the formation of this type of compound.

TABLE 1. Effect of Olefin Structure on Rate of Hydroformylation using dicobaltoctacarbonyl (18).

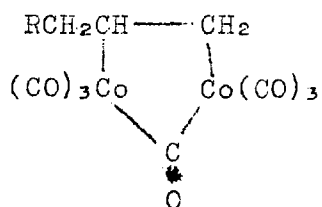
Olefin	Specific Reaction Rate 10 ³ K, min ⁻¹
C-C-C-C-C=C	66
C-C-C-C=C-C	19
C-C-C=C-C C	4.9
C-C=C-C C C	1.4

As early as 1953 Orchin had prepared aldehydes by the reaction of cobalt hydrotetracarbonyl with olefins in the absence of synthesis gas. He also obtained the pyridinium salt of cobalt hydrotetracarbonyl, $(C_5H_5NH)^+(Co(CO)_4)^-$ by treating dicobalt octacarbonyl in pyridine with synthesis gas at 230 atm. and a temperature of 120° C, i.e. conditions under which hydroformylation takes place. It was also shown that the presence of bases, such as triethylamine, suppressed the hydroformylation reaction, presumably by removing cobalt hydrotetracarbonyl as a salt. This was the first direct evidence for the presence and the importance of cobalt hydrotetracarbonyl in the hydroformylation of olefins.

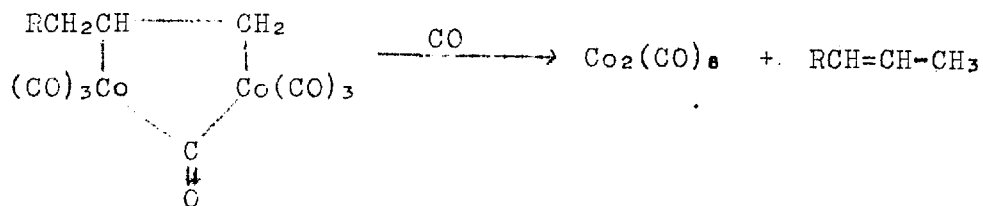
The bridging olefin complex postulated as an intermediate in the hydroformylation reaction was therefore sometimes formulated as (9).



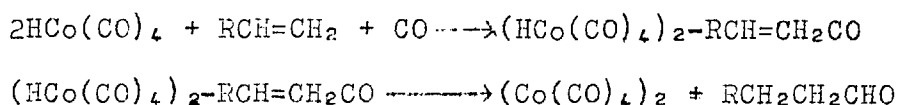
The double bond isomerisation of olefins which takes place during hydroformylation, and when dicobalt octacarbonyl and olefin is heated under pressure of carbonmonoxide only, was considered to be due to the reaction of



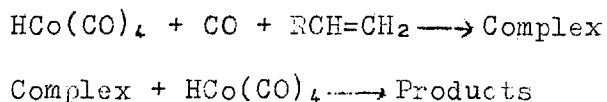
with carbonmonoxide to yield dicobalt octacarbonyl and the most thermodynamically stable forms of the olefin (18).



Further indirect evidence for cobalt hydrotetracarbonyl being the active catalyst was the reaction of olefins with dicobalt octacarbonyl at room temperature and elevated pressures of hydrogen to give 2 moles. of aldehyde for each mole of dicobalt octacarbonyl. This reaction was inhibited by carbonmonoxide, as also was the formation of cobalt hydrotetracarbonyl from dicobalt octacarbonyl and hydrogen (20). Shortly afterwards the presence of cobalt hydrotetracarbonyl in the reaction mixture during hydroformylation was demonstrated (21), by rapid cooling of the reaction vessel in a Dry-Ice bath and analysis of the contents, when it was found that as much as 62% of the cobalt was present as cobalt hydrotetracarbonyl. The rates of reaction of hex-1-ene, hex-2-ene and cyclohexene with cobalt hydrotetracarbonyl were found to be comparable to the rates of hydroformylation of these olefins with dicobalt octacarbonyl at 110° C, being 13:6:1 and 11.4:3:1 respectively (22). Two possible mechanisms were now considered (23) as it now seemed firmly established that $\text{HCo}(\text{CO})_4$ was the active catalytic species.

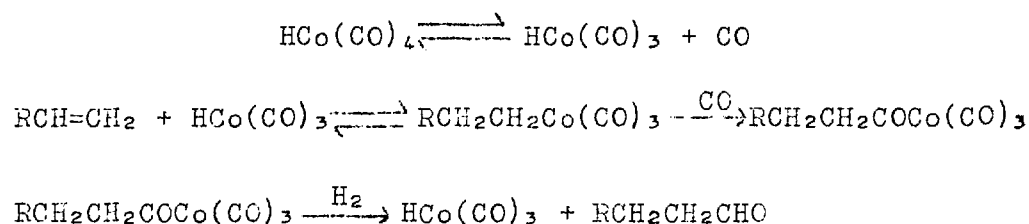


or alternatively



Breslow and Heck (24) confirmed the reaction of cobalt hydrotetracarbonyl with olefin and carbonmonoxide to yield aldehyde and dicobalt octacarbonyl and pointed out that at high olefin concentration absorption of carbonmonoxide approached 1 mole. of carbonmonoxide per mole. of cobalt hydrotetracarbonyl, suggesting that at high olefin concentration all the cobalt is present as $\text{RCH}_2\text{CH}_2\text{COCO}(\text{CO})_4$. They also prepared the compounds $\text{RCo}(\text{CO})_4$ (25) (where R = methyl, ethyl and benzyl) from $\text{NaCo}(\text{CO})_4$ and methyl iodide, triethyloxonium fluoroborate and benzylbromide respectively, which is similar to the method used in the preparation of the first known alkyl metal carbonyl, methylmanganese pentacarbonyl (26). Methyl cobalt tetracarbonyl, which is only stable at low temperatures, was shown to take up one mole. of carbonmonoxide to give a product identical with that obtained by the reaction MeCOBr and $\text{NaCo}(\text{CO})_4$, which is again similar to the method used for the preparation of $\text{MeCoMn}(\text{CO})_5$ (26). The band at 5.8μ in the infra-red spectra of $\text{MeCOCO}(\text{CO})_4$, attributed to an acyl cobalt linkage is also present at lower intensity in

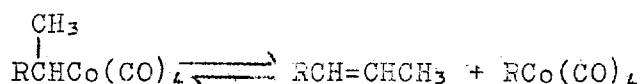
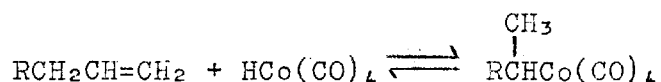
$\text{MeCo}(\text{CO})_4$, suggesting that $\text{MeCo}(\text{CO})_4$ is in equilibrium with $\text{MeCOCO}(\text{CO})_3$ in solution. $\text{MeCOCO}(\text{CO})_4$ was shown to be reduced by cobalt hydrotetracarbonyl to yield acetaldehyde and dicobalt octacarbonyl, but too slowly to be the reaction operating in a normal hydroformylation reaction, $\text{MeCOCO}(\text{CO})_4$ is also reduced with hydrogen at room temperature and elevated pressures. As this reduction is inhibited by high carbon-monoxide pressure it suggests that $\text{MeCOCO}(\text{CO})_3$ and not $\text{MeCOCO}(\text{CO})_4$ is the species being reduced according to the equation:-



with the cobalt present throughout the reaction as the tricarbonyl.

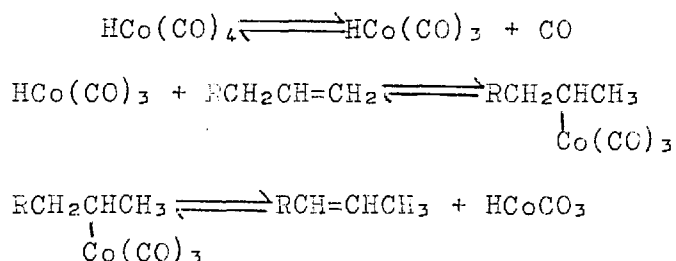
Orchin in a study of the isomerisation of olefins (27) showed that while cobalt hydrotetracarbonyl was an efficient catalyst for the isomerisation of olefins, the isomerisation was suppressed if carried out under an atmosphere of carbon-monoxide. Also when cobalt hydrotetracarbonyl was reacted with low concentrations of olefins to yield aldehydes the ratio of straight chain aldehyde to branched chain aldehyde was much higher if the reaction was carried out under carbon-monoxide than if it was carried out under nitrogen. It was

concluded that the olefin and dissolved carbonmonoxide compete for the cobalt in a nucleophilic displacement of one of the carbonmonoxide ligands on the cobalt hydrotetracarbonyl, and at low olefin concentration the olefin carbonyl complex under the influence of the carbonmonoxide rapidly rearranges to an acylcobalt compound which can then be reduced by uncomplexed cobalt hydrotetracarbonyl, yielding aldehyde with little concomitant isomerisation. The high isomerisation which takes place when the reaction is carried out under nitrogen, has been suggested to result from the frequency of complex formation and dissociation when carbonmonoxide is not present to aid the rearrangement of the complex. The most simple and attractive scheme for explaining the isomerisation of the olefin, consists of addition of cobalt hydrotetracarbonyl to olefin to form an alkyl cobalt tetracarbonyl, followed by splitting out of cobalt hydrotetracarbonyl:-

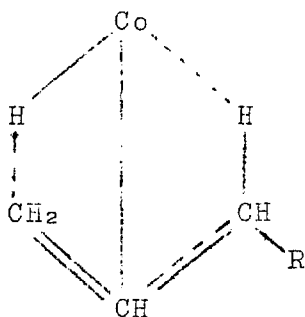


However in reactions under nitrogen with large excess of olefin, i.e. conditions which would maximise the concentration of alkyl cobalt tetracarbonyl, no equilibrium concentration of cobalt hydrotetracarbonyl was found. Furthermore under the above scheme ethyl cobalt tetracarbonyl would be expected to

have an equilibrium concentration of ethylene above it, but no evidence for this was found, in fact treatment of cobalt hydrotetracarbonyl with ethylene leads to complete disappearance of the cobalt hydrotetracarbonyl. The carbonmonoxide inhibition is most easily explained (29) if the isomerisation proceeds via the tricarbonyls rather than the tetracarbonyls this would also explain why ethyl cobalt tetracarbonyl is not in equilibrium with hydrocarbonyl and ethylene.



A further suggestion was that isomerisation proceeds by a donation of metal hydride to the terminal carbon atom with concomitant double bond migration and hydrogen abstraction from the allylic position.

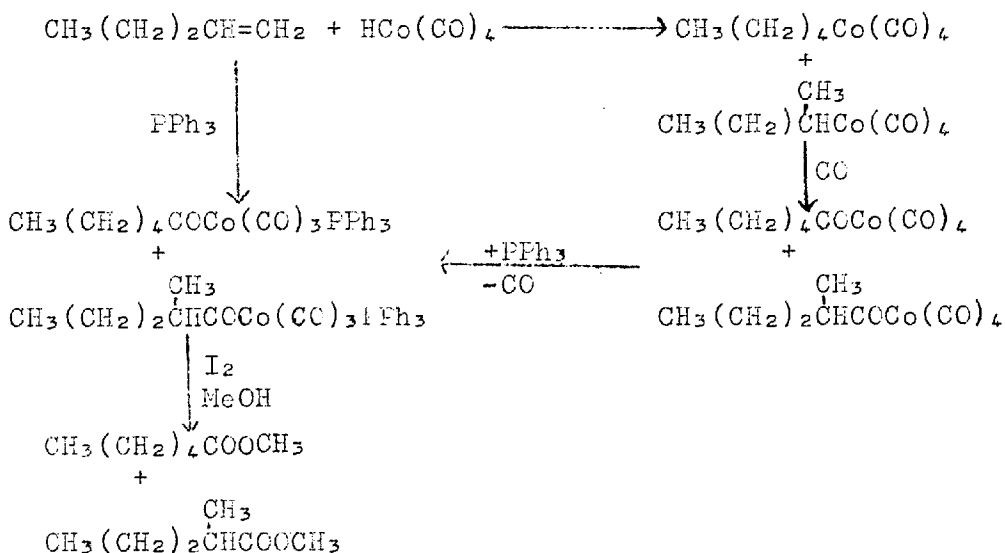


However studies (28) on the catalytic isomerisation of allylbenzene, which is rapidly isomerised by cobalt hydrotetracarbonyl to give trans-propenylbenzene as the major product,

showed that the isomerisation proceeds at the same rate when catalysed with cobalt hydrotetracarbonyl as with cobalt deuterotetracarbonyl, which is strong evidence that the breaking of the Co-H (or Co-D) bond is not involved in the rate determining step. At the end of the reaction very little deuterated propenylbenzene had been formed, and most of the deuterium was still present as cobalt deuterotetracarbonyl. This appears to rule out the possibility of the isomerisation proceeding by either formation of an alkyl intermediate and subsequent splitting out of cobalt hydrotetracarbonyl or a mechanism involving donation of the metal hydride to the terminal carbon atom and hydrogen abstraction from the allylic position. Our own work on isomerisation using $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ has provided strong evidence for the involvement of the Rh-H bond in isomerisation of olefins (see Page 65) and it is possible that because of the difficulties in handling $\text{HCo}(\text{CO})_4$ and $\text{DCo}(\text{CO})_4$ some of the results may not be correct.

Further evidence for the formation of acylcobalt tetracarbonyls in the hydroformylation reaction was obtained by Heck and Breslow (29), when by adding triphenylphosphine to the reaction mixture of olefins and cobalt hydrotetracarbonyl under carbonmonoxide they succeeded in isolating stable crystalline monotriphenylphosphine adducts with properties similar to those of acylcobalt tricarbonyl-triphenylphosphine complexes (30), which were obtained by the

addition of triphenylphosphine to the unstable acyl cobalt tetracarbonyl complexes. By treating these triphenylphosphine acyl cobalt carbonyl complexes obtained from pent-1-ene and cobalt hydrotetracarbonyl at 0° with iodine and methanol they obtained a mixture of isomeric methyl hexanoates, these were analysed by G.l.c. and so the symmetry of the acyl group was determined.

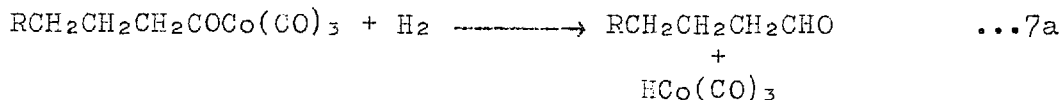
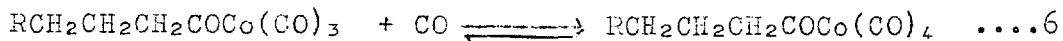
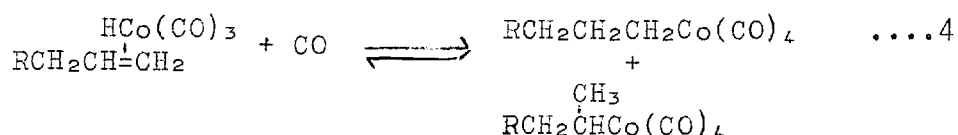
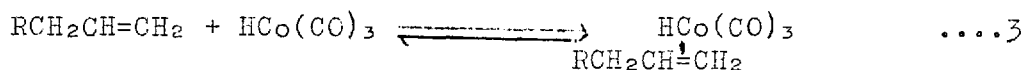
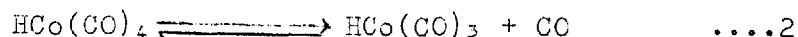
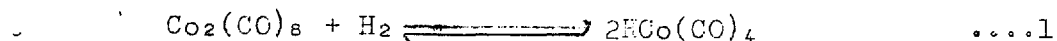


They found that equimolar amounts of methyl n-hexanoate and methyl 2-methylpentanoate were obtained, i.e. approximately the same ratio of branch- to straight-chain product as is obtained in the hydroformylation of pent-1-ene with cobalt hydrotetracarbonyl at 120° (31). Breslow and Heck found however that repeating the experiment with isobutylene instead of pent-1-ene, they obtained methyl trimethylacetate essentially free of methyl 3-methylbutyrate, as in the normal hydroformylation reaction isobutylene yields almost exclusively methyl 3-methyl-

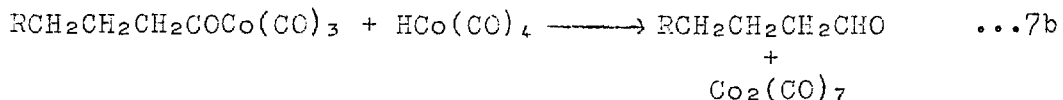
butyrate (18), the addition at 0° is essentially the reverse of that at elevated temperatures. It was also shown that whereas in the conventional hydroformylation reaction methylacrylate gives exclusively methyl 3-formylpropionate (32), on treatment of the methylacrylate-cobalt hydrotetracarbonyl-triphenylphosphine complex obtained at 0° with iodine and methanol a mixture of dimethyl methylmalonate and dimethyl succinate in a ratio of 5:1 was obtained, so that the mode of addition is predominantly the reverse of that at 120° . The suggested explanation for these results is that in the case of isobutylene the high electron density of the double bond leads to an acidic type addition, i.e. Markownikov type addition leading to the branched chain product, while the low density double bond in the methyl acrylate leads predominantly to an hydridic addition and hence a straight chain product. A straight chain alk-1-ene is probably neutral towards hydrocarbonyl addition and hence approximately equimolar amounts of branch-and straight-chain product is obtained. However if the formation of olefin complex, alkyl intermediate and acyl intermediate is reversible, the product obtained at elevated temperatures could reflect the relative stabilities of the intermediates rather than the direction of the original addition. Evidence for this reversibility at high temperatures has been obtained from investigation of ethyl cobalt tetracarbonyl. Although ethyl cobalt tetracarbonyl shows no evidence for dissociation at $0-25^{\circ}$, injection of a solution into a G.l.c. apparatus with an inlet heated at 220° gave an 80%

yield of ethylene with ca. 10% yield of propionaldehyde.

The suggested mechanism for the hydroformylation reaction which best explains the known facts of the reaction is:-



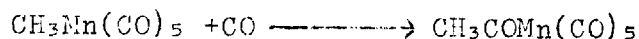
or



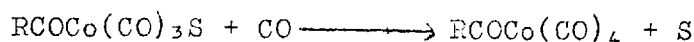
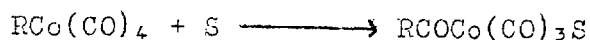
Only the straight-chain alkyl has been followed through from equation 4, equations 5,6,and 7 would also be drawn showing branch chain alkyl and acyl and hence $\text{RCH}_2\text{CH}(\text{CH}_3)\text{CHO}$ in the complete scheme.

Equation 5 is often referred to as an insertion reaction, but it could equally well result from the cleavage of the

cobalt-alkyl bond and a subsequent migration of the alkyl group. There is no direct evidence for either mechanism but a study of the reaction:-



using C^{14} has shown that the carbonmonoxide molecule which inserts is one which is already attached to manganese (33). It has been suggested that in the hydroformylation reaction the insertion is solvent assisted (34).

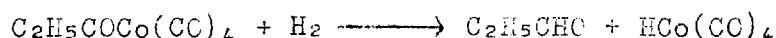
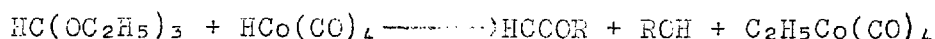


S = Solvent

It is not known whether the final reduction to aldehyde is by hydrogen or cobalt hydrotetracarbonyl, both reactions are known to occur (24,27,29).

Recently Piacenti (35,36) suggested that the branch-chain aldehyde did not result from n-alk-1-ene via isomerisation of the alkyl and acyl intermediates but that the ratio of isomeric aldehydes formed was determined by the nature of the olefin- $\text{HCo}(\text{CO})_4$ complex first formed. His main evidence for this was the reaction of ethylorthoformate with carbonmonoxide and hydrogen in the presence of $\text{Co}_2(\text{CO})_8$ under conditions employed for hydroformylation. This reaction yielded exclusively 1,1-diethoxypropane, no derivatives of isopropionaldehyde were observed. As the reaction is believed to have a mechanism

involving alkyl and acyl cobalt intermediates; as in the hydroformylation reaction one would expect some branched chain products if these compounds were in equilibrium.

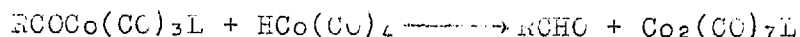


Takegami (37,38,39) however has shown that the isomerisation of the acyltetracarbonyls to be solvent dependent, tetrahydrofuran for example inhibits the isomerisation, so possibly orthoformates also inhibit the isomerisation.

Although strong nucleophiles such as triphenylphosphine, and bases such as pyridine and triethylamine stop hydroformylation under mild conditions through formation of $\text{HCo}(\text{CO})_3\text{PPh}_3$ and $\text{PyH}^+(\text{Co}(\text{CO})_4)^-$, they have been claimed to increase the rate of reaction and the ratio of straight- to branch-chain aldehyde under the drastic conditions normally used industrially (40).

Roos and Orchin (41) showed that the rate of reaction of pent-1-ene with cobalt hydrotetracarbonyl was increased by the addition of the weak nucleophile benzonitrile, also the ratio of straight-chain to branch-chain aldehyde was increased in reactions at 25° and 1 atm. carbonmonoxide. (an earlier patent (42) had claimed increased yields of straight-chain aldehyde

using ketones as solvent). Roos and Orchin suggested that the weak nucleophile (benzonitrile) complexes weakly with the acyl tricarbonyl in competition with the strong nucleophile carbonmonoxide, and cleavage of this tricarbonyl by cobalt hydrotetracarbonyl is rapid. Whereas excess carbonmonoxide fixes the



cobalt in the unreactive tetracarbonyl state and retards cleavage with HCo(CO)_4 .

In view of the great industrial importance of the hydroformylation reaction in the preparation of aldehydes, which can be reduced to the industrially more important alcohols, (indeed industrially the reaction conditions are often arranged so that the aldehyde formed is immediately converted to its corresponding alcohol) it is not surprising that large patent literature has grown up claiming complexes of other metals as catalysts.

Except for rhodium which will be discussed later, all have required much more drastic conditions - higher temperatures and higher pressures than those required for cobalt.

Pentacarbonyl iron has been used both alone when very vigorous conditions were needed and promoted with cobalt when it is claimed comparable conditions to those used in the conventional hydroformylation reaction may be employed (43). From the examples given in these patents it is difficult to decide on the role of the pentacarbonyl iron as the yields are close to those that would be expected from the presence of the cobalt

alone. Some of these patents also indicate tetracarbonyl nickel as an hydroformylation catalyst.

Ruthenium carbonyl catalysts of unspecified stoichiometry (44), usually prepared in situ by the reaction of synthesis gas on ruthenium chloride, have also been indicated, and claimed to give greater ratios of straight-chain aldehyde than cobalt.

Patents exist claiming the use of soluble catalysts of group VIII metals, formed by the interaction of a metal salt and donor ligands such as amines, phosphites and phosphines (45). Examples of all the group VIII metals are given but no stoichiometric compounds were characterised and some of the claims must be regarded as spurious.

CHAPTER I.PREPARATION OF CHLOROCARBONYLBIS(TRIARYLPHOSPHINE)RHODIUM(I)
COMPLEXES.

The chlorocarbonylbis(tertiaryphosphine)rhodium(I) complexes have usually been prepared by the action of the appropriate phosphine on rhodium carbonyl chloride, $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, (46,47,48). This method while simpler than those involving the interaction of tertiary phosphine and rhodium trichloride trihydrate in hot alcoholic solutions of potassium hydroxide, both in the presence (49,50) and absence of carbonmonoxide (51), suffers from the disadvantage of using rhodium carbonyl chloride as a precursor. While rhodium carbonyl chloride can easily be prepared by the interaction of carbonmonoxide and rhodium trichloride trihydrate at 105-110° (52), the method is slow, also the overall reaction to obtain the chlorocarbonylbis(triarylphosphine)rhodium(I) from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (the commercially available form of rhodium) is a two stage process.

It is known that $\text{RhCl}(\text{PPh}_3)_3$, prepared by refluxing $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with a large excess of triphenylphosphine in ethanol (53,54), is an effective reagent for the decarboxylation of aldehydes (55,56) resulting in the formation of chlorocarbonylbis(triphenylphosphine)-rhodium(I) and saturated hydrocarbon.

These reactions have been adapted to give a rapid method for the preparation of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, by adding aqueous

formaldehyde (40% ^W/v) to a refluxing solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and excess triphenylphosphine in ethanol. The reaction has been used to prepare triphenylarsine, tris(p-methylphenyl)phosphine and tris(p-fluorophenyl)phosphine analogues in yields over 85%.

The formaldehyde probably acts as a reducing agent as well as a source of carbonmonoxide, because, whereas both triphenylphosphine and p-fluorophenylphosphine react with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in refluxing ethanol to yield $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RhCl}(\text{P}(\text{p-FC}_6\text{H}_4)_3)_3$ respectively, with the triarylphosphine undoubtedly acting as a reducing agent, $\text{RhCl}(\text{P}(\text{p-MeC}_6\text{H}_4)_3)_3$ cannot be prepared from the interaction of rhodium trichloride with excess tris p-tolylphosphine in refluxing ethanol, good yields of $\text{RhCl}(\text{CO})(\text{P}(\text{p-MeC}_6\text{H}_4)_3)_2$ can be obtained on addition of formaldehyde to the solution. The interaction of excess tri p-tolylphosphine with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ gives, after removal of the ethanol and washing with ether to remove excess unreacted phosphine, a yellow powder which gives non-stoichiometric analysis, but with high (ca. 10%) chlorine content, suggesting that the rhodium is still present in the tri-valent state.

Addition of formaldehyde solution to a refluxing solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1 mole) and triphenylphosphine (2 moles) in ethanol gives no $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$.

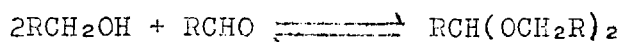
CHAPTER 2.HYDROFORMYLATION USING COMPLEXES OF RHODIUMA) Introduction

Patents (57) have been in existence for some time claiming that, the use of rhodium-cobalt or addition of rhodium salts, enables hydroformylation to be conducted under less drastic conditions than when using cobalt alone. It is assumed that the catalyst is HRh(CO)_4 produced in situ by reductive carbonylation as in the cobalt case. Direct comparisons of pure rhodium and cobalt carbonyls (58, 59) as hydroformylation catalysts have shown that rates of hydroformylation are significantly higher ($\times 10^2$ to 10^3) when using rhodium. Rhodium however gives worse ratios of straight chain to branch chain aldehyde than cobalt (59) possibly because rhodium carbonyl is reported to hydroformylate alk-2-enes faster than alk-1-enes and to isomerise alk-1-enes to alk-2-enes to a much greater extent than cobalt (59). Rhodium carbonyl has been used preparatively in a number of cases (60). However no rhodium compounds, other than the simple carbonyls have been used, and nothing is known about the mechanism, or the stoichiometry of the rhodium complexes that actually catalyse hydroformylation.

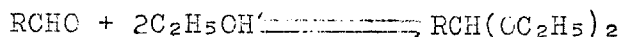
B) Hydroformylation of alkenes using trans-chlorocarbonyl bis(triphenylphosphine)rhodium(I) and similar complexes

(i) Qualitative studies. This work began with studies on chlorotris(triphenylphosphine)rhodium(I), which is an exceedingly effective catalyst for the homogeneous hydrogenation of olefins (61), it had already been shown (62) that triphenylphosphine, pyridine and stannous chloride complexes of rhodium catalysed the hydroformylation of olefins under quite mild conditions (ca. 70°, 100 atms.). Since it was known that $\text{RhCl}(\text{PPh}_3)_3$ and carbonmonoxide react rapidly (61) to give $\text{trans-RhCl}(\text{CO})\text{-(PPh}_3)_2$ and that triphenylphosphine complexes of rhodium(III) are reduced to this compound by carbonmonoxide and hydrogen, it appeared that the carbonyl species was the actual catalyst. This complex may not only be recovered quantitatively from the reaction mixture when hydroformylating with $\text{RhCl}(\text{PPh}_3)_3$ but it can be used directly at temperatures > 55° and pressures > 10 atms.

When carrying out hydroformylation reactions with these complexes carbonmonoxide was always introduced into the catalyst/olefin solution before addition of hydrogen to avoid hydrogenation and isomerisation of the olefin (see Page 50). The reactions were usually carried out in benzene, when the product was always the aldehyde, none of the corresponding alcohol or acetal formed by the reactions



was detected. If however the reaction is carried out in ethanol or a benzene-ethanol mixture some of the aldehyde is recovered as its diethyl acetal



The use of ethanol was avoided where possible as the formation of acetals is an undesirable complication in the estimation of aldehyde. Although none of the aldehyde was reduced to alcohol during the hydroformylation, the corresponding alcohols could be obtained by reduction of the reaction mixtures at the end of the hydroformylation by the use of H_2 alone at pressures above 50 atms. and temperatures above 100° .

A number of olefins were hydroformylated using trans- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, There was no significant difference in the ratios of straight- to branch-chain aldehyde when using alk-1-enes remaining ca. 2.7, except in the case of propene, (see Table 2).

Using complexes of general formulae $\text{RhX}(\text{CO})(\text{PR}_3)_2$ where $\text{X} = \text{Cl}, \text{Br}$ or I , and $\text{R} =$ aryl or alkyl, for the hydroformylation of pent-1-ene there was no significant difference in the ratio of straight- to branch-chain aldehyde, some variation in yield, i.e. rate of reaction was observed. However the ratio of straight- to branch-chain aldehyde was approximately halved when the corresponding triphenylarsine complex $\text{RhCl}(\text{CO})(\text{AsPh}_3)_2$ was used as catalyst (see Table 3).

Although very little hydroformylation occurred using $\text{RhCl}_3 \cdot (\text{CO})(\text{PPh}_3)_2$, ca. 50% of it was reduced to the normally effective

hydroformylation catalyst $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ during the reaction.

TABLE 2. Hydroformylation of various olefins using trans-bis(triphenylphosphine)chlorocarbonylrhodium(I). Catalyst 7.2×10^{-5} mole in benzene, (4ml.). Olefin 0.027 mole, (3ml.). Temperature 80° ; time 17 hrs. Total pressure 100 atms. with $\text{CO}:\text{H}_2$ ratio 1:1.

Alkene	Conversion %	Aldehyde:
		<u>Straight-chain</u> <u>Branch-chain</u>
propene	100	1.8
but-1-ene	100	2.7
pent-1-ene	100	2.8
hex-1-ene	100	2.8
cis/trans pent-2-ene	100	all branched
cis/trans hex-2-ene	100	all branched
cyclohexene	43 ^a	cyclohexaldehyde

^a Unreacted olefin was present as cyclohexene only.

TABLE 3. Hydroformylation of pent-1-ene using trans-halogeno-carbonylbis(tertiaryphosphine)rhodium(I) complexes. Catalyst, 7.2×10^{-5} mole in benzene, (4ml.). Pent-1-ene, 0.027 mole (3ml.) Temperature 70° ; time 16 hrs. Total pressure 100 atm. CO:H₂=1:1.

Catalyst	Conversion%	Aldehyde: <u>straight</u> branched
RhCl(CO)(PPh ₃) ₂	100	2.7
RhCl(PPh ₃) ₃ ^a	100	2.8
RhBr(CO)(PPh ₃) ₂	100	2.8
RhI(CO)(PPh ₃) ₂	83 ^b	2.7
RhCl(CO)(AsPh ₃) ₂	100	1.3
RhCl(CO)(PEt ₃) ₂	88 ^b	2.6
RhCl(CO)(PEt ₂ Ph) ₂	92 ^b	2.7
RhCl(CO)(P(p-MeC ₆ H ₄) ₃) ₂	100	2.8
RhCl(CO)(P(p-MeCC ₆ H ₄) ₃) ₂	100	2.7
RhCl(CO)(P(p-FC ₆ H ₄) ₃) ₂	100	2.7
RhCl ₃ (CO)(PPh ₃) ₂	5 ^b	-
RhCl ₃ (PEt ₂ Ph) ₃	none detected	-
Rh ₂ (CO) ₄ Cl ₂	80 ^c	0.7
RhCl ₃ .3H ₂ O ^d	ca. 80 ^c	0.7

- a) RhCl(CO)(PPh₃)₂ recovered at end of reaction
- b) Recovered olefin was exclusively pent-1-ene
- c) Recovered olefin was predominantly cis/trans pent-2-ene
- d) Reaction carried out in benzene-ethanol, presumably an in situ formation of Rh₂(CO)₄Cl₂ occurs when the carbon-monoxide is introduced; part of the hexaldehyde and α -methyl-valeraldehyde was present as their diethyl acetals.

(2) Quantitative studies. These were carried out by hydroformylating a solution of pent-1-ene (25 ml., 0.229 mole) in benzene (225 ml.), using an autoclave fitted with a device for removing liquid samples. (See experimental for full details of procedure). Samples were taken at intervals and the concentration of pent-1-ene in these samples was determined by G.l.c. Taking the concentration of pent-1-ene at time 0 to be a mole L^{-1} , and concentration at time t to be $a-x$ mole L^{-1} plots of t vs $\ln \frac{a}{a-x}$ were obtained, where x is mole L^{-1} of pent-1-ene converted to aldehyde.

a). Effect of catalyst concentration. Three hydroformylations of pent-1-ene were carried out at 70° under a total pressure of 1000 p.s.i. (67 atms.). The quantities of $\text{trans-RhCl(CO)(PPh}_3)_2$ used were; 200 mg. (1.16×10^{-3} mole L^{-1}), 400 mg. (2.32×10^{-3} mole L^{-1}) and 800 mg. (4.64×10^{-3} mole L^{-1}). The results are tabulated in table 4.

From figure 1 (page 37) it can be observed that the plots of t vs $\ln \frac{a}{a-x}$ do not pass through the origin, i.e. there is a substantial inhibition period.

The plots of the slopes of the lines (k), 1.16×10^{-3} mole L^{-1} , 1.36×10^{-5} ; 2.32×10^{-3} mole L^{-1} , 2.78×10^{-5} ; and 4.64×10^{-3} mole L^{-1} , 5.71×10^{-5} sec^{-1} : (Figure 2 page 38) shows that the rate is pseudo first order with respect to catalyst over the range of concentration studied. The ratio of straight- to branch-chain aldehyde remained constant for all three concentrations. In all samples the hydrocarbon was

present exclusively as pent-1-ene.

TABLE 4. Effect of concentration of $\text{trans-RhCl(CO)(PPh}_3)_2$ on rate of hydroformylation. Pent-1-ene (25 ml., $0.916 \text{ mole L}^{-1}$) in benzene (225 ml.) Temperature 70° . Total pressure 1000 p.s.i. $\text{H}_2:\text{CO} = 1:1$.

(i) $1.16 \times 10^{-5} \text{ mole L}^{-1}$

Time hrs.	x	$\ln \frac{a}{(a-x)}$	t (sec. $\times 10^{-3}$)
1	0.014	0.0039	3.6
2	0.049	0.0555	7.2
3	0.067	0.0762	10.8
4	0.102	0.1177	14.4
5	0.107	0.1241	18.0
6.5	0.203	0.2508	23.4
7	0.203	0.2508	25.2
8	0.247	0.3141	28.8
9	0.283	0.3696	32.4
10.1	0.315	0.4212	36.4

(ii) 2.32×10^{-3} mole L^{-1}

Time hrs.	x	$\ln \frac{a}{(a-x)}$	t (sec. $\times 10^{-3}$)
1	0.022	0.0246	3.6
2	0.153	0.1831	7.2
3	0.124	0.1458	10.8
4	0.213	0.2646	14.4
5	0.269	0.3478	18.0
5.5	0.301	0.3984	19.8
6	0.331	0.4486	21.6
6.5	0.372	0.5214	23.4

(iii) 4.64×10^{-3} mole L^{-1}

Time hrs.	x	$\ln \frac{a}{(a-x)}$	t (sec. $\times 10^{-3}$)
1	0.052	0.0583	3.6
2	0.155	0.1887	7.2
3	0.354	0.4878	10.8
4	0.440	0.6543	14.4
4.75	0.513	0.8205	17.1
5.5	0.583	1.0119	19.8
6.25	0.636	1.1850	22.5
7	0.677	1.3436	25.2

Figure 1. Effect of Concentration of $\text{trans-RhCl}(\text{CO})(\text{PPh}_3)_2$.

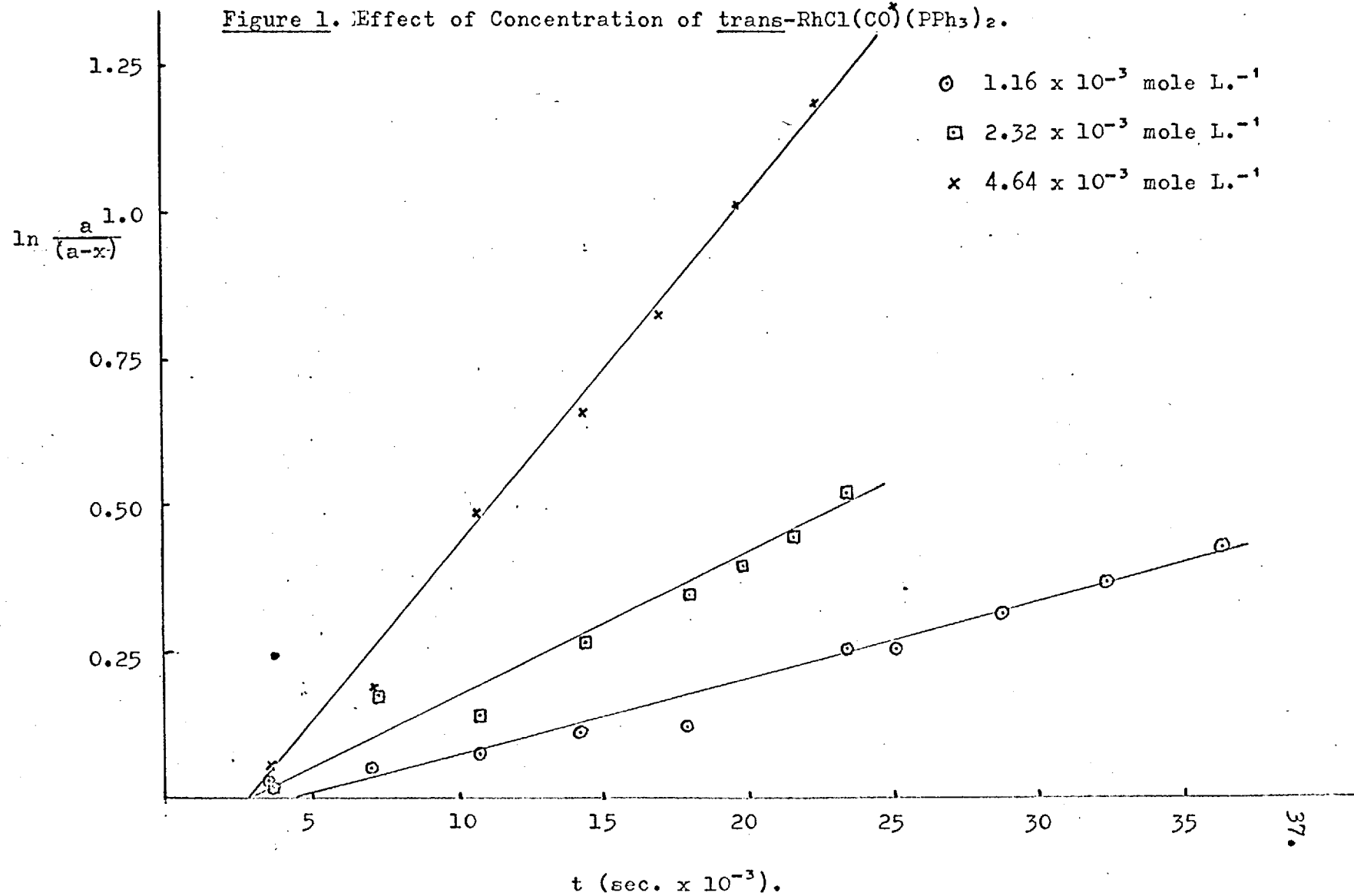
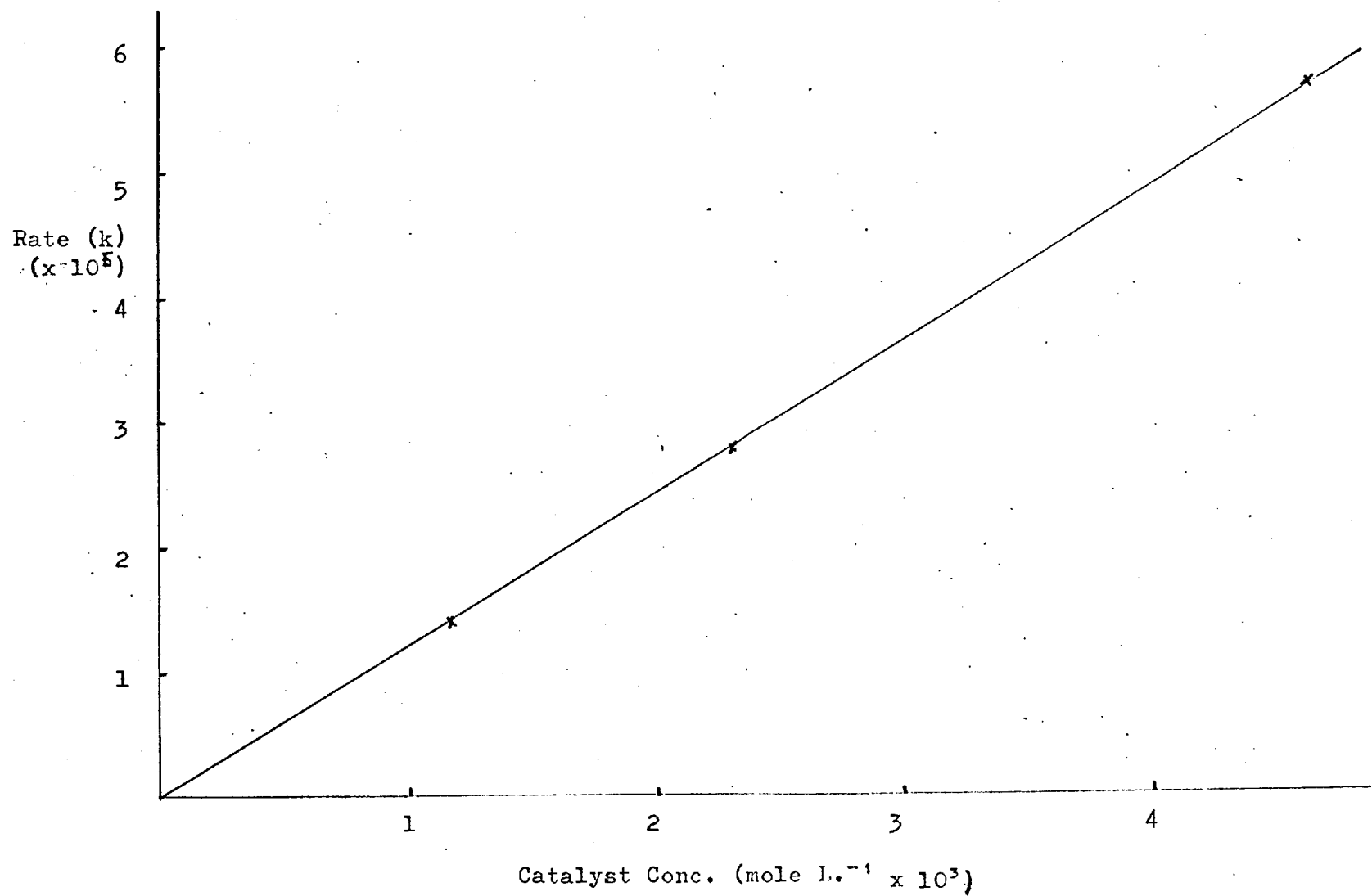


Figure 2. Rate (k) vs trans-RhCl(CO)(PPh₃)₂ Concentration.



b). Effect of increasing the partial pressure of carbonmonoxide.

Two hydroformylations of pent-1-ene were carried out under a total pressure of 1200 p.s.i. (80 atms.). The gas mixtures used were $\text{H}_2:\text{CO}:\text{N}_2$, 1:1:1 and $\text{H}_2:\text{CO}$, 1:2. Nitrogen was used in the first reaction so that the total pressure was the same in both cases. The results are tabulated in Table 5.

TABLE 5. Effect of partial pressure of carbonmonoxide.

Pent-1-ene (25 ml., 0.916 mole L^{-1}) in benzene (225 ml.).

Catalyst trans- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (800 mg. 4.64×10^{-3} mole L^{-1}).

Temperature 70° . Total pressure 1200 p.s.i.

(i) $\text{H}_2:\text{CO}:\text{N}_2$, 1:1:1.

Time hrs.	x	$\ln \frac{a}{a-x}$	t (sec. $\times 10^{-3}$)
2	0.093	0.1069	7.2
3	0.192	0.2351	10.8
4	0.313	0.4180	14.4
5.3	0.420	0.6135	19.2
6.3	0.512	0.8188	22.8

(ii) H₂:CO, 1:2.

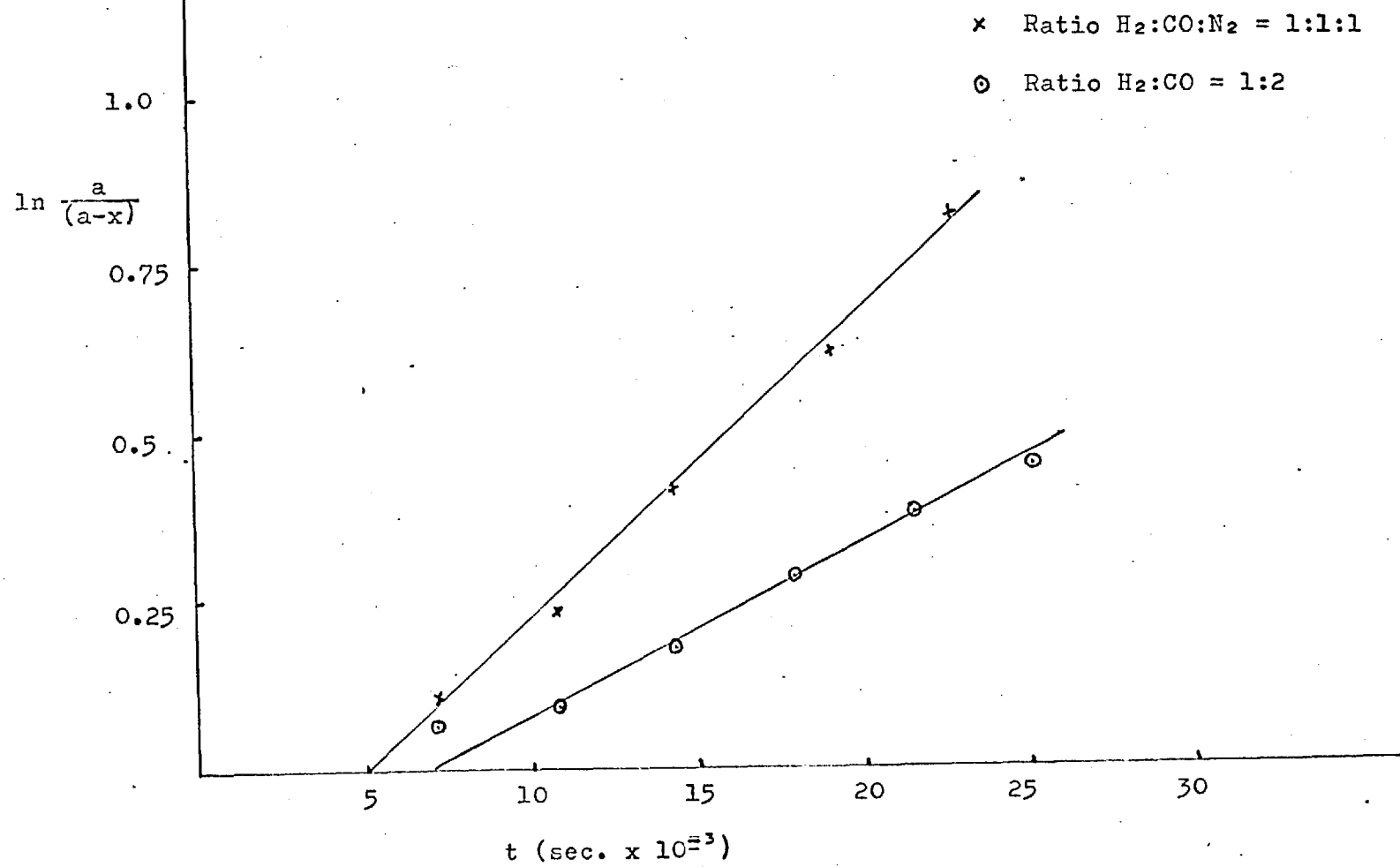
Time hrs.	x	$\ln \frac{a}{a-x}$	t (sec. x 10 ⁻³)
2	0.056	0.0631	7.2
3	0.080	0.0919	10.8
4	0.146	0.1739	14.4
5	0.222	0.2777	18.0
6	0.284	0.3710	21.6
7	0.329	0.4447	25.2

From Figure 3 (Page 41) it can be observed that again the plots of t vs. $\ln \frac{a}{a-x}$ do not pass through the origin. The plots of the slopes of the lines (k) show that increasing the partial pressure of carbonmonoxide has an inhibiting effect on the reaction, $k = 2.5 \times 10^{-5} \text{ sec}^{-1}$ for the reaction with the high partial pressure of carbonmonoxide, which is little more than half that found for the reaction where the partial pressure of the CO and H₂ were equal, ($k = 4.5 \times 10^{-5}$).

c) Effect of variations of X in trans-RhX(CO)(PPh₃)₂

Two experiments were carried out using trans-RhBr(CO)-(PPh₃)₂ and trans-RhI(CO)(PPh₃)₂. The same catalyst concentration ($4.64 \times 10^{-3} \text{ mole. l}^{-1}$) and the same conditions were employed as outlined from trans-RhCl(CO)(PPh₃)₂ in Table 5(i).

Figure 3. Effect of Increasing the Partial Pressure of Carbonmonoxide.



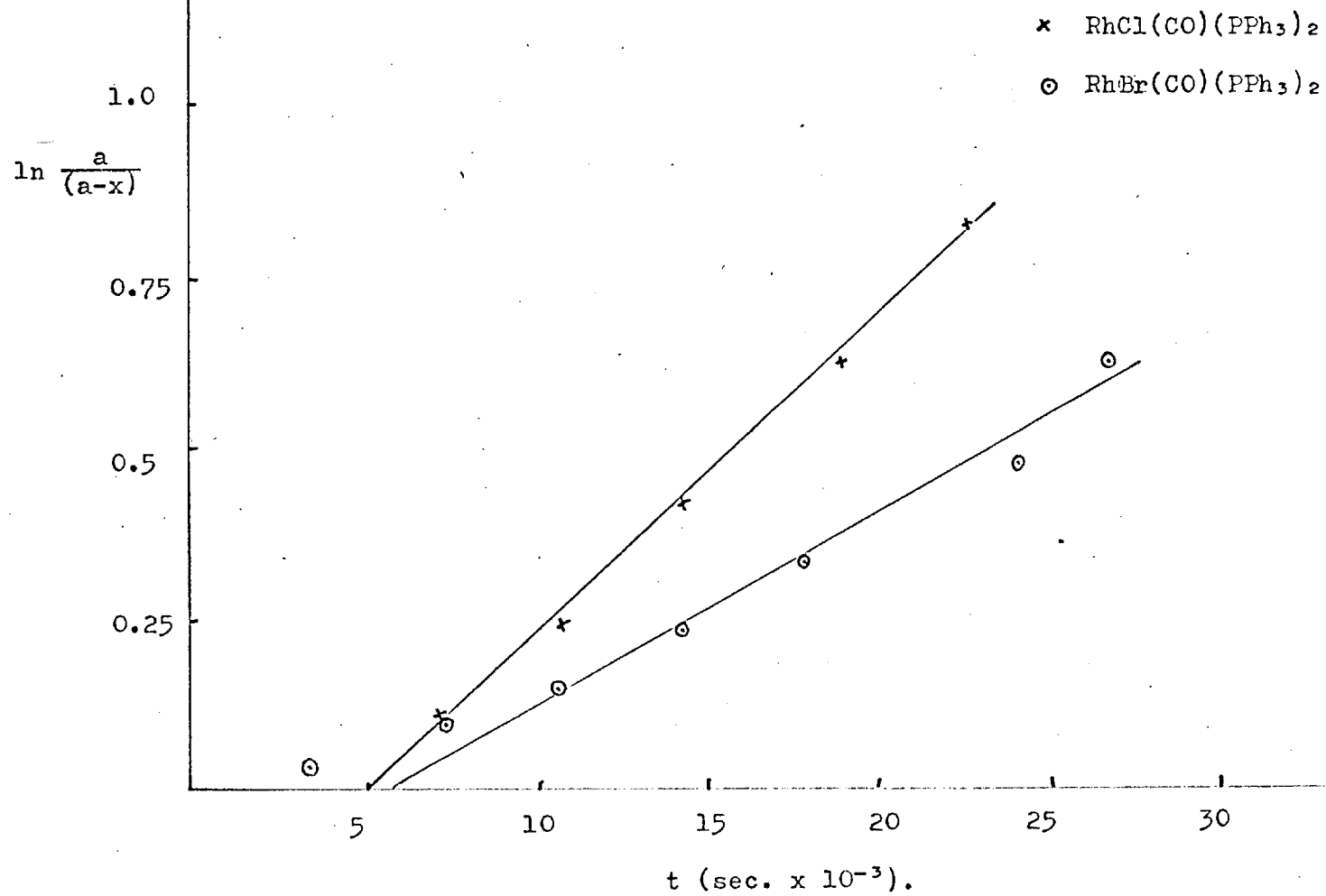
The results for $\text{trans-RhBr(CO)(PPh}_3)_2$ are tabulated in Table 6. The rate of reaction using $\text{trans-RhI(CO)(PPh}_3)_2$ was too slow to obtain a plot as only 15% of the pent-1-ene was converted to aldehydes after 6 hours, compared with 35% and 50% for the bromide and chloride respectively.

TABLE 6. $\text{Trans-RhBr(CO)(PPh}_3)_2$ as hydroformylation catalyst. Pent-1-ene (25 ml., 0.916 mole. L^{-1}) in benzene (225 ml.) catalyst $\text{trans-RhBr(CO)(PPh}_3)_2$ (850 mg. 4.64×10^{-3} mole. L^{-1}). Temperature 70° . Total pressure 1200 p.s.i. $\text{H}_2:\text{CO}:\text{N}_2 = 1:1:1$.

Time hrs.	x	$\ln \frac{a}{a-x}$	t (sec. $\times 10^{-3}$)
1	0.27	0.296	3.6
2	0.096	0.1104	7.2
3	0.125	0.1467	10.8
4	0.192	0.2351	14.4
5	0.261	0.3352	18.0
6.75	0.403	0.5800	24.3
7.5	0.426	0.6254	27.0

A comparison of plots of $\ln \frac{a}{a-x}$ vs t for x = Cl and Br is shown in Figure 4. The rate of reaction is in the order x = Cl, > Br, > I. The ratio of straight- to branch-chain aldehyde remained constant and no isomerisation or hydrogenation of the pent-1-ene occurred.

Figure 4. Effect of Variation of X in trans-RhX(CO)(PPh₃)₂



(d) Effect of variation of R in $\text{trans-RhCl(CO)(PR}_3)_2$. Three complexes were used, R = p-FC₆H₄-, C₆H₅-, and p-MeOC₆H₄-. These three were chosen so that no steric factors would be introduced in the change of ligand, but changes of π -acidity would be introduced. The complexes when R = p-FC₆H₄-, and R = p-MeOC₆H₄- were run at the same catalyst concentration and conditions as outlined for $\text{trans-RhCl(CO)(PPh}_3)_2$ in Table 5. The results are tabulated in Table 7.

TABLE 7. Effect of variation of R in $\text{trans-RhCl(CO)(PR}_3)_2$ pent-1-ene (25 ml., 0.916 mole. L⁻¹) in benzene (225 ml.). Temperature 70°. Total pressure 1200 p.s.i. H₂:CO:N₂ = 1:1.

(i) $\text{trans-RhCl(CO)(P(p-FC}_6\text{H}_4)_3)_2$

Time hrs.	x	$\ln \frac{a}{(a-x)}$	t (sec. x 10 ⁻³)
2	0.074	0.0846	7.2
3	0.093	0.1069	10.8
4	0.158	0.1887	14.4
5	0.184	0.2239	18.0
6	0.224	0.2806	21.6
7	0.313	0.4179	25.2

(ii) trans-RhCl(CO)(P(p-MeOC₆H₄)₃)₂

Time hrs.	x	$\ln \frac{a}{(a-x)}$	t (sec. x 10 ⁻³)
2	0.1337	0.1579	7.2
3	0.2382	0.4466	10.8
4	0.3939	0.5817	14.4
4.5	0.4351	0.6439	16.2
5	0.5102	0.8135	18.0
5.5	0.5551	0.9309	19.8
6	0.5899	1.0331	21.6
6.5	0.6385	1.1960	23.4

From figure 5 (page 46) it can be seen that the order of reaction is p-MeOC₆H₄- > C₆H₅- > p-FC₆H₄-. The ratio of straight- to branch-chain aldehyde remained ca. 2.7 in all three cases, and no isomerisation of the pent-1-ene occurred.

(e) Effect of temperature. A reaction was carried out at 80°, the same olefin concentration, catalyst concentration and pressure was used as outlined in table 4. (See Table 8).

Increasing the temperature by 10° approximately doubles the rate of reaction (see figure 6, page 47). The slopes of the plots (k) at 70° and 80° were 2.78 x 10⁻⁵ sec⁻¹ and 5.71 x 10⁻⁵ sec⁻¹, respectively. The inhibition period was still present at the higher temperature, but the ratio of straight- to branch-chain aldehyde was not affected, neither was there any isomerisation or hydrogenation of the pent-1-ene.

Figure 5. Effect of Variation of R- in $\text{trans-RhCl(CO)(PR}_3)_2$.

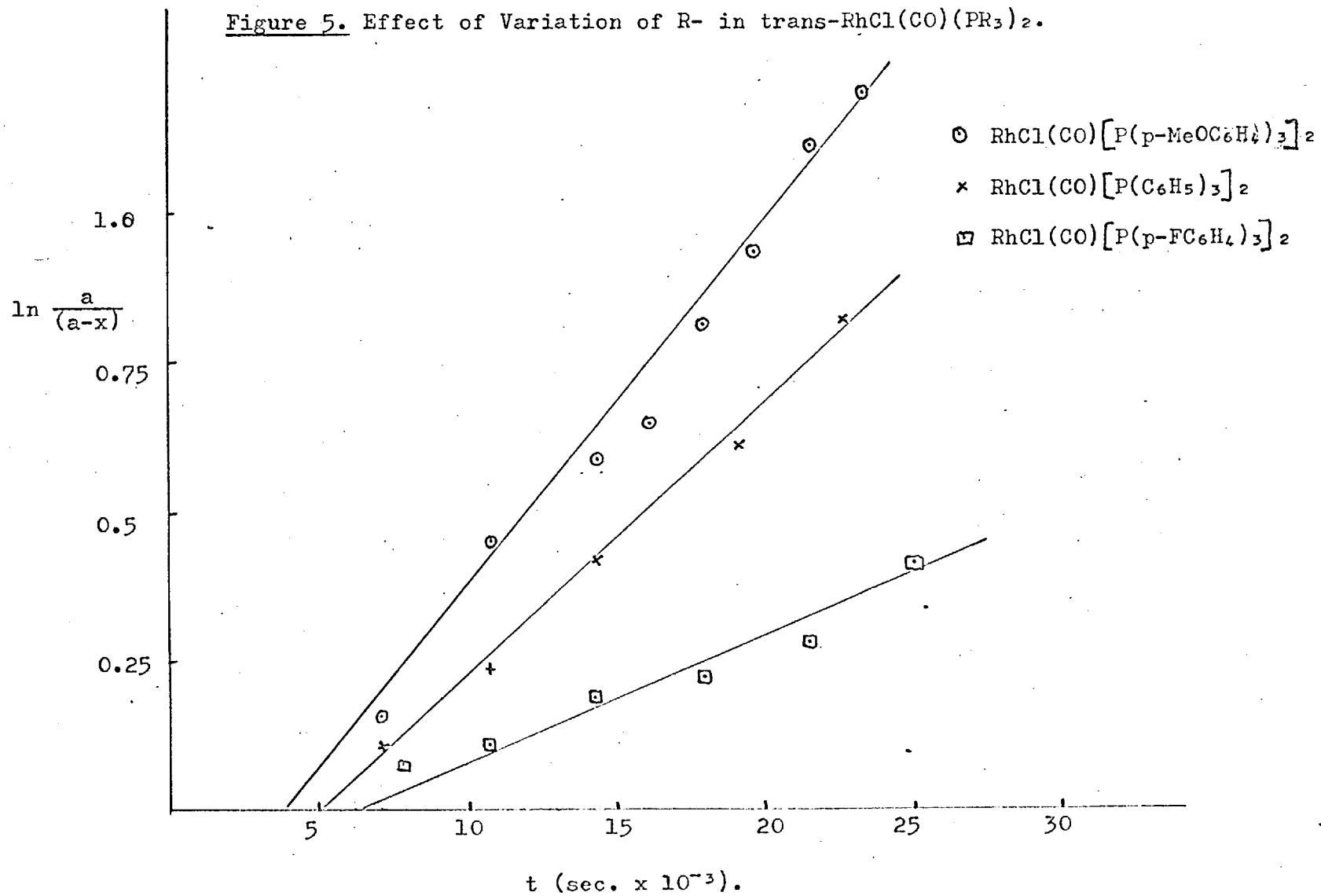


TABLE 8. Effect of temperature. Pent-1-ene (25 ml., 0.196 mole L⁻¹) in benzene (225 ml.) Temperature 80°. Total pressure 1000 p.s.i. H₂:CO = 1:1.

Time hrs.	x	$\ln \frac{a}{(a-x)}$	t (sec. x 10 ⁻³)
1	0.049	0.0555	3.6
2	0.109	0.1267	7.2
3	0.223	0.2791	10.8
4	0.313	0.4550	14.4
4.5	0.425	0.6239	16.2
5.5	0.514	0.8238	19.8

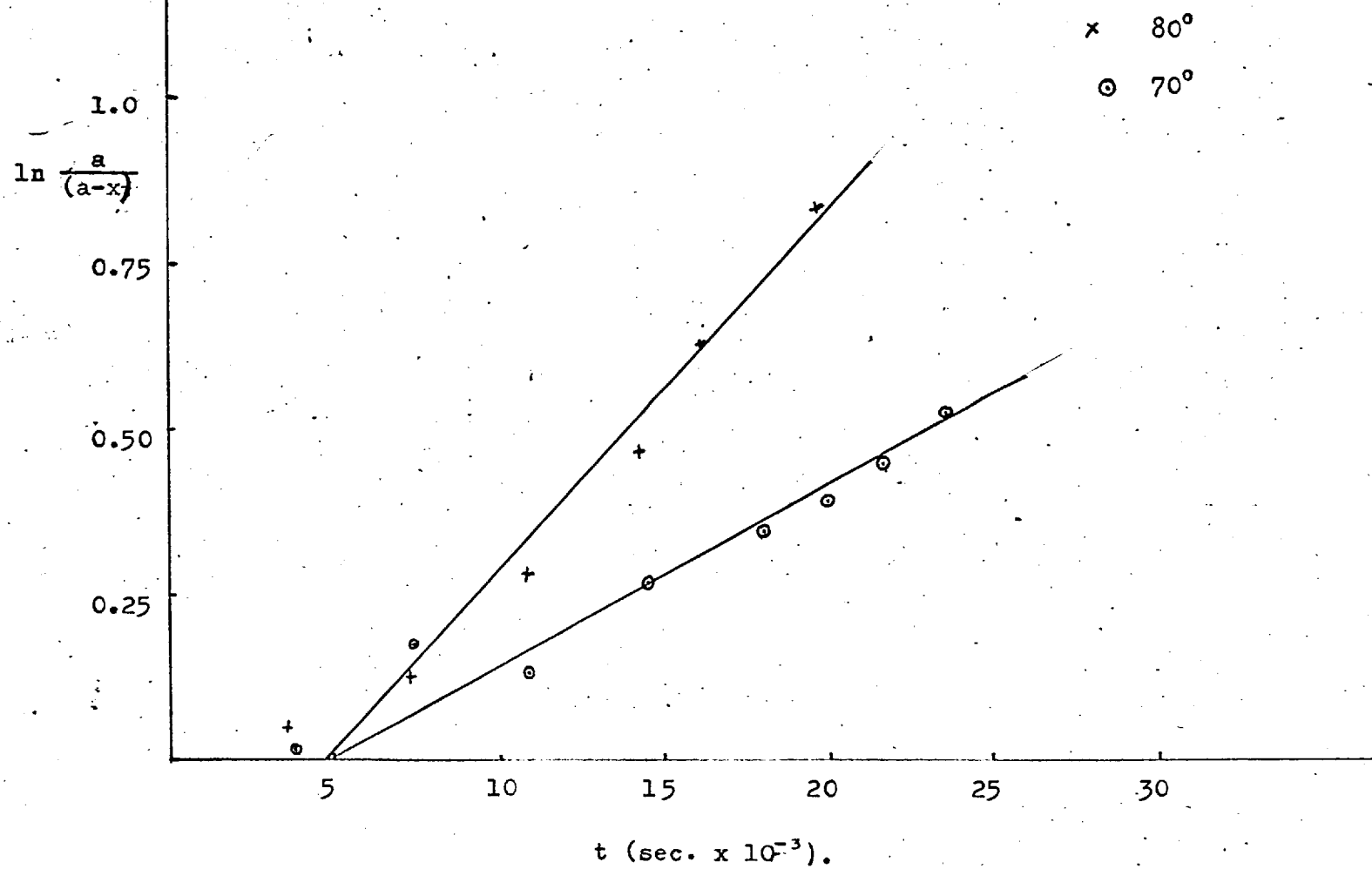
(3) Effect of additives.

(a) Carbondisulphide. To an hydroformylation of pent-1-ene catalysed by RhCl(CO)(PEt₂Ph)₂ was added carbondisulphide.

The solution at the end of the reaction was the normal yellow colour, no red coloration due to the formation of the diethylphenylphosphine-carbondisulphide complex was observed. The diethylphenylphosphine analogue was used because triphenylphosphine does not form a complex with carbondisulphide.

(b) Propyliodide. To an hydroformylation of pent-1-ene catalysed by RhCl(CO)(PEt₂Ph)₂ was added propyliodide. At the end of the reaction no diethylphenylpropylphosphonium iodide was recovered from the reaction mixture. The diethylphenylphosphine was used because triphenylphosphine only undergoes quaternisation reactions with great difficulty.

Figure 6. Effect of Temperature.



(c) Hydrogen chloride. Hydrogen chloride gas was passed for a few seconds into a solution of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (50 mg., 7.2×10^{-5} mole.) and pent-1-ene (3 ml., 0.027 mole.) in benzene (4 ml.). After heating this solution at 80° for 16 hours under a total pressure of 100 atms. with $\text{CO}:\text{H}_2$ ratio of 1:1, no aldehyde was detectable by G.l.c.

(d) Hydrogen chloride acceptors. Addition of organic bases, e.g. triethylamine and pyridine causes a great increase in rate of hydroformylation using $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ as catalyst, the ratio of straight to branch chain aldehyde is however unaltered. Two reactions in the autoclave fitted with the sampling device were carried out using $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (400 mg., 4.64×10^{-3} mole. L^{-1}), pent-1-ene (25 ml., 0.916 mole., L^{-1}) and 225 ml. solvent, at 70° under a total pressure 1200 p.s.i., $\text{H}_2:\text{CO}:\text{N}_2 = 1:1:1$. Using pure pyridine as solvent, 95% conversion of pent-1-ene to hexaldehydes took place in 105 min.; using triethylamine 0.7 mole. L^{-1} in benzene as solvent, 95% conversion took place in 75 minutes; under these conditions in pure benzene 50% conversion takes place in 360 minutes. The reaction is almost complete during the time of the inhibition period observed in the reactions without base.

Addition of base also lowers the temperature at which hydroformylation is catalysed by $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, ca. 5% of the pent-1-ene was hydroformylated when a solution of $\text{RhCl}(\text{CO})-$

(PPh₃)₂ (50 mg., 7.2×10^{-5} mole.), pent-1-ene (3 ml., 0.027 mole.) and triethylamine (2 g., 0.02 mole.) in benzene (4 ml.), was kept at room temperature 20-25° for 18 hours under 100 atms. CO + H₂ (ratio = 1:1). There is no detectable hydroformylation in the absence of amine under these conditions.

In all the above experiments the ratio of straight- to branch- chain aldehyde was not significantly different from that obtained in the absence of amine, also the unreacted hydrocarbon was exclusively pent-1-ene.

At the end of these base assisted hydroformylations the reaction mixture was very pale yellow, in contrast to the deeper yellow solution of RhCl(CO)(PPh₃)₂ observed in the absence of base. Very fine white needle like crystals were observed in suspension in the reaction mixture which were removed by filtration and washed with hot benzene. Identification by M.Pt. and I.R. showed them to be, in the case of the pyridine assisted reactions pyridenium-hydrochloride and in the case of the triethylamine reactions, triethylammoniumchloride. The pale yellow solutions however rapidly darkened on exposure to air, turning black; isolation of the complex present in this pale yellow solution has not been possible. However if an excess of triphenylphosphine is added at the start of the reaction, the solution is no longer air sensitive at the end of the reaction and the well known complex RhH(CO)(PPh₃)₃ (63) can be isolated. Repeating

the experiment with $\text{RhBr}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhI}(\text{CO})(\text{PPh}_3)_2$ gives $\text{RhHCO}(\text{PPh}_3)_3$ and triethylammonium bromide and iodide respectively.

No conversion of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ to $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ occurred when hydrogen was passed through a refluxing solution of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ at 1 atm. in benzene-triethylamine solutions in the presence of excess triphenylphosphine.

If a benzene solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is treated with HCl gas at 1 atm. it is rapidly and quantitatively converted to $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. Also treatment of a solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (50 mg., 5.4×10^{-5} mole.) with triethylammonium-chloride (100 mg., 7.3×10^{-4} mole.) in triethylamine (2 ml., 0.014 mole.) and benzene 4 ml. for 18 hours at 70° under H_2 (60 atms.) a mixture of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ is obtained.

4) Isomerisation of olefins with trans-chlorocarbonylbis-(triphenylphosphine)rhodium(I).

In the presence of hydrogen alone trans- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ in benzene catalyses hydrogenation and isomerisation of alkenes under conditions that readily give hydroformylation, i.e. 60 atms. and 70° ; even under 1 atm. of hydrogen at 70° in sealed glass tubes double bond migration is catalysed (Table 9).

This isomerisation of olefin is suppressed in the presence of carbonmonoxide, no pent-2-one has been detected in any of the samples analysed during the quantitative studies.

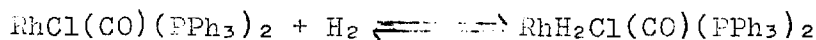
TABLE 9. Hydrogenation and isomerisation of pent-1-ene using $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ in benzene at 70° . Molar ratio catalyst/pent-1-ene = 0.0027. Yields %.

Conditions	Pent-1-ene	Pent-2-ene	Pentene
60 atm. H_2 , 1.25 hrs.	-	90	10
60 atm. CO , 1.25 hrs.	100	-	-
1 atm. H_2 , 18 hrs.	10	90	-
1 atm. N_2 , 18 hrs.	100	-	-

$\text{Rh}_2(\text{CO})_4\text{Cl}_2$ however catalyses the isomerisation of alkenes in the presence of hydrogen-carbonmonoxide mixtures (see Table 3, Page 33). Also in an hydroformylation using $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ 7.2×10^{-5} mole. and pent-1-ene (3 ml. 0.027 mole.) at 70° under 100 atms. H_2 + CO ratio 1:1, after 6 hours reaction, the unreacted olefin (74%) consisted of cis-pent-2-ene (26%) trans-pent-2-ene (67%) and pent-1-ene (7%).

5) Discussion.

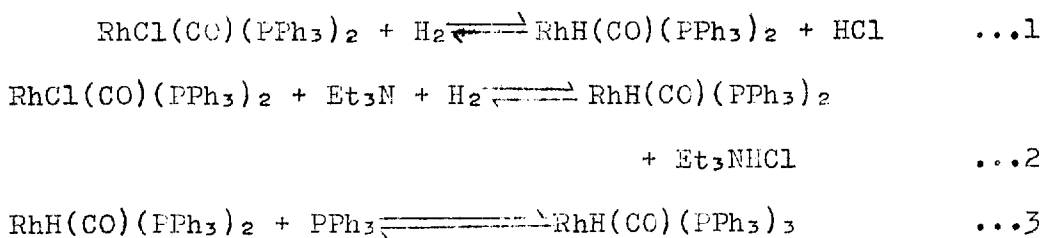
If it is assumed that the first reaction of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ under hydroformylation conditions is (by comparison with the iridium analogue (64)) addition of hydrogen.



The rhodium is then co-ordinately saturated and there^{iv} is no point of attack for olefin, so it would appear that one or more of the ligands must be dissociated from the complex before reaction with olefin can occur. Loss of carbonmonoxide would

be surprising under the high pressures of carbonmonoxide employed, also no evidence for loss of phosphine was obtained.

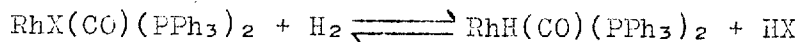
The inhibition period always observed in the absence of base must be compared with the inhibition period observed (12) in the cobalt system when using metallic cobalt. It suggests that $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ is not the active catalyst. The reactions in the presence of HCl (when no hydroformylation occurred) and of organic base (when the catalytic activity was greatly enhanced, and base hydrochloride was formed) clearly show that the following equilibria are set up in the reaction mixture, and that hydroformylation, hydrogenation and isomerisation reactions are due to the formation of the hydride species.



In the absence of amine equilibrium (1) will be set up, but on opening the autoclave and releasing the hydrogen, only $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ will be recovered. Equilibrium (2) will be set up in the presence of amine but in this case cooling and releasing the hydrogen will lead to recovery of the equilibrium mixture. The dissociation of $\text{Rh}(\text{CO})\text{H}(\text{PPh}_3)_3$ (3) is well known (63).

As the same active catalytic intermediate $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ is formed regardless of the nature of X in $\text{RhX}(\text{CO})(\text{PPh}_3)_2$ it

must be concluded that effect of varying X is to move the position of the equilibrium in the reaction.



Whether the variation in catalytic activity observed when R in $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ was changed is due to it having an effect on the position of the equilibrium in this reaction, or whether the nature of R in $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ affects the catalytic activity of this species is not known.

Study of the ruthenium complex $\text{RuCl}_2(\text{PPh}_3)_3$ has yielded another example of base catalysed hydride formation (65).

Although in the presence of hydrogen alone $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ catalyses both isomerisation and hydrogenation of olefins, no isomerisation of olefins takes place in the presence of carbon-monoxide, so the branch-chain aldehyde is not formed by isomerisation of alk-1-ene to give alk-2-ene followed by hydroformylation of the alk-2-ene to give branch-chain aldehyde. This is not however the case with $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ when the unreacted olefin is recovered as the alk-2-ene; the greater yield of branch-chain aldehyde, here as in the reactions using rhodium carbonyl (58) is evidently due to more facile isomerisation, followed by hydroformylation of the isomerised olefins.

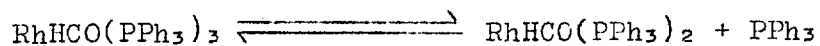
There is no isomerisation of straight-chain aldehydes under hydroformylation conditions in the presence of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, so that branch-chain aldehyde does not arise this way.

A) Hydroformylation of Alkenes using hydridocarbonyltris-(triphenylphosphine)rhodium(I)

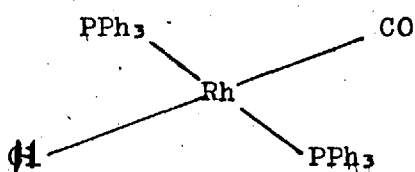
(1) Preparation and reactions of hydridocarbonyltris(triphenylphosphine)rhodium(I).

Hydridocarbonyltris(triphenylphosphine)rhodium(I) was first prepared by Vaska (63) by the addition of hydrazine to a suspension of trans-chlorocarbonylbis(triphenylphosphine)-rhodium(I) in a solution of excess triphenylphosphine in ethanol. It was however found that the reaction proceeded much more quickly and smoothly if sodium borohydride was used instead of hydrazine. The iridium analogue hydridocarbonyltris(triphenylphosphine)iridium(I) is also prepared more easily by the addition of sodium borohydride rather than hydrazine to a suspension of trans-chlorocarbonylbis(triphenylphosphine)iridium(I) in a solution of excess triphenylphosphine in ethanol. Vaska also showed by molecular weight determinations that whereas the iridium analogue was undissociated in solution the rhodium analogue was highly dissociated in benzene solution giving molecular weights approximately half that calculated.

The n.m.r. of the rhodium analogue gives a broad line at τ 19.9, this hydride line is undoubtedly broad due to the rapid equilibrium in solution:-

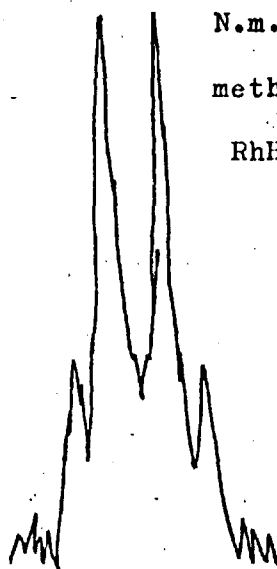


If the n.m.r. is examined in a low M.Pt. solvent, e.g. CH_2Cl_2 at low temperature, below -10° a quartet with relative intensities 1:3:3:1 split by 14 c.p.s. is observed (see Figure 7). This is consistent with a square planar trans structure for the dissociated species.



The hydride being split by the rhodium and the two cis phosphines.

FIGURE 7.

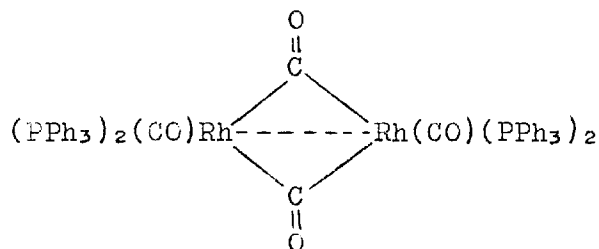


N.m.r. spectra at 100 Mc/sec. in methylene chloride at -20° of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$.

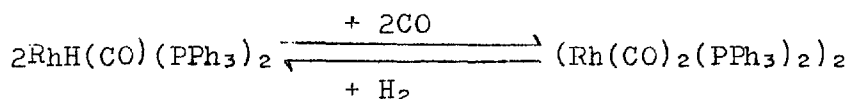
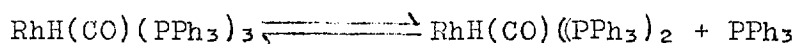
LaPlaca (66) has shown the undissociated $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, in the solid state to have a trigonal bipyramid structure with the three phosphines in the plane and the hydrogen and carbonmonoxide above and below the plane.

When carbonmonoxide is passed through a solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ in benzene the high field line due to the hydride in the n.m.r. decreases in size and finally disappears. The solution I.R. shows a strong absorption at 1770 cm^{-1} besides absorption at $1900\text{--}2000\text{ cm}^{-1}$. If the passage of carbonmonoxide is continued and the benzene allowed to evaporate away, a yellow crystalline solid is obtained. This compound is very unstable and elemental analysis has not been possible. The I.R. in nujol shows $\sqrt{\text{CO}}$ 2017 (w) , 1992 (str) , 1800 (w) , $1770\text{ (str)}\text{ cm}^{-1}$, no Rh-H stretch was obtained. The interaction of $\text{RhD}(\text{CO})(\text{PPh}_3)_3$ with CO gives a compound with identical spectrum. By examination of the gas above the solution using mass spectrometry, it was shown that deuterium^e is lost when carbonmonoxide interacts with $\text{RhD}(\text{CO})(\text{PPh}_3)_3$. If however after carbonmonoxide has been passed for ca 15 min. and the solution obtained which shows the strong absorption at 1770 cm^{-1} , hydrogen is passed through the solution, or if the yellow unstable compound (see above) is immediately after filtration dissolved in a solution of triphenylphosphine in benzene and hydrogen passed through the solution the parent compound $\text{RhH}(\text{CO})-(\text{PPh}_3)_3$ is obtained.

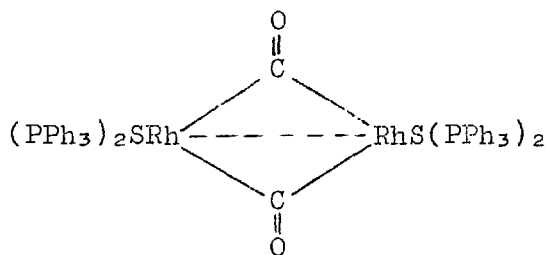
The unstable yellow complex is apparently a dimeric species formulated as:



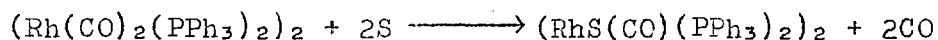
isoelectronic with dicobalt octacarbonyl (67), and is formed by the reversible reactions.



If carbonmonoxide is passed through a benzene solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ for ca 15 min., ethanol added and the solution evaporated in a stream of nitrogen, a deep red solution is obtained, from which red crystals are precipitated. These crystals slowly decompose but not rapidly enough to prevent elemental analysis being carried out. It has only one carbonyl stretching frequency in the I.R. $\sqrt{\text{CO}} = 1720 \text{ cm}^{-1}$. A similar compound can be obtained if carbonmonoxide is passed through a solution of $\text{RhHCO}(\text{PPh}_3)_3$ in CH_2Cl_2 for ca 15 min., then the solution evaporated in a stream of nitrogen, the solution immediately turns red and red crystals are obtained, they also only have one carbonyl stretching frequency in the I.R. $\sqrt{\text{CO}} = 1739 \text{ cm}^{-1}$. These compounds are formulated as:

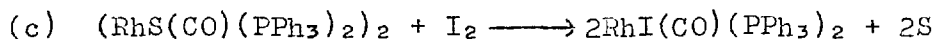
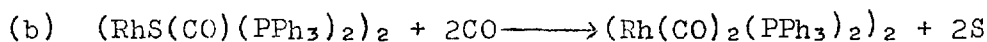
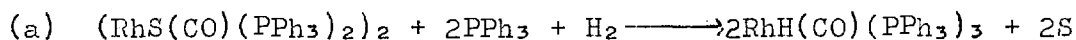


formed by the reaction



where S = ethanol or methylenechloride.

Evidence for the structure of these compounds has come from their reactions with hydrogen, carbonmonoxide and iodine. Benzene solutions of these complexes (a) in the presence of triphenylphosphine absorb one mole. of hydrogen per mole of complex to give $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, (b) absorb two moles of carbonmonoxide per mole. of complex to give a solution with an I.R. spectrum identical with that obtained by passing carbonmonoxide through a benzene solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and (c) interaction with iodine gives $\text{RhI}(\text{CO})(\text{PPh}_3)_2$



The n.m.r. of benzene solutions of $(\text{RhCH}_2\text{Cl}_2(\text{CO})(\text{PPh}_3)_2)_2$ and $(\text{RhEtOH}(\text{CO})(\text{PPh}_3)_2)_2$ give a spectrum of methylene chloride and ethanol respectively, identical with that observed for free

methylene chloride and ethanol in benzene solution, suggesting that the CH_2Cl_2 and ethanol is free in solution.

When carbonmonoxide is bubbled through a benzene solution of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$, a slow reaction takes place, and the stable complex $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ is obtained $\text{Ir-H} = 2030 \text{ cm}^{-1}$, $\nu \text{ CO}$ 1975 and 1910 cm^{-1} .

(2) Hydroformylation at elevated pressures.

Following the discovery of the formation of the hydride species by the interaction of hydrogen and trans- $\text{RhCl}(\text{CO})-(\text{PPh}_3)_2$, $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ was used directly as an hydroformylation catalyst. A solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (65 mg., 7.2×10^{-5} mole.) in pent-1-ene (3 ml. 0.027 mole.) and benzene (4 ml.) was kept at 25° for 17 hours under a total pressure of 100 atm. with $\text{CO}:\text{H}_2$ ratio 1:1, 25% of the pent-1-ene was hydroformylated, a ratio of straight- to branch- chain aldehyde of 3 was obtained.

Two reactions were carried out in an autoclave fitted with a device for taking samples during the reaction. Both reactions were carried out using a solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (260 mg. 1.16×10^{-3} mole. L^{-1}) and pent-1-ene (25 ml. 0.916 mole. L^{-1}) in benzene (225 ml.) at 50° . Both reactions were pressurised to 1200 p.s.i., with (a) $\text{CO}:\text{H}_2:\text{N}_2 = 1:1:1$ and (b) $\text{CO}:\text{H}_2 = 2:1$. The solution of $\text{Rh}(\text{CO})(\text{PPh}_3)_3$ was saturated with carbonmonoxide before adding olefin, to prevent isomerisation. Plots of $\ln \frac{a(a-x)}{x}$ vs t were obtained as before (Page 34).

The results are tabulated in Table 10.

TABLE 10. Hydroformylation of Pent-1-ene using $\text{RhH}(\text{CO})(\text{PPh}_3)_3$.
Catalyst (260 mg. 1.16×10^{-3} mole. L^{-1}) olefin 25 ml. (0.916 mole. L^{-1}), Benzene 225 ml. Temperature 70° . Total pressure 1200 p.s.i.

(i) $\text{H}_2:\text{CO}:\text{N}_2 = 1:1:1$.

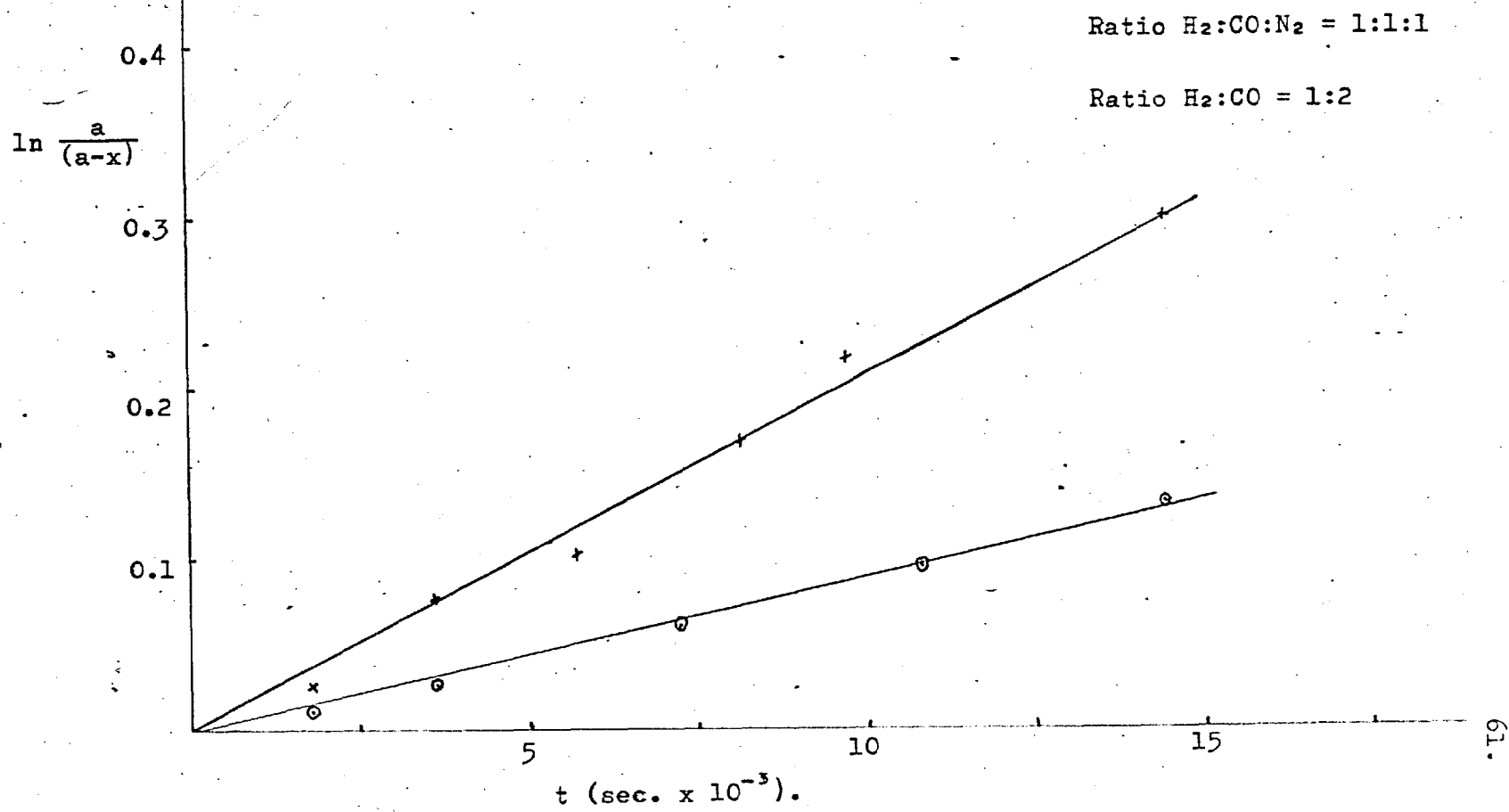
Time hrs.	x	$\ln a(a-x)^{-1}$	$t(\text{sec.} \times 10^{-3})$
0.5	0.029	0.0322	1.8
1	0.061	0.0810	3.6
1.6	0.091	0.1043	5.7
2.25	0.143	0.1700	8.1
2.75	0.180	0.2190	9.7
4	0.239	0.3020	14.4

(ii) $\text{CO}:\text{H}_2 = 2:1$

Time hrs.	x	$\ln \frac{a}{a-x}$	$t(\text{sec.} \times 10^{-3})$
0.5	0.014	0.0157	1.8
1	0.027	0.0295	3.6
2	0.059	0.0668	7.2
3	0.087	0.0984	10.8
4	0.116	0.1356	14.4

From Figure 8 (Page 64) it can be seen that using

Figure 8. Hydroformylation of Pent-1-ene using $\text{RhH}(\text{CO})(\text{PPh}_3)_3$.



$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ as catalyst the plot of t vs $\ln a(a-x)^{-1}$ now passes through the origin, suggesting that this is the active catalyst or immediately gives the active catalyst on treatment of its solution with hydrogen and carbonmonoxide. Also from the slopes of the lines (k) it can be seen that the rate is approximately halved ($\text{H}_2:\text{CO}:\text{N}_2 = 1:1:1$, $20.8 \times 10^{-6} \text{ sec.}^{-1}$, $\text{CO}:\text{H}_2 = 2:1$, $9.4 \times 10^{-6} \text{ sec.}^{-1}$) when the partial pressure of carbonmonoxide is doubled, (cf. effect of high partial pressure of carbonmonoxide on rate of catalysis with $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$) (see Page 39).

(3) Hydroformylation at 1 atm.

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is also an effective catalyst for the hydroformylation of olefins at room temperature and 1 atm. pressure. When a mixture of hydrogen and carbonmonoxide is bubbled through a benzene solution of alkene containing $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, rapid hydroformylation occurs, however both the rate of reaction and the ratio of straight- to branch-chain aldehyde is effected by the ratio of hydrogen to carbonmonoxide so reproducible results could not be obtained by this method. This is perhaps not surprising considering the lability of the equilibria involved. Reproducible results for comparative purposes were obtained by saturating with carbonmonoxide at 25° for 20 min. a solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (100 mg. 1.1×10^{-4} mole.) in benzene (2 ml.) to convert it all to the dimer $(\text{Rh}(\text{CO})_2(\text{PPh}_3)_2)_2$, the olefin (1.8×10^{-3} mole.)

was then added and hydrogen bubbled slowly into the solution for 10 min. although the reaction was apparently complete after ca 2 min. The solution was then analysed by G.l.c. Because of the small amount of aldehyde to be detected, the benzene used was purified by means of the nickel clathrate compound, $\text{Ni}(\text{CN})_2\text{NH}_3\text{C}_6\text{H}_6$, (68) to remove toluene and xylenes which interfered with the estimation of aldehyde. The solution was saturated with carbonmonoxide before adding the olefin because $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is an extremely effective catalyst for the isomerisation of olefins. This process on a solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ can apparently be repeated indefinitely without loss of catalyst.

Using this technique alk-1-ene gave 95% of the straight chain aldehyde. The yield of aldehyde on catalyst, assuming one mole aldehyde per mole rhodium was a fraction over 100%, this is probably due to some of the carbonmonoxide dissolved in the benzene being involved in the reaction. The yield by assuming that one of the carbonmonoxides on each rhodium and all the carbonmonoxide dissolved in the benzene could be converted to aldehyde was of the order of 90%. One would hardly expect yields of 100% on carbonmonoxide as some of the carbonmonoxide in solution would be quickly swept out by the hydrogen during the conversion of the carbonmonoxide on the rhodium to aldehyde.

Addition of excess triphenylphosphine suppresses the reaction and lower yields of aldehyde based on rhodium are obtained.

It is possible that this reaction may have utility in preparative organic chemistry, where it is required to convert $R-CH = CH_2$ to $R-CH_2CH_2CHO$ without subjecting the rest of the molecule (R) to extremes of temperature or harsh chemicals.

Cis-alk-2-enes reacted slower than alk-1-ene and trans-alk-2-enes reacted slower than cis-alk-2-enes. All alk-2-enes examined gave exclusively branched chain aldehyde (see Table 11).

TABLE 11. Hydroformylation at 25° and 1 atm. using $RhH(CO)-(PPh_3)_3$ (1×10^{-4} mole) in benzene (2 ml.). Solution saturated with carbonmonoxide (20 min.) prior to introduction of olefin (1.8×10^{-3} mole); hydrogen was then bubbled for 10 min. Yield assumes one mole aldehyde per mole rhodium.

Alkene	Yield %	Aldehyde: <u>Straight</u> Branched
pent-1-ene	104	20
pent-1-ene(a)	23	20
cis-pent-2-ene	61	(b)
trans-pent-2-ene	10	(b)
hex-1-ene	102	21
cis + trans-hex-2-ene	43	(b)

(a) 9.5×10^{-4} mole (i.e. 9 fold excess) triphenylphosphine present.

(b) all branched.

Hydroformylation under the above conditions, of a mixture of hex-1-ene and cis/trans-hex-2-ene, gave a ratio of straight- to branch-chain aldehyde of 19, suggesting that the hex-1-ene had reacted preferentially, as hex-1-ene alone gave a ratio of 21.

Hydroformylation of hex-1-ene at 1 atm. but at 50° gave a ratio of straight- to branch-chain aldehyde of only ca 9, while when alk-1-ene was added to a benzene solution of $\text{RhH(CO)(PPh}_3)_3$ which had been saturated with carbonmonoxide and while at 25° the solution was quickly pressurised to 30 atms. with hydrogen, a ratio of 10 was obtained.

(4) Hydrogen atom exchange and olefin isomerisation using hydridocarbonyltris(triphenylphosphine)rhodium(I).

When a solution of $\text{RhD(CO)(PPh}_3)_3$ (24 mg., 2.6×10^{-5} mole) in benzene (0.3 ml.) is treated with pent-1-ene or hex-1-ene (9×10^{-5} mole) at 25°, the high field line in the n.m.r. ca 19 due to the Rh-H grows with an apparent half life of ca 20 sec. The addition of triphenylphosphine (70 mg., 2.6×10^{-4} mole, i.e. 9 fold excess) reduced the rate of exchange and an half life of ca 45 min. was obtained. This strongly suggests that the exchange reactions proceed via the dissociated species $\text{RhH(CO)(PPh}_3)_2$ and not $\text{RhH(CO)(PPh}_3)_3$.

Pent-2-ene also undergoes exchange reactions with $\text{RhD(CO)-(PPh}_3)_3$, using conditions exactly as outlined for pent-1-ene, in the absence of excess triphenylphosphine an half life of ca 60 min. was obtained.

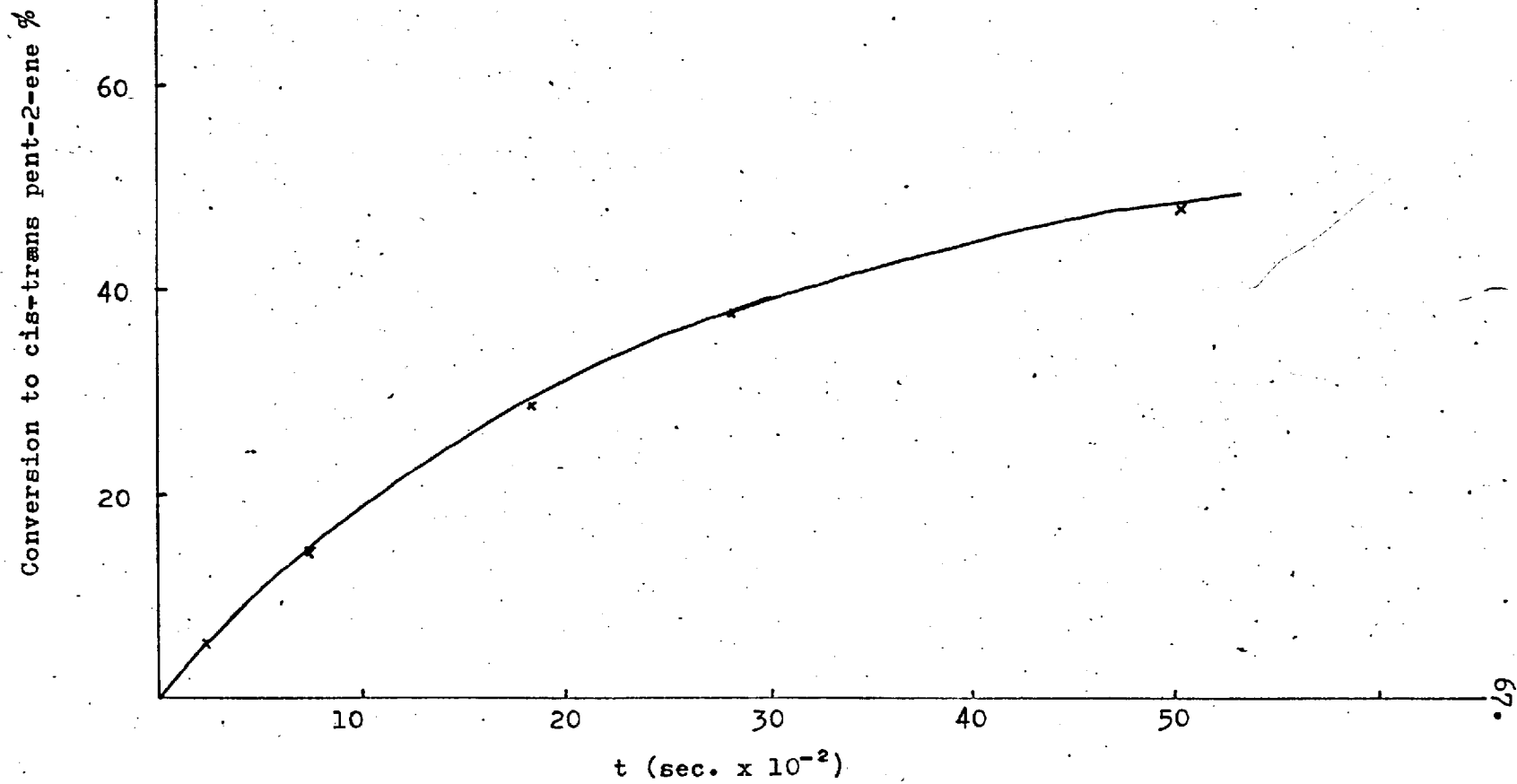
Although pent-1-ene is isomerised by solutions of $\text{Rh}(\text{CO})\text{H}(\text{PPh}_3)_3$ to a mixture of cis and trans pent-2-ene, the rate of isomerisation is considerably slower than the rate of exchange indicating that every reaction between alk-1-ene and catalyst does not lead to isomerisation. Samples of a solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (50 mg., 5.2×10^{-5} mole) and pent-1-ene (1 ml., 9×10^{-3} mole) in benzene (4ml.) were taken at intervals and analysed by G.l.c. The percentage of the pent-1-ene isomerised to cis/trans-pent-2-ene was:- 4min., 6%; 12 min., 18.5%; 31 min., 29%; 47 min., 37.5%; and 84 min., 47.5% (see figure 8, page 67).

Like the exchange reactions isomerisation is inhibited by excess triphenylphosphine, addition of triphenylphosphine (140 mg., 5.2×10^{-4} mole, i.e. 9 fold excess), reduced the isomerisation to 13% in 22 hrs. Again indicating that the dissociated species $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ and not $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is the catalyst. Cis-pent-2-ene is isomerised to trans-pent-2-ene but this isomerisation is very slow, under the same conditions used for pent-1-ene only ca. 10% of the cis-pent-2-ene was isomerised to trans-pent-2-ene in 60 min. No pent-1-ene was detected in the pent-2-ene isomerisation reactions.

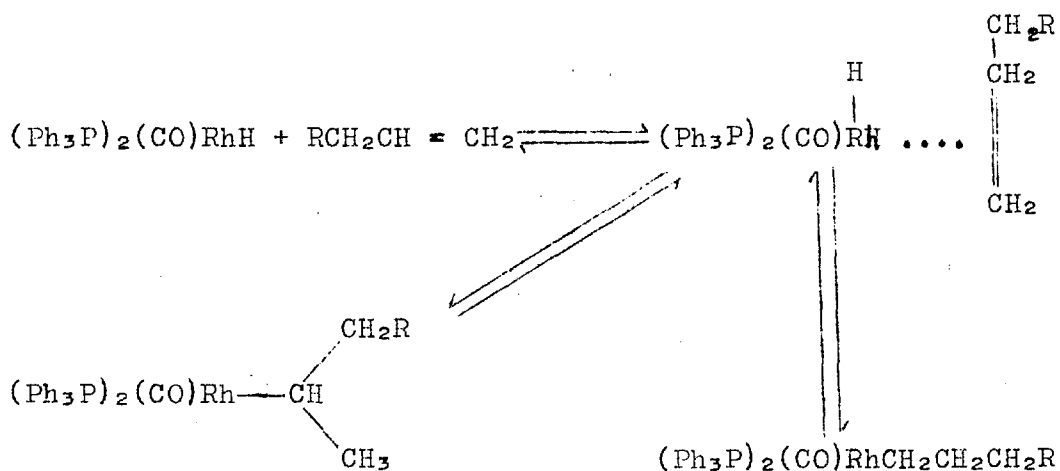
These experiments indicate that an alkyl intermediate is formed reversibly with the dissociated hydrido species via an hydrido- π -alkene intermediate (69, 70).

In the absence of rotation in the intermediate hydrido- π -alkene complex hydrogen abstraction can only occur from the β -carbon of the $\text{Rh}-\text{CH}_2\text{CH}_2\text{R}$ group, which would lead to ~~the alk-1-ene~~ alk-1-ene, and the isomerisation must be attributed to the direct

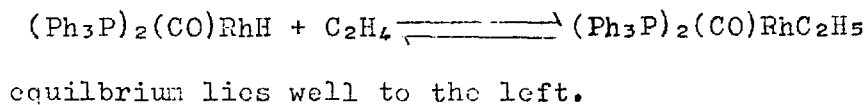
Figure 9. Isomerisation of Pent-1-ene using $\text{RhH}(\text{CO})(\text{PPh}_3)_3$



addition to give an $\text{Rh}-\text{CH}(\text{CH}_3)\text{CH}_2\text{R}$ group from which hydrogen can be abstracted either from $\beta\text{-CH}_3$ to reform the alk-1-ene or from the β -methylene group to give alk-2-ene.



The formation of the alkyl intermediate has not been proved spectroscopically. A benzene solution of $\text{RhH}(\text{CO})-(\text{PPh}_3)_3$ under 40 atms. of ethylene in an n.m.r. tube shows no $\text{Rh}-\text{C}_2\text{H}_5$ spectrum. This contrast with the detection of the alkyl produced by interaction of C_2H_4 with $\text{RhHCl}_2(\text{PPh}_3)_2$ (70) and $(\text{RuHCl}(\text{PPh}_3)_2)_2$ (65), suggesting that the reaction



These observations and suggested mechanisms agree with those of Cramer (71) published during the course of this work.

(5) Discussion.

The generally accepted steps involved in the hydroformylation of alkenes using cobalt catalysts have been outlined in the introduction.

For the rhodium system under investigation the following observations require explanation:

- (a) There is no isomerisation or hydrogenation of alkenes under hydroformylation conditions.
- (b) The selectivity for alk-1-enes is not so pronounced in the hydroformylation reaction as for isomerisation and hydrogen atom exchange.
- (c) The yields of straight chain aldehyde from alk-1-enes are exceptionally high at 25° and 1 atm. pressure, but are lower at higher temperatures and pressures.
- (d) All of the known catalytic reactions of $\text{RhH(CO)(PPh}_3)_3$ are inhibited by excess triphenylphosphine, and hydroformylation is also inhibited by increased partial pressure of carbonmonoxide.
- (e) The difference in behaviour of $\text{RhH(CO)(PPh}_3)_3$ compared to pure rhodium carbonyl and to cobalt and iridium catalysts.

The basic steps of the mechanism for hydroformylation with cobalt can be adapted with little change. Thus it can be assumed that there are always cis site transfers of the hydrido group to coordinated alkene, of the alkyl group so produced to coordinated carbonmonoxide to form an acyl group, and of hydride to acyl to give aldehyde.

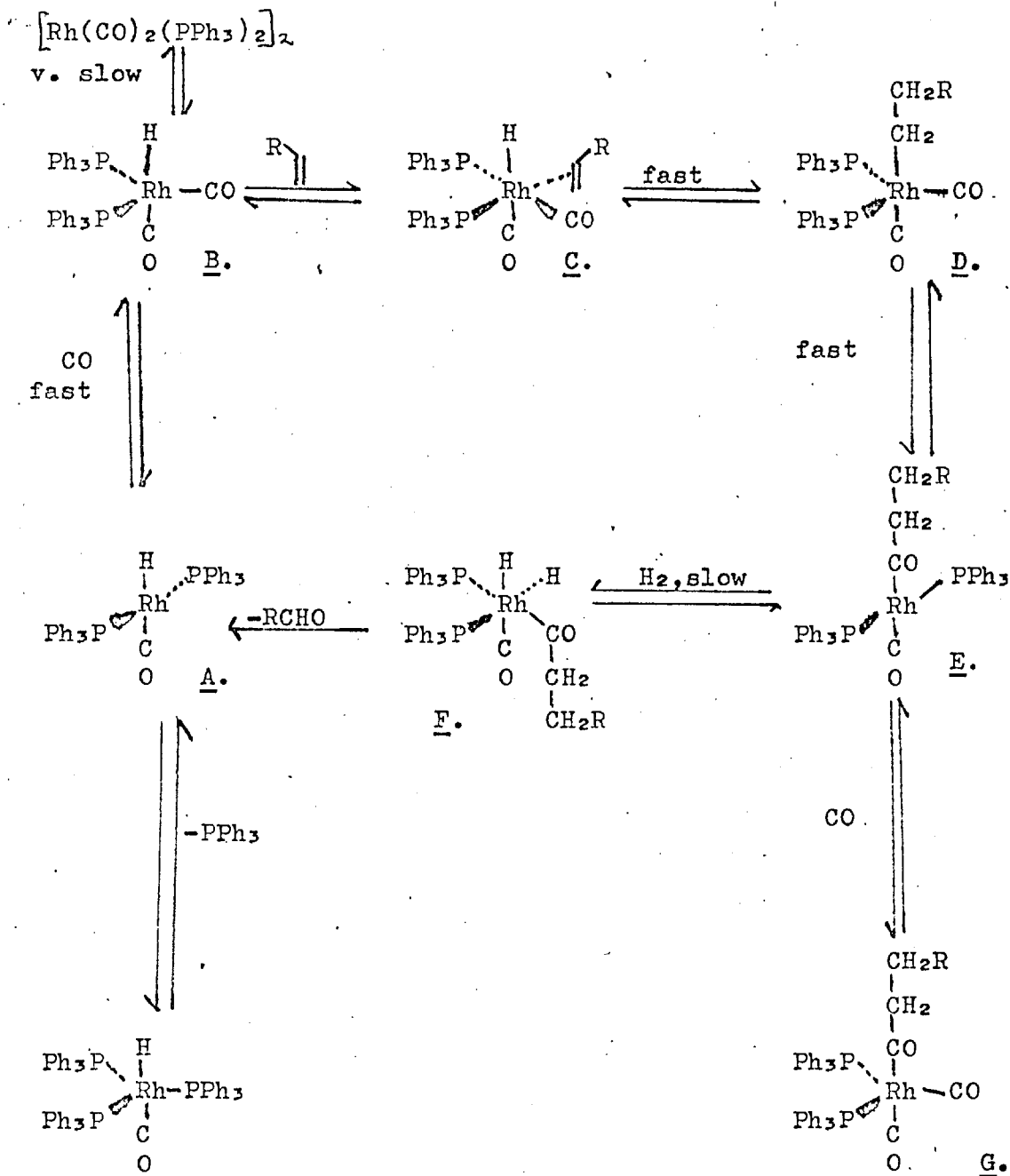
It seems reasonable to propose that the rate determining step is that involving oxidative cis addition of molecular hydrogen to a square rhodium(I) acyl complex, since the other species involved are rhodium(I) species, this is the only step which involves a change in both the oxidation state of the metal as well as a change in the coordination number. This step will be especially sensitive to the nature of the metal and the ligands bound to it (61). The ease of oxidisability would be expected to be in the order $\text{Co} < \text{Rh} < \text{Ir}$; for a given metal, and the effect of ligands should be $\text{CO} < \text{P(alkyl)}_3 < \text{P(aryl)}_3$ and, considering the substituted aryls, substitution by an electron withdrawing group e.g. para-fluoro, should allow less facile activation of hydrogen than an electron releasing group e.g. para-methoxy.

Two main ^c schemes which cannot be distinguished with the present information can be devised. Scheme 1 (page 71), involves an associative attack of alkene on the dicarbonyl species $\text{RhH(CO)}_2(\text{PPh}_3)_2$ (72). Scheme 2 (page 72), involves a dissociative mechanism similar to the dissociation of cobalt hydridotetracarbonyl to cobalt hydridotricarbonyl postulated for the cobalt system. In scheme 2 either triphenylphosphine or carbonmonoxide could be the group which dissociates.

Initial addition of the hydrido species to alkenes. The hydrogen atom exchange and isomerisation reactions of alkenes proceed via attack of the alkene on the species $\text{RhH(CO)}(\text{PPh}_3)_2$ (Scheme 1,A).

SCHEME 1.

71.



In the presence of carbonmonoxide however the species $\text{Rh}(\text{CO})_2(\text{PPh}_3)_2$ (Scheme 1,B; Scheme 2,4) predominates (72) but although in this case, the initial attack of alkene forms an alkyl, the transfer reaction to give acyl (Scheme 1, D $\rightarrow$ E; Scheme 2, E $\rightarrow$ F) must be so fast that exchange and isomerisation reactions are not competitive.

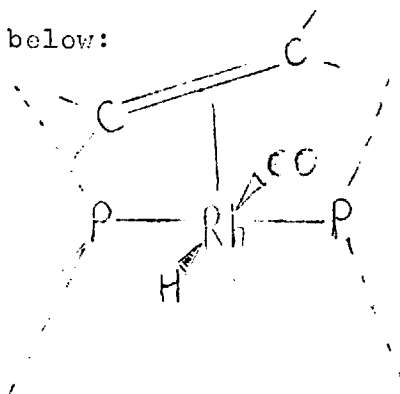
In the reversible addition (69,70,71) of $\text{L}_n\text{M}-\text{H}$ to alkene to give an alkyl complex, there are two main factors which are not independent.

(a) The direction of addition may be Markownikov or anti-Markownikov and only the former leads to isomerisation. It may be assumed that the direction of addition will depend in part on the polarity of the M-H bond. The presence on the metal of ligands of high π -acidity such as carbonmonoxide which will increase the polarity in the direction $\overset{\delta^-}{\text{M}}-\overset{\delta^+}{\text{H}}$ (in the extreme case the anion is formed e.g. $\text{Co}(\text{CO})_7^-$), and so increase the extent of Markownikov addition. The information for this is only based on qualitative observations. $\text{HCo}(\text{CO})_4$ is a strong acid in water whereas $\text{CoH}(\text{CO})_3\text{PPh}_3$ has an acid dissociation constant of only ca. 10^{-7} . The former is known (29) to react with pent-1-ene to give approximately equal amounts of the isomeric acyl cobalt carbonyls. Comparable studies are not available for the phosphine complex, but it is reported in the patent literature (40) that hydroformylation by octacarbonyl dicobalt in the presence of tertiaryphosphines, where phosphine

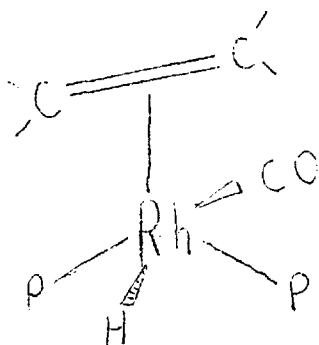
substituted carbonyl species will be involved, gives much higher ratio of straight- to branch-chain aldehyde.

(b) The presence of bulky ligands such as R_3P can generate substantial steric inhibition to the formation of the metal alkyl, especially where R is aryl, and such inhibition will not arise in the pure carbonyl species. The steric interaction will be at a maximum when such groups are trans to each other and mutually cis to the hydrido group or the alkyl formed from it as in Scheme 1, A. When R_3P groups are cis as in Scheme 1, B, the steric inhibition to alkyl formation will be minimised. The high selectivity in hydrogen atom exchange is probably due to this steric hindrance in the $RhH(CO)(PPh_3)_2$ species. The steric effect could either operate in the approach of the alkene to form an intermediate alkene complex, or in the transfer step to form the alkyl group.

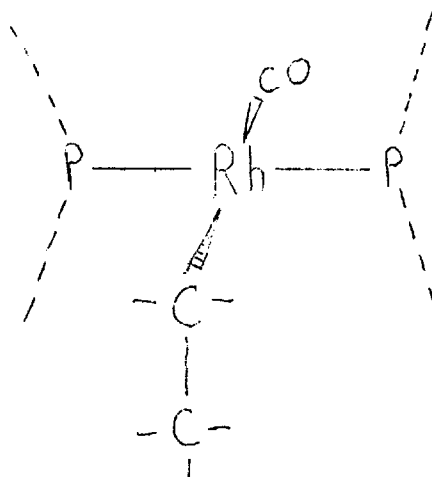
As the alkene approaches the square complex it could experience repulsion from the phenyl groups of the trans- PPh_3 groups which by rotating will be sweeping out a cone as can be seen below:



Thus the orientation of the bound alkene and the subsequent shift to the four centre transition state could be determined, since free rotation could be prevented. However in the approach of the alkene and formation of the alkene complex, the groups on the alkene will be bending away and back from the direction of approach, also the triphenylphosphine ligands will be moving towards their positions in the pentacoordinate intermediate hydrido alkene complex.



In passing from the hydrido alkene complex to the square alkyl intermediate the triphenylphosphine ligands will be returning to their square trans positions, with the alkyl group mutually cis to them. It would appear that unless this alkyl group is one with an α -methylene group, i.e., $\text{Rh-CH}_2\text{-}$ formed by anti-Markownikov addition, there will be steric hindrance due to the bulky phosphine groups. Markownikov addition to RCH=CH_2 or addition of alk-2-ene or cycloalkene, will lead to formation of a $\text{Rh-CH(R}^1\text{)-}$, or worse, $\text{Rh-C(R}^1\text{)(R}^{1'}\text{)-}$, the steric hindrance will be a minimum for $\text{R}^1 = \text{CH}_3$.



This is consistent with the observation that although the rate of isomerisation of pent-1-ene to pent-2-ene (which can only occur by Markownikov addition) is much slower than hydrogen atom exchange of pent-1-ene (which can occur by both Markownikov and anti-Markownikov addition), it is faster than the hydrogen atom exchange reactions of pent-2-enes. The observation that pent-1-ene is isomerised to a mixture of equal amounts of cis and trans pent-2-enes suggests that there is rotation round the Rh-C bond in the alkyl group $\text{Rh-CH(CH}_3\text{)CH}_2\text{C}_2\text{H}_5$.

The direction of addition will be affected by a combination of electronic and steric factors, both being governed by the nature of the metal and the ligands. At high temperature a decrease in the importance of steric factors would be expected.

Associative vs dissociative mechanism. It would appear unlikely in the hydroformylation mechanism that the initial

attack of the olefin is on the square species trans-RhH(CO)-(PPh₃)₂, were this so, an higher selectivity towards RCH = CH₂ would be expected as in the hydrogen atom transfer reactions.

If it is assumed that the olefin does not make a direct attack on the Rh-H bond but the alkyl intermediate is formed via an hydrido alkene complex there are two ways in which an olefin can attack RhH(CO)₂(PPh₃)₂. The associative attack (Scheme 1) is the simplest. The main objection to this scheme is that for a d⁸ species the effective atomic number rule is thus exceeded, but it should be remembered that this is a very short lived species.

The associative step accounts for the small specificity in hydroformylation between alk-1-ene and alk-2-enes, because of the reduction of steric hinderance in the formation of the alkyl from RhH(CO)₂(PPh₃)₂ (Scheme 1, B→C), where the Ph₃P groups are cis.

Considering the dissociative pathway for the initial attack it is clear that we cannot accept attack on a square complex RhH(CO)(PPh₃)₂ with trans phosphine groups for the reasons discussed above. If one carbonmonoxide dissociates from RhH(CO)₂(PPh₃)₂ it is required that the resulting transient species should have cis phosphines. Since there seems no reason why the dissociation of RhH(CO)(PPh₃)₃ in solution should not also produce a cis-phosphine species, in which case selectivity in hydrogen atom exchanges would not occur, it

seems more reasonable to propose a dissociation of a phosphine molecule as in Scheme 2. (Although no evidence for dissociation of PEt_2Ph was found when $\text{RhCl}(\text{CO})(\text{PEt}_2\text{Ph})$ was used as catalyst it should be remembered that the CS_2 complex of phosphines is in equilibrium with CS_2 and phosphine in solution, and in the presence of HCl and propyliodide the diethylphenylphosphonium-chloride would be formed much more readily than diethylphenyl-propylphosphonium iodide). Scheme 2 requires more stages to reach the critical square acyl intermediate $\text{Rh}(\text{COR})(\text{CO})(\text{PPh}_3)_2$, which then undergoes oxidative addition of hydrogen, than Scheme 1, but has the advantage that only 4 and 5 coordinate rhodium(I) species are involved. Either scheme, if it is assumed that alkyl transfer to carbonmonoxide to give acyl is much faster than the oxidative addition of hydrogen to the alkyl or to the reaction leading to double bond migration is consistent with the lack of hydrogenation and isomerisation of alkene under hydroformylation conditions.

Inhibition. It would appear from the hydrogen atom exchange and isomerisation experiments that excess triphenylphosphine suppresses the dissociation of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ so that any process depending on the presence of $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ will be inhibited. Similarly carbonmonoxide could inhibit hydroformylation by formation of the yellow dimer, $(\text{Rh}(\text{CO})_2(\text{PPh}_3)_2)_2$ but probably more likely is inhibition in the reactions Scheme 1, $\text{E} \rightarrow \text{G}$, Scheme 2, $\text{F} \rightarrow \text{H}$, which would block the rate-determining

oxidative addition reaction.

Aldehyde ratios. A mixture of straight and branched chain aldehyde can be obtained from an alk-1-ene either by initial addition to give terminal or secondary alkyls, or by isomerisation of alkyl or acyl intermediates, irrespective of the initial direction of the addition.

The latter type of reaction would proceed via the equilibria $\text{hydride} \rightleftharpoons \text{alkyl} \rightleftharpoons \text{acyl}$ so that a straight chain alkyl or acyl would eliminate alk-1-ene while a branched alkyl could eliminate either alk-1-ene or alk-2-ene, so if this were a significant pathway for branched aldehyde formation, the unconverted alkene should contain alk-2-ene, especially as alk-2-ene is hydroformylated less readily than alk-1-ene. It is possible however that the eliminated alkene could remain coordinated in the hydrido- π -alkene intermediate.

If it is assumed that in the hydroformylation of pent-1-ene at 25° and 1 atm., where the straight- to branch-chain aldehyde ratio is ca. 20, that the mode of initial addition is the determining factor, support for this is provided by the fall in the ratio to ca. 9 at 50°. The free energy of activation for anti-Markownikov addition of $\text{L}_n\text{Rh-H}$ to an alk-1-ene will be slightly smaller, (by ΔE_a) than that for Markownikov addition. Since the addition ratio will be proportional to $e^{-E_a/RT}$, the ratio should decrease with increasing temperature, as observed. If the aldehyde ratio were dependent on acyl re-arrangement,

the opposite would probably be expected, as in the cobalt system, temperature increases are believed (37, 38, 39) to favour terminal acyl, which are more difficult to isomerise than their branch chain isomers.

The observation that the ratio of straight-to branch-chain aldehyde is only of the order of 3, in reactions conducted under pressures of carbonmonoxide and hydrogen even at room temperature could be due to the dissociative scheme being the one in operation and mechanisms involving both loss of triphenylphosphine and carbonmonoxide being possible, depending on the reaction conditions. The reactions under 1 atm. were conducted with fairly concentrated solutions of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ where the concentration of triphenylphosphine in solution will be relatively high compared with the concentration of carbonmonoxide, however in the high pressure reactions, where more dilute solutions of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ were used, the concentration of triphenylphosphine will be very small compared with the concentration of carbonmonoxide. In the first case Scheme 2 could be operating with loss of carbonmonoxide to give square hydridocarbonyl species with cis triphenylphosphines, while at higher pressures triphenylphosphine could be lost yielding a square hydridodicarbonyltriphenylphosphine species. The former species would from the argument developed on Page 73 give a less polar Rh-H bond and less chance of Markownikov addition, whereas the latter species would give a more polar

Rh-H bond and more chance of Markownikov addition. This still does not however explain why when a high pressure of hydrogen is introduced to a solution of $\text{RhHCO}(\text{PPh}_3)_3$ saturated with carbonmonoxide to which alk-1-ene has been added a lower ratio of straight chain aldehyde is obtained than when hydrogen is introduced slowly at 1 atm.

The difference in behaviour between rhodium and iridium catalysts will be discussed in Chapter 3.

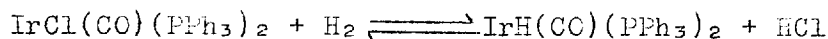
CHAPTER 3.HYDROFORMYLATION USING COMPLEXES OF OTHER METALS1) Iridium

Although iridium complexes have been indicated in the patent literature (45) as hydroformylation catalysts no stoichiometric complexes were characterised. The simple iridium carbonyls have been compared with cobalt carbonyls and rhodium carbonyls (58) and found to be less effective than either.

Following the successful hydroformylation of olefins with trans-RhCl(CO)(PPh₃)₂, hydroformylation of pentene-1 was attempted using the iridium analogue trans-IrCl(CO)(PPh₃)₂, using conditions under which hydroformylation readily occurs with the rhodium analogue, i.e. 16 hours at 80° under 100 atm. of H₂:CO (1:1) the hexacoordinate IrH₂Cl(CO)(PPh₃)₂ complex was recovered, and very little aldehyde was obtained. It was subsequently reported (73) that more drastic conditions, i.e. temperatures of 140° are required.

Although treating IrCl(CO)(PPh₃)₂ in the presence of triphenylphosphine and triethylamine with hydrogen (100 atm.) at 70° for 16 hours gives an approximate equimolar mixture of IrH(CO)(PPh₃)₃ and IrH₂Cl(CO)(PPh₃)₂ (the rhodium analogue under these conditions gives an almost quantitative yield of

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$, failure of the reaction:-



to lie further enough to the right hand side is not the only reason for its poor performance as an hydroformylation catalyst, as $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ is also a poor hydroformylation catalyst.

A solution of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (50 mg., 7×10^{-5} mole) and pent-1-ene (3 ml., 0.027 mole) in benzene (4 ml.), yielded only 10% aldehyde after 16 hours at 80° under a total pressure of 100 atms.

$\text{H}_2:\text{CO} = 1:1$.

2) Iron.

The observation that pentacarbonyl iron is a poor hydroformylation catalyst (43) was confirmed. After 16 hours at 110° under a total pressure of 100 atms. of a 1:1 mixture of carbonmonoxide and hydrogen, a solution of pent-1-ene (3 ml., 0.027 mole) in benzene (4 ml.) in the presence of $\text{Fe}(\text{CO})_5$ (0.4 ml., 0.003 mole) was hydroformylated to an extent of only 4%. In a reaction carried out under identical conditions except for the addition of triphenylphosphine (1 g.) the yield of aldehyde was increased to 31%. A small amount of yellow solid was isolated from the reaction mixture whose I.R. and melting point indicated a mixture of bis(triphenylphosphine)-tricarbonyliron and triphenylphosphinetetracarbonyliron. Cotton has reported (76) that a mixture of bis(triphenylphosphine)-tricarbonyliron and triphenylphosphinetetracarbonyliron is

obtained on heating pentacarbonyl iron with triphenylphosphine at 110° . In view of these reactions $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ and $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ were used alone as hydroformylation catalysts, they were found to give markedly increased yields of aldehyde compared with $\text{Fe}(\text{CO})_5$ under the same conditions. The $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ and the $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ can be recovered unchanged at the end of the reaction. The ratio of straight- to branch-chain aldehyde was ca. 2.7 in all cases. (See table 12).

3) Ruthenium.

Unspecified ruthenium carbonyl complexes have been indicated (44) in the patent literature as hydroformylation catalysts. Following the success of the ruthenium complexes $\text{tris}(\text{triphenylphosphine})\text{dichlororuthenium(II)}$ and $\text{tetrakis}(\text{triphenylphosphine})\text{-dichlororuthenium(II)}$ as catalysts for the homogeneous hydrogenation of olefins (65,77) they were tried without success as hydroformylation catalysts. However, they react rapidly with carbonmonoxide to give the stable, hexacoordinate dicarbonyl complex $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$.

This reaction of carbonmonoxide with $\text{RuCl}_2(\text{PPh}_3)_3$, has been used to give a quicker route to the effective hydroformylation catalyst (77) $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$. This complex was first prepared by Collman (78) by the interaction of carbonmonoxide and $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$, in the presence of zinc, with dimethylformamide as solvent. The $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ was prepared by treating hydrated ruthenium chloride, in a methanol solution

of triphenylphosphine with carbonmonoxide at 60 p.s.i. for 30 hours. $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ can however be prepared by the interaction of carbonmonoxide and $\text{RuCl}_2(\text{PPh}_3)_3$ in the presence of zinc in dimethylformamide. $\text{RuCl}_2(\text{PPh}_3)_3$ can easily be prepared by the interaction of hydrated ruthenium trichloride and triphenylphosphine in methanol (79).

TABLE 12. Hydroformylation by iron and ruthenium complexes. Pent-1-ene (3 ml., 0.027 mole), benzene (4 ml.), 100 atms. $\text{H}_2:\text{CO} = 1:1, 110^\circ$ for 16 hours.

Complex	mole ratio $\frac{\text{catalyst}}{\text{olefin}}$	conversion % ^a
$\text{Fe}(\text{CO})_5$	0.11	4
$\text{Fe}(\text{CO})_5 + \text{PPh}_3$	0.11	31
$\text{Fe}(\text{CO})_4\text{PPh}_3$	0.0044	30
$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$	0.0028	37
$\text{RuCl}_2(\text{PPh}_3)_3$	0.0015	5
$\text{RuCl}_2(\text{PPh}_3)_4$	0.0015	5
$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$	0.0026	80

^a In all cases straight- to branch-chain aldehyde ratio is ca 2.7.

$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ is the most efficient ruthenium hydroformylation catalyst that has yet been reported. An 80% yield of aldehyde was obtained on treating a solution of pent-1-ene (3 ml., 0.027 mole) in benzene (4 ml.) in the presence of

$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (50 mg., 7×10^{-5} mole), at 110° for 16 hours under 100 atms. $\text{H}_2:\text{CO}$ (1:1). (See Table 12).

4) Nickel.

Despite patent claims (45), no detectable amounts of aldehydes were obtained using the nickel complexes $\text{NiX}_2(\text{PR}_3)_2$, where $\text{X} = \text{Cl}$ or Br , $\text{R} = \text{n-C}_4\text{H}_9$ or C_2H_5 , at temperatures up to 195° and a total pressure of 100 atms. $\text{H}_2:\text{CO} = 1:1$.

5) Differences between cobalt, rhodium and iridium as hydroformylation catalysts.

The low activity of the iridium complexes compared to the analogous rhodium complexes is most probably due to the greater stability of pentacoordinate iridium(I) and octahedral iridium(III) species. Thus dissociation to provide sites for activation of substrates probably occurs to a much smaller degree than in the corresponding rhodium complexes.

Indeed, although $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is dissociated in benzene solution, $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ is not (63) also the dicarbonyl, $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ is stable, and can be easily prepared by passing carbonmonoxide into a benzene solution of $\text{IrH}(\text{CO})-(\text{PPh}_3)_3$, the analogous rhodium compound $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ has only been observed in solution inequilibrium with other rhodium species (72), also an acyl species $\text{Ir}(\text{COCH}_3)(\text{CO})_2(\text{PPh}_3)_2$ comparable to G of Scheme 1 has been characterised (74), a stable methoxycarbonyl, $\text{Ir}(\text{CO}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2$ is also known (75).

The main reason for the greater activity of rhodium carbonyl catalysts than cobalt carbonyl catalysts (58) is probably due to the greater ease of oxidative addition of hydrogen to the rhodium(I) acyl complexes. If the suggestion (80) that the larger size reduces the crowding of the ligands were true, iridium would be expected to be even better, which it is not.

Whereas no acyl intermediates have been isolated from the rhodium systems nor have they been observed spectroscopically, the acyl cobalt tetracarbonyls have been observed spectroscopically (24) and the triphenylphosphine acyl cobalt carbonyl complexes have been prepared (29, 30), suggesting that these species are more stable than those of rhodium and hence require more drastic conditions for dissociation.

EXPERIMENTAL.1). Apparatus.

Simple elemental microanalyses were by the Microanalytical Laboratories of Imperial College. N.m.r. were carried out on a Varian Associates 43100 Spectrometer at 56.4 Mc/sec., unless otherwise stated. Infra-red spectra were recorded in nujol mulls on a Grubb Parsons Spectromaster unless otherwise stated. Mass-spectra were obtained by using an A.E.I. MS-9 spectrometer. Vapour phase chromatographs were obtained from a Perkin Elmer F.11 gas Chromatograph with flame ionisation detection. The stationary phase was carbowax for aldehydes, squaline and silver nitrate-diethyleneglycol for hydrocarbons; calibrations were made using standard samples. Melting points were determined on a Kofler hot stage and are uncorrected.

2). Materials.

The rhodium chloride, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was from Johnson Matthey Ltd.; the only transition metal impurity is believed to be possibly a trace of iridium (81). Triphenylphosphine (Albright & Wilson Ltd.) was recrystallised from benzene-ethanol before use. The other phosphines were prepared by the Grignard reaction. The but-1-ene (Matheson Lecture bottle) and propylene (I.C.I.) were used without purification. All other olefins were from Rock-Light, they were freed from peroxides by passage through an alumina column and distillation over sodium. The benzene used in the low pressure hydroformylation reactions was

purified via the nickel clathrate compound (68), to remove small amounts of toluene and xylene which interfered in the estimation of yields of aldehydes by G.l.c.

3). Preparations.

(a). Bis(triphenylphosphine)carbonylchlororhodium(I).

To a solution of triphenylphosphine (7.2 g., 0.027 mole) in hot ethanol (300 ml.) was added a solution of rhodium trichloride trihydrate (2 g. 0.0075 mole) in ethanol (70 ml.), when the solution cleared, sufficient formaldehyde solution 40% ^w/v HCHO (ca. 10 ml.) was added to give a pale yellow solution from which crystals of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ separated out. The yellow microcrystals were obtained by filtration and recrystallised from benzene. Yield 4.54 g. (85% on rhodium trichloride). (Found: C, 64.7; H, 4.5; Cl, 5.0. $\text{C}_{37}\text{H}_{30}\text{ClOP}_2\text{Rh}$ requires C, 64.4; H, 4.4; Cl, 5.1%).

(b). Bis(triphenylphosphine)carbonylbromorhodium(I).

This was prepared in essentially quantitative yield by the interaction of carbonmonoxide and tris(triphenylphosphine)-bromorhodium(I). (Found: C, 60.4; H, 4.2; Br, 10.6. $\text{C}_{37}\text{H}_{30}\text{BrCO-P}_2\text{Rh}$ requires C, 60.4; H, 4.1; Br, 10.9%).

(c). Bis(triphenylphosphine)carbonyliodorhodium(I).

This was prepared in essentially quantitative yield by the interaction of carbonmonoxide and tris(triphenylphosphine)iodorhodium(I). (Found: C, 57.1; H, 4.0; I, 16.1. $\text{C}_{37}\text{H}_{30}\text{IOP}_2\text{Rh}$ requires C, 56.8; H, 3.8; I, 16.2%).

(d). Bis(triethylphosphine)carbonylchlororhodium(I), bis-(diethylphenylphosphine)carbonylchlororhodium(I) and bis-(tri-p-methoxyphenylphosphine)carbonylchlororhodium(I).

These were prepared by the interaction of the appropriate phosphine with $(\text{Rh}(\text{CO})_2\text{Cl})_2$ (47).

(e) Bis(tri-p-methylphenylphosphine)carbonylchlororhodium(I).

To a hot solution of para-tolylphosphine (1.8 g., 0.0053 mole) in ethanol (80ml.) was added a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.5 g., 0.0019 mole) in ethanol (30 ml.), when the solution cleared, formaldehyde solution 40% w/v HCHO (ca. 4 ml.) was added until a pale yellow solution was obtained, from which microcrystals of $\text{RhCl}(\text{CO})((\text{p-MeC}_6\text{H}_4)_3\text{P})_2$ separated out, these were removed by filtration and recrystallised from benzene. Yield 1.25 g. (84% on rhodium trichloride). (Found: C, 66.5; H, 5.3; Cl, 4.5. $\text{C}_{43}\text{H}_{42}\text{ClOP}_2\text{Rh}$ requires C, 66.4; H, 5.4; Cl, 4.6%).

(f) Reaction of rhodium trichloride and para-methylphenylphosphine.

To a hot solution of para-methylphenylphosphine (4 g., 0.0012 mole) in ethanol (90 ml.) was added a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.5 g., 0.0019 mole) in ethanol (40 ml.), a burgundy red solution was obtained on refluxing this solution, but no crystals were deposited, even after 3.5 hours at reflux. The solvent was removed by evaporation under reduced pressure and the resulting yellow-brown solid after washing with ether gave non-stoic-

hiometric analysis. (Found: C, 61.12; H, 5.42; Cl, 10.17%).
(g). Bis(tri-p-fluorophenylphosphine)carbonylchlororhodium(I).

To a hot solution of para-fluorophenylphosphine (1.85 g., 0.0053 mole) in ethanol (80 ml.) was added a solution of rhodium trichloride (0.5 g., 0.0019 mole) in ethanol (30 ml.), when the solution cleared formaldehyde solution 40% ^w/v HCHO (ca. 4ml.) was added until a pale yellow solution was obtained from which microcrystals of $\text{RhCl}(\text{CO})((\text{p-FC}_6\text{H}_4)_3\text{P})_2$ were deposited, these were removed by filtration and recrystallised from benzene. Yield 1.3 g. (86% on rhodium trichloride), m.p. 162-163°, ν CO = 1984 cm^{-1} . (Found: C, 55.8; H, 3.3; Cl, 4.4. $\text{C}_{37}\text{H}_{24}\text{F}_6\text{ClOP}_2\text{Rh}$ requires C, 55.6; H, 3.0; Cl, 4.5%).

(h). Tris(tri-p-fluorophenylphosphine)chlororhodium(I).

To a hot solution of para-fluorophenylphosphine (3.6 g., 0.0106 mole) in ethanol (90 ml.) was added a solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.5 g., 0.0019 mole) in ethanol (20 ml.). On refluxing the burgundy red solution that was obtained, orange crystals were obtained after ca. 2 min. at reflux. These were removed by filtration and washed with ethanol. Yield 1.85 g. (90% on rhodium trichloride). (Found: C, 59.8; H, 3.7; P, 8.6; Cl, 3.1. $\text{C}_{54}\text{H}_{36}\text{F}_9\text{ClP}_3\text{Rh}$ requires C, 59.6; H, 3.3; P, 8.6; Cl, 3.3%).

(i). Bis(triphenylarsine)carbonylchlororhodium(I).

To a hot solution of triphenylarsine (2.05 g., 0.0053mole) in ethanol (100ml.) was added a solution of rhodium trichloride

(0.5 g., 0.0019 mole) in ethanol (20 ml.), 5 ml. of formaldehyde solution 40% w/v HCHO was immediately added, a pale yellow solution was obtained from which yellow crystals of $\text{RhCl}(\text{CO})_2(\text{AsPh}_3)_2$ were obtained, these were removed by filtration and recrystallised from benzene. Yield: 1.15 g. (78% on rhodium trichloride). (Found: C, 56.7; H, 3.6; Cl, 4.3. $\text{C}_{37}\text{H}_{30}\text{Cl}_2\text{OAs}_2\text{Rh}$ requires C, 57.0; H, 3.9; Cl, 4.6%).

(j) Tris(triphenylphosphine)carbonylhydridorhodium(I).

To a stirred, heated suspension of bis(triphenylphosphine)-carbonylchlororhodium(I) (1 g., 0.0014 mole) in a solution of triphenylphosphine (1.5 g., 0.0057 mole) in ethanol (100 ml.) was added sodium borohydride in ethanol until a sample of the yellow precipitate contained no $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (Analysed by I.R.). The yellow precipitate was removed by filtration and recrystallised from benzene-ethanol. Yield 1.2 g. (90%). (Found: C, 72.6; H, 5.0; P, 10.2. $\text{C}_{55}\text{H}_{46}\text{P}_3\text{ORh}$ requires C, 72.7; H, 5.0; P, 10.1%).

(k). Reactions of tris(triphenylphosphine)hydridocarbonylrhodium(I) with carbonmonoxide.

Carbonmonoxide freed from iron carbonyls by passage through active carbon was passed into a solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ in benzene for ca. 20 min., on evaporating the benzene at room temperature in a stream of carbonmonoxide an unstable yellow compound was obtained. ($\sqrt{\text{CO}}$ 2017, 1992, 1800, and 1770 cm^{-1}). No elemental analysis was obtained.

A solution of $\text{RhD}(\text{CO})(\text{PPh}_3)_3$ (prepared by passing deuterium through a benzene solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ until the Rh-H stretch disappeared in the I.R., removing the benzene and recrystallising from benzene-ethanol) in benzene was introduced into a glass tube sealed at one end and fitted with a tap at the other end. The solution after being de-gassed by careful evacuation was frozen in liquid nitrogen and evacuated, carbonmonoxide was introduced to a pressure of ca. 0.75 atm. After warming to room temperature the tube was vigorously shaken for 20 minutes. Examination of the gas in the tube by mass spectra showed the presence of deuterium. The I.R. of the benzene solution remaining in the tube after treatment with more carbonmonoxide was identical with that of a benzene solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ treated with carbonmonoxide, also the same yellow solid was obtained on evaporating the benzene in a stream of carbonmonoxide.

(1). Bis- μ -dicarbonylbis(triphenylphosphine)ethanoldirrhodium(O).

Ethanol was added to the yellow solution obtained by passing carbonmonoxide through a benzene solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$. A stream of nitrogen was then passed through this solution which immediately went red, on evaporating off the benzene in a stream of nitrogen the product was obtained as a red crystalline solid. (ν_{CO} 1720 cm^{-1}). (Found: C, 66.6; H, 5.3; P, 8.9; O, 4.3. $\text{C}_{78}\text{H}_{72}\text{P}_4\text{O}_4\text{Rh}_2$ requires C, 66.8; H, 5.2; P, 8.8; O, 4.6%).

(m). Bis- μ -dicarbonyl(bistriphenylphosphine)methylenechloride-rhodium(0).

Carbonmonoxide was passed through a methylene chloride solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ for ca. 15 min., nitrogen was then bubbled through the solution which immediately changed from yellow to red. On evaporating the methylene chloride in a stream of nitrogen, the product was obtained as a red crystalline solid (ν_{CO} 1739 cm^{-1}). (Found: C, 61.5; H, 4.4; P, 8.2; Cl, 9.6. $\text{C}_{76}\text{H}_{64}\text{P}_4\text{Cl}_4\text{O}_2\text{Rh}_2$ requires C, 61.4; H, 4.4; P, 8.4; Cl, 9.6%).

(n). Reactions of bis- μ -dicarbonyl(bistriphenylphosphine)-methylenechloride-rhodium(0).

(i). With carbonmonoxide. $(\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{CH}_2\text{Cl}_2)_2$ (0.12 g.) was added to benzene (5 ml.) in a catalytic hydrogenation apparatus under an atmosphere of carbonmonoxide, the solution rapidly changed from red to yellow and 3.62 cc. (at N.T.P.) of carbonmonoxide was absorbed. For the absorption of one carbonmonoxide per rhodium, 3.63 cc. (at N.T.P.) of carbonmonoxide would be required. The solution I.R. was identical with that obtained by passing carbonmonoxide through a solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$.

(ii). With hydrogen in the presence of triphenylphosphine. $(\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{CH}_2\text{Cl}_2)_2$ (0.1574 g.) was added to benzene (5 ml.) in a catalytic hydrogenation apparatus, the benzene contained triphenylphosphine (0.25 g.), under a atmosphere of hydrogen.

2.26 cc. of hydrogen (at N.T.P.) was absorbed. For the absorption of one mole of hydrogen per mole of complex 2.38 cc. (at F.T.P.) of hydrogen is required. At the end of the reaction the solution which had changed from red to yellow was evaporated to dryness and the resulting yellow solid was washed with ether to yield $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (0.155 g., 81% theory).

(iii). With iodine. A solution of iodine in benzene was added carefully to a benzene solution of $(\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{-CH}_2\text{Cl}_2)_2$ (0.2 g.). The red colour of the solution gradually disappeared, a yellow solution was obtained, from which $\text{RhI}(\text{CO})(\text{PPh}_3)_2$ (0.18 g., 86% theory) was obtained.

(o). Tris(triphenylphosphine)carbonylhydrido-iridium(I).

To a stirred heated suspension of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (0.5 g., 0.00064 mole) in a solution of triphenylphosphine (1 g., 0.0038 mole) in ethanol (100 ml.), was added sodium borohydride in ethanol. The addition of sodium borohydride was continued until a sample of the precipitate contained no $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (Analysed by I.R.). The product was obtained by filtration and recrystallised from benzene-ethanol. Yield 0.59 g., 91% theory). (Found: C, 65.8; H, 4.5; P, 9.1. $\text{C}_{55}\text{H}_{46}\text{P}_3\text{OIr}$ requires C, 65.8; H, 4.6; P, 9.2%).

(p). Bis(triphenylphosphine)dicarbonylhydrido-iridium(I).

This was obtained as a white crystalline solid in essentially quantitative yield, by the interaction of tris(triphenylphosphine)carbonylhydrido-iridium(I) and carbonmonoxide in benzene.

(~~IR~~-H 2030 cm^{-1} ; CO 1975, 1910 cm^{-1}). (Found: C, 59.2; H, 4.1; O, 4.0; P, 8.1. $\text{C}_{38}\text{H}_{31}\text{O}_2\text{P}_2\text{Ir}$ requires C, 59.0; H, 4.0; O, 4.1; P, 8.0%).

(g). Bis(triphenylphosphine)tricarbonylruthenium(O).

A solution of tris(triphenylphosphine)dichlororuthenium(II) (0.5 g.) in dimethylformamide (10 ml.) in the presence of zinc dust (1.0 g.) was kept at 100° for 20 hours under 100 atm. of carbonmonoxide. After cooling and filtering, the dimethylformamide was evaporated off under reduced pressure and the product washed with ether. Yield 0.33 g. (88%). (Found: C, 65.8; H, 4.2; O, 6.9; P, 8.7. $\text{C}_{39}\text{H}_{30}\text{O}_3\text{P}_2\text{Ru}$ requires C, 66.0; H, 4.3; O, 6.8; P, 8.7%).

4). Hydroformylation reactions.

(a). These were normally carried out in 25 ml. stainless steel autoclaves (Baskerville and Lindsay Ltd.). Each reaction was carried out at least twice in different autoclaves, to guard against spurious results due to small amounts of catalyst left in the autoclaves from previous reactions. The autoclave with solvent, alkene and catalyst was flushed with carbonmonoxide and then pressurised to the required level, the carbonmonoxide was always introduced before the hydrogen. The autoclave was heated in an electric oven without agitation. After the required reaction time the autoclave was cooled and the products analysed immediately by G.l.c.

(b). The rate studies on pent-1-ene were carried out using a

Parr Series 4500 one-litre autoclave (stainless steel type 316) fitted with a stirrer and dip-leg which enabled samples to be withdrawn from the autoclave during the reaction. The catalyst, pent-1-ene, benzene and amine where required were introduced, after a carbonmonoxide purge, carbonmonoxide was introduced to the required pressure. The autoclave was raised to the desired temperature and the hydrogen and where necessary nitrogen were introduced. Immediately before introducing the hydrogen a liquid sample was removed and checked by G.l.c. for double bond migration in the pent-1-ene. Further liquid samples were taken at intervals (ca. 1 ml.) and the conversion of pent-1-ene to aldehyde was calculated by G.l.c. analysis, and the unreacted hydrocarbon was checked for hydrogenation and double bond migration by G.l.c. After each sample was taken a small amount of either hydrogen or carbonmonoxide was introduced down the dip-leg, to ensure that the next sample taken was not contaminated with solution which had been left in the cool part of the dip-leg when the previous sample had been taken.

(c). Atmospheric reactions were carried out in sample tubes fitted with self sealing serum caps. Gases were introduced through thin-bore stainless steel tubing and liquids from hypodermic syringes.

The $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and triphenylphosphine where necessary were weighed into a sample tube, which was sealed with a serum cap and purged with carbonmonoxide using thin-bore tubing.

Benzene was then introduced via an hypodermic syringe and the passage of carbonmonoxide was continued for 20 min. to convert all the rhodium to the dimeric species $(\text{Rh}(\text{CO})_2(\text{PPh}_3)_2)_2$.

Alkene was then introduced using a 100 μ L. Hamilton syringe, Hydrogen was then bubbled through this solution for 10 min., The solution was then analysed for aldehydes by G.l.c.

5). Hydrogen atom exchange reactions.

A solution of $\text{RhD}(\text{CO})(\text{PPh}_3)_3$ with triphenylphosphine, where necessary, in benzene in a n.m.r. tube, was set in the spectrometer, the alkene was injected into this solution using a 10 μ L. Hamilton syringe. The growth of the line at τ 19, due to the Rh-H was observed.

6). Isomerisation reactions.

The $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ with triphenylphosphine where necessary was weighed into a sample tube, which was sealed with a serum cap. The tube was purged with nitrogen and the benzene and alkene were introduced via hypodermic syringes. Samples were removed at intervals through the serum cap and analysed by G.l.c.

7). Reactions of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ with ethylene.

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (24 mg., 2.6×10^{-5} mole) in benzene (0.3 ml.) in a thick walled n.m.r. tube was attached to a vacuum line and sufficient ethylene was condensed in to give a pressure of ca. 40 atms. at room temperature. The tube was then sealed with a flame and examined by n.m.r. No Rh- C_2H_5 spectrum was observed. The experiment was repeated with a small amount of

carbonmonoxide bubbled through the solution before introducing the ethylene, no $\text{Rh-C}_2\text{H}_5$ or $\text{Rh-CO-C}_2\text{H}_5$ spectrum was observed.

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