F. J. McQUILLIN

HOMOGENEOUS HYDROGENATION IN ORGANIC CHEMISTRY

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PREFACE

Organic chemistry is constantly concerned with effecting reactions at a particular centre in a complex molecule, and if possible with a high and predictable level of stereoselectivity. In the light of much accumulated experience within organic chemistry it is usually possible to assess the likelihood of alternative reaction pathways at least qualitatively. However, well based expectations can be falsified, and the experiments directed to the synthesis of vitamin B_{12} which led to Woodward's recognition of orbital symmetry control in organic chemistry are an instructive example. Our limitations in this respect are very much accentuated in the case of heterogeneous reactions, which present additional problems, and except for very well studied instances, heterogeneous catalysis has remained a relatively empirical area of chemistry. Knowledge in this area has, however, been greatly improved by the development of transition metal complexes which replicate the catalytic properties of the metals, and are effective in a homogeneous reaction system. This development has advanced our understanding of catalysis by making it possible to interpret reactions in strictly molecular terms. In addition, these homogeneously active complexes are frequently more selective than their heterogeneous metallic counterparts either in discriminating between different functional centres in a molecule or in offering better stereoselectivity.

Homogeneous catalysts have now been devised for a number of organic chemical reactions, including hydrogenation, carbonylation, polymerisation, and isomerisation and dismutation of alkenes. The potential, and limitations of these methods within organic chemistry will, however, emerge only by wider application in the laboratory. This text is concerned with homogeneous hydrogenation, and its aim is to make the existing information on homogeneous hydrogenation catalysis more directly available to the practicing chemist. The underlying principles of catalytic hydrogenation are considered, but most emphasis is placed on examples, and on ex-

perimental conditions for the use of homogeneous catalysts. For this reason attention has been concentrated on catalytically active complexes which are readily prepared, and for which organic chemical applications have been examined. A number of metal complexes which exhibit activity as hydrogenation catalysts have not been included since they have, as yet, found no distinct area of application. Discussion of these catalysts may be found in reviews, notably in B. R. James's 'Homogeneous Hydrogenation', in the *Chemical Society's Specialist Periodical Reports on Organometallic Chemistry* and in the article by Harmon, Gupta and Brown in *Chemical Reviews* 73, 21 (1973). Useful articles on hydrogenation by R. Coffey and by A. Andreetta, F. Conti and G. F. Ferrari also appear in *Aspects of Homogeneous Catalysis*, Vol. 1, ed. by R. Ugo.

I am grateful to my colleague Dr N. A. Hughes and to Professor B. R. James for reading the text and for a number of useful suggestions.

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CHAPTER I

GENERAL PRINCIPLES

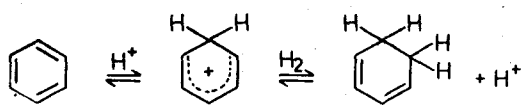
1. The Activation of Hydrogen

Although the reaction: alkene + hydrogen → alkane is thermodynamically allowed, hydrogen is a rather stable molecule not easily susceptible to polarisation, and in consequence reaction with an alkene is not observed in absence of a catalyst. Concerted addition is also symmetry disallowed.

Polarisation of the hydrogen molecule may indeed be observed [1], but only under rather severe circumstances. Thus the equilibrium:

$$Me_3CH + H^+ \rightleftarrows Me_3\overset{+}{C} + H_2$$

has been established for solutions in $HF—SbF_5$, and examined both by the rate of evolution of hydrogen or of the formation of isobutane, or of ^2H-isobutane, from reaction of *t*-butyl cation with hydrogen or deuterium [1]. Similar observations [1a] have been recorded for the reaction of benzene and hydrogen in presence of $HF—TaF_5$ as the acidic medium. Hydrogenation to give cyclohexane is regarded as resulting from a sequence of protonation and hydride transfer:



However, although these observations demonstrate polarisation leading to heterolysis of the hydrogen molecule, the reaction requires a very highly acidic medium.

A complementary base induced polarisation of hydrogen has also been realised experimentally [2]. Benzophenone may be reduced by means of hydrogen in presence of potassium *t*-butoxide in *t*-butanol. The reaction

sequence may be represented:

$$t\text{-BuO}^- + H_2 \rightleftarrows t\text{-BuOH} + H^-$$
$$Ph_2CO + H^- \rightleftarrows Ph_2CHO^-$$
$$Ph_2CHO^- + t\text{-BuOH} \rightleftarrows Ph_2CHOH + t\text{-BuO}^-.$$

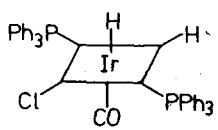
Nitrobenzene has also been reduced by this system. However, the reaction conditions for reduction, viz. 130–230 °C, 75–100 atm pressure of H_2, are again very severe.

By contrast various of the transition metals, such as platinum, palladium, rhodium, nickel, and now also a range of soluble transition metal complexes, are able to catalyse the activation of hydrogen and hydrogenation of olefins or other acceptors at the ordinary temperature and 1 atm hydrogen pressure.

The most essential element in this catalysis is the conversion of hydrogen into a transition metal hydride. In this context, the reversible formation of a dihydride (2) from reaction of hydrogen with *trans*-carbonylchloro *bis* (triphenylphosphine) iridium (I) (1) proved a particularly significant observation [3].

$$\underset{(1)}{\textit{trans}\ IrCl(CO)(PPh_3)_2} + H_2 \rightarrow \underset{(2)}{IrH_2Cl(CO)(PPh_3)_2} \qquad \text{(i)}$$

The dihydride (2) could be characterised [4] by infrared bands due to the metal hydride ligands, ν_{IrH} 2222, 2098 cm^{-1}, and by ^1H n.m.r. hydride signals: τ 28.4, 17.3, each as a 1:2:1 triplet due to $^1H—^{31}P$ coupling, i.e. consistent with structure (3). Each hydride ligand is *cis* to two phosphorus groups, but the hydrides, which are respectively *trans* to Cl and CO ligands exhibit both different infrared frequencies and different n.m.r. chemical shifts.



(3)

A further important general point to emerge from studies with carbonyl *bis* (triphenylphosphine) iridium complexes is that as the halogen is varied, the rate of reaction with hydrogen increases [5] viz., Cl < Br < I. Also as the

base properties of the phosphine are increased by introducing electron donating para substituents into the phenyl groups, e.g. *p*-MeO or *p*-Me, reaction with hydrogen is facilitated [6]. This emphasises the important influence of the totality of the ligand groups on the process of hydride formation, and on the properties of the hydrido complex which is formed.

In the transition metal hydrides, of which (3) is but one example, the metal hydride bond is covalent and not markedly polar, although in certain carbonyl hydrides such as $FeH_2(CO)_4$, the stability of the metal carbonyl anion, i.e. $[FeH(CO)_4]^-$ or $[Fe(CO)_4]^{2-}$ may render the hydride somewhat acidic [7].

Thermodynamic measurements on reaction (i) [5], and on a parallel instance of transition metal hydride formation shown in reaction (ii), indicate [8] a metal-hydrogen bond energy of ca. 250 kJ mol^{-1}.

$$2[Co(CN)_5]^{3-} + H_2 \rightarrow 2[HCo(CN)_5]^{3-} \qquad \text{(ii)}$$

It is of interest that the value is of much the same order as estimates of the binding energy for hydrogen on the surface of various transition metals [9].

The ability of a catalytic complex to activate hydrogen and form a metal hydride, as in equation (i), is a necessary, but not, in itself, a sufficient condition for catalytic hydrogenation of for example an olefin. For hydrogen transfer to such an acceptor the olefin must also generally be co-ordinated to the metal. Inspection of the structure of the hexa-coordinated dihydride (3) indicates that this co-ordinatively saturated species can accept an olefin ligand only after displacement of one of the ligands already present. The ligands are strongly bound and for this reason carbonylchloro *bis* (triphenylphosphine) iridium (I) (1) under hydrogen is not a particularly effective hydrogenation catalyst [10, 11]. In toluene solution at 70–80° and 1 atm H_2, slow hydrogenation by $IrCl(CO)(PPh_3)_2$ was observed for ethylene, propylene and for other simple olefins, but only over many hours. Nevertheless, this particular hydride-forming complex is both important historically, and also in drawing attention to the dual requirement for an effective catalyst to co-ordinate both hydrogen and the hydrogen acceptor.

From this conclusion it is also evident that the hydrogenation reaction may in principle follow either a sequence: (a) L_n·metal hydride + olefin → complex → alkane, known as the hydride route of reaction, or (b): L_n·metal + olefin → complex which with hydrogen → hydrido olefin complex → alkane,

known as the unsaturate route of reaction (L_n signifies the remaining ligands in the complex).

Kinetic studies [12] with $IrCl(CO)(PPh_3)_2$ have been interpreted in terms of a sequence of type (b), i.e. *via* the unsaturate route:

$$IrCl(CO)(PPh_3)_2 + \text{olefin} + \text{solvent} \rightleftarrows IrCl(CO)(PPh_3)(\text{olefin}) + PPh_3$$

$$\xrightarrow{H_2} IrH_2(Cl)(CO)(PPh_3)(\text{olefin}) \rightarrow \text{alkane} + IrCl(CO)(PPh_3)(\text{solvent}).$$

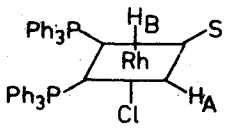
This reaction sequence also draws attention to an important role of the solvent in homogeneous catalysis not only in solvating the various components of the system, but in temporarily occupying a co-ordination site at the metal complex, albeit with only weak bonding and assisting ligand displacement.

This discussion of the behaviour of $IrCl(CO)(PPh_3)_2$ is an appropriate introduction to considering the behaviour of the related rhodium complexes e.g. $RhCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$. Unlike its iridium analogue (1), $RhCl(CO)(PPh_3)_2$ gives no evidence of hydride formation [13] in solution under 1 atm H_2. The $RhCl(PPh_3)_3$ complex, on the other hand, readily forms a dihydrido-derivative in solution, and equally important is a concomitant dissociation to a small extent of a phosphine ligand, viz.:

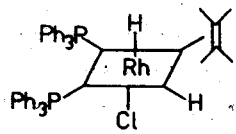
$$\underset{(4)}{RhCl(PPh_3)_3} + H_2 \rightleftarrows RhH_2Cl(PPh_3)_3 \overset{-PPh_3}{\rightleftharpoons} \underset{(5)}{RhH_2Cl(PPh_3)_2} \qquad \text{(iii)}$$

Although reaction (iii) is part of a kinetically complex [14] system which will be discussed more fully later, the immediately important point is that complex (5) is effectively five co-ordinate, and hence has a free site for co-ordination of an olefinic ligand.

The dihydro complex (6) *bis* (triphenylphosphine) dihydridochlororho-



(6)



(7)

dium, has been isolated and fully characterised [15]. It shows characteristic ν_{RhH} absorption (2078, 2013 cm^{-1}), δ_{Rh-H} (785 cm^{-1}), and ^1H n.m.r. signals: τ 28.2, 21.5, 18.8 which are consistent with structure (6), i.e. with marked $^1H—^{31}P$ coupling to H_A and small $^1H—^{31}P$ coupling to H_B. In solution the sixth co-ordination position in (6) is considered to be occupied by a weakly held solvent molecule (S), and a crystalline solvate, $RhH_2Cl(PPh_3)_2$. CH_2Cl_2 with dichloromethane has indeed been isolated. This easily displaced solvent molecule provides a site for co-ordination of an olefinic acceptor, as in (7). This catalyst has indeed proved very effective for homogeneous hydrogenation [16], viz.:

$$RhCl(PPh_3)_3 + H_2 \overset{-PPh_3}{\rightleftharpoons} RhH_2Cl(PPh_3)_2 \rightleftarrows RhH_2(\text{alkene})Cl(PPh_3)_2 \rightarrow \text{alkane} + RhCl(PPh_3)_2.$$

The reaction sequence reforms $RhCl(PPh_3)_2$ which then re-enters the catalytic cycle. It will be evident, however, that although an intermediate such as (7) is sterically well arranged to permit hydrogen transfer from rhodium to carbon, polarisation of the olefin through co-ordination, as well as a nice balance of Rh—H and C—H bond energies is also necessary to permit a rapid catalytic process of low activation energy.

Chloro*tris*(triphenylphosphine)rhodium (I) (4), which is commonly referred to as Wilkinson's complex, has proved extremely valuable not only as a catalyst, but as a means of clarifying our understanding of catalytic hydrogenation. The iridium analogue, $IrCl(PPh_3)_3$, also reacts readily to form a dihydride:

$$\underset{(8)}{IrCl(PPh_3)_3} + H_2 \rightleftarrows \underset{(9)}{IrH_2Cl(PPh_3)_3}$$

but in this case there is no detectable accompanying phosphine dissociation. The hydride (9) is not active as a catalyst for hydrogenation since there is no readily available vacant site for olefin co-ordination [17]. This interpretation is confirmed by the observation [18] that chloro*bis*(triphenylphosphine)iridium(I) (10) is found to be active for the hydrogenation of alkenes. Reaction may be formulated either by analogy with the rhodium analogue,

via a dihydride (11), which still retains a free co-ordination site, or possibly through reaction of an olefin co-ordinate (12) with hydrogen.

$$\underset{(10)}{IrCl(PPh_3)_2} + H_2 \rightleftarrows \underset{(11)}{IrH_2Cl(PPh_3)_2}$$

$$IrCl(\text{olefin})(PPh_3)_2 + H_2 \rightleftarrows \underset{(12)}{IrH_2Cl(\text{olefin})(PPh_3)_2} \rightarrow$$

$$\rightarrow \text{alkane} + IrCl(PPh_3)_2$$

Ruthenium also yields a catalytically active hydride complex, $RuHCl(PPh_3)_3$, i.e. chlorohydrido*tris*(triphenylphosphine)ruthenium(II) [19]. This differs from the rhodium and iridium complexes (6) and (11) above in that it is a monohydride. There is also a difference in the mode of formation. The dihydrides $RhH_2Cl(PPh_3)_2$ and $IrH_2Cl(PPh_3)_3$ or $IrH_2Cl(CO)(PPh_3)_2$ are formed by direct addition of hydrogen, so that the formal oxidation level of the metal is increased by two units. The ruthenium monohydride $RuHCl(PPh_3)_3$ is obtained by displacement from the dichloride:

$$RuCl_2(PPh_3)_3 + H_2 \rightarrow RuHCl(PPh_3)_3 + HCl$$

The process is assisted by use of a solvent such as ethanol which solvates the hydrogen chloride formed, or by an added base, e.g. triethylamine which removes HCl. Sodium borohydride reduction is, however, a more convenient method of preparation.

From molecular weight [19a] and spectral [19b, 19c] measurements there is evidence for phosphine dissociation from $RuCl_2(PPh_3)_3$ in solution:

$$RuCl_2(PPh_3)_3 \rightleftarrows RuCl_2(PPh_3)_2 + PPh_3.$$

This would leave free, or solvated, two co-ordination sites which permits halogen displacement *via* formation of a dihydride, i.e. following the pattern of hydrogen addition shown by the rhodium and iridium complexes considered above, viz.:

$$RuCl_2(PPh_3)_2 + H_2 \rightleftarrows RuH_2Cl_2(PPh_3)_2$$
$$\xrightarrow{-HCl} RuHCl(PPh_3)_2 \xrightarrow{PPh_3} RuHCl(PPh_3)_3.$$

A series of ruthenium hydrido complexes, $RuH(OCOR)(PPh_3)_3$ containing a carboxylate residue in place of chloride as the anionic ligand have also

been described [20], and shown to be effective homogeneous catalysts for hydrogenation. The survey has covered complexes containing anionic ligands —OCOR where R = Me, Et, *n*-Pr, *i*-Pr, CMe_3, Ph, CH_2Cl and CF_3. In the solid state, these carboxylate derivatives appear to be rather less air sensitive than the chloro complex, $RuHCl(PPh_3)_3$, but these complexes as a group are found to be highly oxygen sensitive in solution [20].

A monohydrido-rhodium complex which is also active as a catalyst for homogeneous hydrogenation is carbonylhydrido*tris*(triphenylphosphine) rhodium (I) [21], $RhH(CO)(PPh_3)_3$, which is conveniently available by sodium borohydride reduction of the corresponding chloride:

$$RhCl(CO)(PPh_3)_3 \xrightarrow{NaBH_4} RhH(CO)(PPh_3)_3.$$

This hydride is characterised [21] by ν_{RhH} 2000 cm^{-1}, and by a ^1H n.m.r. hydride signal as a doublet of quartets: τ 19.69, J_{PH} 14, J_{RhH} 1 Hz at $-35°$, which however, broadens at higher temperatures due to phosphine exchange arising from dissociation:

$$RhH(CO)(PPh_3)_3 \rightleftarrows RhH(CO)(PPh_3)_2 + PPh_3.$$

Hence, there is good evidence that in solution carbonylhydrido *tris*(triphenylphosphine)rhodium (I) will provide a species with free co-ordination sites, in principle capable of accepting an olefinic ligand. This is also clearly established by the observed [21] rapid ^1H—^2H exchange of the hydrido complex in benzene solution under deuterium, a process which presumably involves phosphine dissociation, deuterium addition, elimination of HD, and re-coordination of phosphine:

$$RhH(CO)(PPh_3)_3 \rightleftarrows RhH(CO)(PPh_3)_2 + PPh_3$$
$$\overset{D_2}{\rightleftarrows} RhHD_2(CO)(PPh_3)_2 \rightleftarrows RhD(CO)(PPh_3)_2 +$$
$$+ HD \xrightarrow{PPh_3} RhD(CO)(PPh_3)_3.$$

2. Mode of Reaction of Hydrido-Complexes with Alkenes

Although further examples of practically useful homogeneous catalyst systems will be considered below it is convenient at this point to examine the catalytic hydrogenation reaction sequence in terms of the fully characterised hydrido complexes which have already been described.

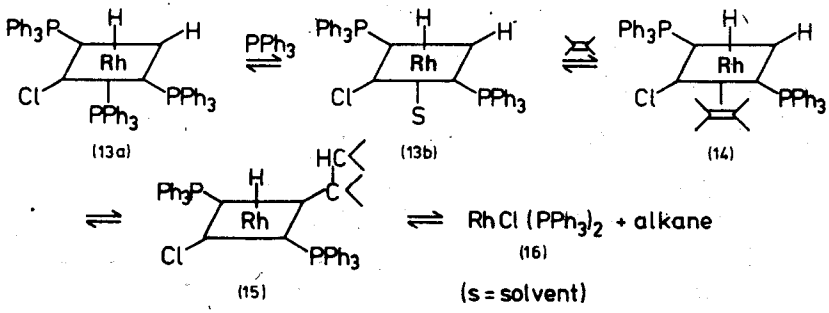
The most thoroughly investigated example is the dihydride (6) derived from chloro*tris*(triphenylphosphine)rhodium (I). The behaviour of this complex also serves to illustrate the difference between the two possible routes of hydrogenation catalysis, namely (i) formation of a hydride followed by co-ordination of alkene, or (ii) co-ordination of alkene followed by reaction with hydrogen.

Since all the ligands co-ordinated to a metal centre determine the energy levels, and since a hydride and an alkene ligand are not identical in their electronic effects, sequences (i) and (ii) are not necessarily equally facile. This principle is well illustrated by the observation [15] that whereas $RhCl(PPh_3)_3$ reacts rapidly with hydrogen and the derived hydride, $RhH_2Cl(PPh_3)_2$, hydrogenates ethylene, $RhCl(PPh_3)_3$ forms a co-ordinate with ethylene, $RhCl(C_2H_4)(PPh_3)_2$, which it is reported [15] fails to activate hydrogen at 1 atm pressure i.e.:

$$RhH_2Cl(PPh_3)_2 + C_2H_4 \longrightarrow RhCl(PPh_3)_2 + C_2H_6$$
$$RhCl(C_2H_4)(PPh_3)_2 + H_2 \not\longrightarrow C_2H_6.$$

The explanation [15] is considered to lie in the marked π-acid properties of ethylene as a ligand, which reduces the reactivity of the metal centre towards hydrogen. However, formation of the ethylene complex is reversible, and ethylene dissociation will clearly reopen the alternative route of reaction *via* the dihydride, $RhCl(H_2)(PPh_3)_2$. This may explain the observed hydrogenation of ethylene by $RhCl(PPh_3)_3$ under certain circumstances [22], and the catalytic activity of the ethylene complex, $RhCl(C_2H_4)(PPh_3)_2$ in the hydrogenation of other alkenes [23].

A reaction sequence indicating the principal steps for hydrogenation with $RhCl(PPh_3)_3$ may be outlined:



Scheme 1.

There is good evidence, discussed later, that the two hydrogens of the dihydride (13) are transferred sequentially in a two step process, and that stage (14)→(15) leading to the transient rhodium alkyl intermediate is reversible. In (13) the environments of the two hydride ligands are non-equivalent, and in any case, with an unsymmetrically substituted alkene, hydrogen transfer to the two terminii would be expected to occur at different rates. With this rhodium complex, however, stage (15)→(16) is generally very fast, and the intrinsic reversibility of stage (14)→(15), which is considered more fully under the heading of catalysed olefin isomerisation, generally has no important consequences.

The kinetics of hydrogenation using $RhCl(PPh_3)_3$ generally support the reaction sequence outlined above. The rate data are found [15] to fit reasonably the general relation:

$$-\mathrm{d}[\text{olefin}]/\mathrm{d}t = \frac{(k_1K_1 + k_2K_2)[H_2][\text{olefin}][RhCl(PPh_3)_3]}{1 + K_1[H_2] + K_2[\text{olefin}]}$$

where K_1, K_2 and k_1, k_2 are defined in the reaction scheme:

$$\begin{array}{ccc} RhCl(PPh_3)_3 + H_2 & \overset{K_1}{\rightleftharpoons} & RhH_2Cl(PPh_3)_2 \\ K_2 \uparrow\downarrow \text{(olefin)} & & \text{(olefin)} \uparrow\downarrow k_1 \\ RhCl(\text{olefin})(PPh_3)_2 & \xrightarrow[H_2]{k_2} & RhCl(PPh_3)_2 + \text{alkane} \end{array}$$

and k_2 is ~ 0, i.e. the olefin complex does not contribute to the reaction.

Close examination, however, has revealed that the behaviour of chloro-*tris*(triphenylphosphine)rhodium (I) in solution is rather complex [22, 24b]. It has been shown that $RhCl(PPh_3)_3$ dissociates in solution:

$$RhCl(PPh_3)_3 \rightleftarrows RhCl(PPh_3)_2 + PPh_3$$

and that although this equilibrium lies far to the left ($K = 1.4 \times 10^{-4}$ M), the dissociated species reacts very rapidly with hydrogen:

$$RhCl(PPh_3)_2 + H_2 \rightleftarrows RhH_2Cl(PPh_3)_2.$$

In the presence of the phosphine in solution this chlorodihydrido *bis*(tri-

phenylphosphine) rhodium (III) is in equilibrium with the six co-ordinate $RhH_2Cl(PPh_3)_3$:

$$RhH_2Cl(PPh_3)_2 + PPh_3 \rightleftarrows RhH_2Cl(PPh_3)_3$$

which has also been characterised [22].

These reactions are rapid and appear to contribute the principal components concerned in hydrogenation with $RhCl(PPh_3)_3$ in absence of any appreciable excess of phosphine. The complex $RhCl(PPh_3)_2$ reacts with hydrogen some 10^4 times more rapidly than does $RhCl(PPh_3)_3$:

$$RhCl(PPh_3)_3 + H_2 \rightleftarrows RhH_2Cl(PPh_3)_3.$$

Chloro*bis*(triphenylphosphine) rhodium (I) also generates a chloride bridged dimer:

$$RhCl(PPh_3)_3 \rightleftarrows RhCl(PPh_3)_2 + PPh_3$$

$$2RhCl(PPh_3)_2 \rightleftarrows (Ph_3P)_2Rh\begin{matrix}Cl\\ \diagup\ \diagdown\\ Cl\end{matrix}Rh(PPh_3)_2.$$

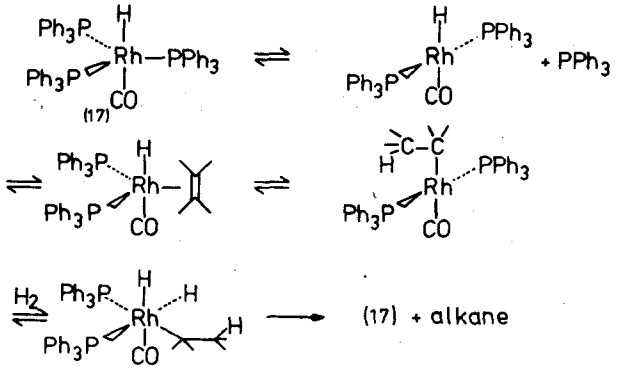
This dimer also reacts with hydrogen to give a dihydro-derivative [22].

$$[RhCl(PPh_3)_2]_2 + H_2 \rightleftarrows (PPh_3)_2RhH_2\begin{matrix}Cl\\ \diagup\ \diagdown\\ Cl\end{matrix}Rh(PPh_3)_2.$$

However, although the hydride from the dimer is catalytically quite effective [22] its rate of formation is slow compared with the rate of formation of $RhH_2Cl(PPh_3)_2$ which is the main reactive species in hydrogenation.

It is evident that these equilibria will be rather sensitive to any excess phosphine which may contaminate a preparation of $RhCl(PPh_3)_3$.

The sequence outlined for catalysis by chloro*tris*(triphenylphosphine) rhodium (I) may be taken as a typical for a catalytically active dihydrido complex, but for a monohydrido catalyst the reaction sequence is necessarily somewhat different. Thus for catalysis of hydrogenation by $RhH(CO)(PPh_3)_3$ (17) the following reaction sequence has been proposed [21] as being in best agreement with the experimental observations.



Scheme 2.

Hydrogenation with the mono hydrido catalyst $RuHCl(PPh_3)_3$ may also be accommodated within a reaction sequence similar to Scheme 2. Chlorohydrido *tris*(triphenylphosphine) ruthenium (II) does not complex strongly with terminal alkenes [19a], but in $CDCl_3$ solution with ethylene under pressure (~35 atm) the ^1H n.m.r. spectrum viz.: τ 9.0 (triplet) and 7.96 (quartet) gave evidence for formation of an ethyl complex:

$$RuHCl(PPh_3)_3 + C_2H_4 \rightleftarrows RuCl(C_2H_5)(PPh_3)_3$$

accompanied by a colour change from red-violet to brown.

3. The Metal-Alkyl Intermediate

In the reaction sequences outlined in Schemes 1 and 2 there are essentially two different steps in hydrogen transfer to the alkene, namely (i) metal hydride addition across the olefinic bond of the co-ordinated alkene: MH +  $\rightarrow$ M—C—CH, and (ii) insertion of a hydride ligand into a metal-alkyl bond: H—M—C—CH $\rightarrow$ M + alkane. With the catalytically very efficient complexes based on rhodium or ruthenium the alkyl intermediate M—C—CH has not been isolated i.e. step (ii) is fast. However, with hydridopentacyanocobaltate (III) ion which has long been known as a catalyst