The Preparation and Properties of Tris(triphenylphosphine)halogenorhodium(I) and Some Reactions thereof including Catalytic Homogeneous Hydrogenation of Olefins and Acetylenes and their Derivatives

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Tris(triphenylphosphine)chlororhodium(I), $RhCl(PPh_3)_3$, has been prepared by the interaction of an excess of triphenylphosphine with rhodium(III) chloride hydrate in ethanol; the corresponding bromide and iodide are also described. The dissociation of the complex in various solvents has been investigated, and its reactions with hydrogen, ethylene, and carbon monoxide and aldehydes studied. Dihydrido- and ethylene complexes have been isolated and studied by nuclear magnetic resonance (n.m.r.) spectroscopy. Approximate values for the formation constants of ethylene and propylene complexes have been obtained; the latter is lower by a factor of over 10^3. By electron spin resonance spectroscopy, the complex $RhCl(PPh_3)_3$ has been shown to contain trace amounts of a paramagnetic species, probably a rhodium(II) complex.

In homogeneous solution the tris(triphenylphosphine) complexes are exceedingly active catalysts for the rapid and homogeneous hydrogenation, at *ca.* 1 atmosphere of hydrogen pressure and room temperature, of unsaturated compounds containing isolated olefinic and acetylenic linkages.

The rates of hydrogenation of hept-1-ene, cyclohexene and hex-1-yne have been studied quantitatively and the dependence on factors such as substrate and catalyst concentration, temperature, and pressure determined. The data can be accommodated by a rate expression of the form:

$$\text{Rate} = \frac{K\,p[S]\,[A]}{1 + K_1 p + K_2[S]}$$

where [S] and [A] are the olefin and catalyst concentrations, respectively, and p is the concentration of hydrogen in solution.

From the data for cyclohexene the activation energy for the rate determining step is $E_a = 22{\cdot}9$ kcal. mole^{-1} ($\Delta H^\ddagger = 22{\cdot}3$ kcal. mole^{-1}) and the value of $\Delta S^\ddagger = 12{\cdot}9$ e.u.

It is shown that the rate of hydrogen–deuterium exchange under selected conditions is quite slow compared with the rates of hydrogenation of olefins and, furthermore, that when H_2–D_2 mixtures are used in the reactions, alkanes and dideuteroalkanes are the major products. Reductions of maleic and fumaric acids with deuterium shows that *cis*-addition occurs preferentially. Similarly, in the reduction of hex-2-yne to n-hexane, *cis*-hex-2-ene is found to be the major olefin intermediate.

A mechanism for the hydrogenation is proposed in which the metal complex serves as a template to which a hydrogen molecule and an olefin molecule are briefly co-ordinated before transfer of one to the other takes place. The low kinetic isotope effect (rate H_2/rate $D_2 = 0{\cdot}9$) suggests that synchronous breaking of Rh–H bonds and making of C–H bonds takes place in the transition state involving two simultaneous three-centre interactions.

The activation of molecular hydrogen by transition-metal ions or complexes in homogeneous solution is well known.[1] However, only very few systems have proved to be useful for the catalytic homogeneous hydrogenation of unsaturated compounds. One of the most versatile catalysts, but one which has the disadvantage of being soluble only in water, is the cobalt(II)–cyanide system; it allows the reduction of conjugated double bonds, as in butadiene, α,β-unsaturated acids and aldehydes, but isolated ethylenic linkages are unaffected.[2] A series of Ziegler-type catalysts soluble in organic solvents allows hydrogenation of olefinic hydrocarbons,[1c] while a chloroplatinate(II)–trichlorostannate(II) complex is effective for ethylene and acetylene.[3] It has been claimed that higher olefins are not reduced in ethanolic solution,[4a] although in the presence of triphenylphosphine, platinum–tin complexes can hydrogenate the methyl ester of soy bean oil.[4b]

It has long been known that molecular hydrogen in the presence of soluble rhodium(III) ammines could reduce quinone.[5] However, rapid deposition of metal occurs, a complication also encountered in the reduction of ferric ion by hydrogen in the presence of hexachlororhodate(III) ion.[6]

During our studies on the use of reducing agents for the catalytic preparation of rhodium(III) complexes from $RhCl_3,3H_2O$, it was observed[7] that molecular hydrogen could act as a catalyst, *e.g.*, for the preparation of *trans*-[Rh py$_4$ Cl$_2$]Cl from pyridine solutions of rhodium trichloride (which contain mainly 1,2,6-Rh py$_3$ Cl$_3$). Furthermore, it was found that 1,2,6-Rh py$_3$ Cl$_3$ in ethanol can slowly catalyse the reduction of hex-1-ene by hydrogen at atmospheric pressure (or more rapidly at higher pressures) without metallic rhodium being deposited.

In order to stabilise the catalyst complex more effectively towards reduction to the metal, and in the hope of obtaining a system catalytically more efficient than the ones employing pyridine, we studied rhodium

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[1] (*a*) J. Halpern, *Adv. in Catalysis*, 1959, **11**, 301; (*b*) J. Halpern and R. S. Nyholm, *Proc. 3rd Internat. Cong. Catal.*, W. M. H. Sachter, G. C. A. Schuitt, and P. Zwietering, eds., vol. I, North Holland Pub. Co., Amsterdam, 1965, p. 25, 146; (*c*) M. F. Sloane, A. S. Matlack, and D. S. Breslow, *J. Amer. Chem. Soc.*, 1963, **85**, 4014, and references therein.

[2] J. Kwiatek and J. K. Seyler, *J. Organometallic Chem.*, 1965, **3**, 421, and references therein.

[3] R. D. Cramer, E. L. Jenner, R. V. Lindsay, jun., and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1963, **85**, 1691.

[4] (*a*) G. C. Bond and I. Hellyer, *Chem. and Ind.*, 1965, 35; (*b*) J. C. Bailar, jun., and H. Itatani, *Inorg. Chem.*, 1965, **5**, 1618.

[5] M. Iguchi, *J. Chem. Soc. Japan*, 1939, **60**, 1287.

[6] R. F. Harrod and J. Halpern, *Canad. J. Chem.*, 1959, **37**, 1933.

[7] R. D. Gillard, J. A. Osborn, P. B. Stockwell, and G. Wilkinson, *Proc. Chem. Soc.*, 1964, 284.

complexes of the stronger π-acceptor ligands such as tertiary phosphones and arsines. Our first studies[8] were made using a rhodium(III) complex stabilised by triphenylphosphine. During the preparation of this phosphine complex we found that when an excess of triphenylphosphine was used, a rhodium(I) complex, $RhCl(PPh_3)_3$, results. This rhodium(I) complex, and the corresponding bromide and iodide, have proved to be the most effective catalysts yet recognised for the homogeneous hydrogenation at normal temperatures and pressures of a variety of unsaturated compounds containing both double and triple bonds.[9]

Although patent claims[10] have been made that solutions of various metallic salts in phosphites could act as homogeneous hydrogenation catalysts, stoicheiometric compounds were not characterised, nor were phosphine ligands studied. Since our first publications[7-9] Vaska has extended his work on hydrogen uptake by square complexes and in preliminary notes[11,12] reports that ethylene, propylene and acetylene can be slowly hydrogenated at 40—60° by the use of $IrCl(CO)(PPh_3)_2$ or at 20—40° by $IrH(CO)(PPh_3)_3$ and $OsHCl(CO)(PPh_3)_3$. As we shall show later, the square carbonyl complexes are very much less efficient catalysts than $RhCl(PPh_3)_3$.

Although hydroformylation reactions of olefins can be effected using rhodium(III) complexes,[8] the rhodium(I) complex again is a more effective catalyst, and can also be used for acetylene hydroformylation.[13] As we shall show later, $RhCl(PPh_3)_3$ is converted by carbon monoxide at 1 atmosphere pressure to $RhCl(CO)(PPh_3)_2$, so that the active hydroformylation catalyst, is, in fact this well known complex; this was confirmed by its direct use. The only previous literature reference to the use of rhodium catalysts is a recent one describing a comparison of rhodium carbonyl with cobalt carbonyl in the conventional hydroformylation process.[14] Although patent claims for the use of solid-state rhodium catalysts exist, the claims involving soluble catalysts,[15] *i.e.*, Group VIII salts of transition metals in the presence of donor ligands such as R_3P, wherein the metal is specifically stated to be in an oxidation state of 0 or -1, provide no examples of the use of rhodium complexes. Indeed, not only were authentic stoicheiometric compounds both unspecified and characterised, but we have shown that some of the claims cannot be reproduced.

In the present Paper we discuss the properties of tris(triphenylphosphine)halogenorhodium(I) complexes, $RhX(PPh_3)_3$, (X = Cl, Br, or I), and their use as homogeneous hydrogenation catalysts; most of the detailed studies have been made on the chloride. These particular complexes have proved more convenient than any other previously known catalyst systems for allowing the mechanism of the catalytic process to be studied. In succeeding Papers we shall describe hydroformylation and hydrogenation studies, using rhodium(III) and other Group VIII metal complex catalysts.

(A) *Tris(triphenylphosphine)chlororhodium*(I) *and its Properties.*—(a) *Preparation and physical properties.* When rhodium(III) chloride hydrate and an excess (*ca.* 6 mols) of triphenylphosphine are dissolved in boiling ethanol, reduction occurs and the dark, burgundy-red, crystalline complex, $RhCl(PPh_3)_3$, is obtained A large excess of triphenylphosphine is essential to prevent the formation of a bridged dimer (see below) and to further the reduction of the rhodium(III) species formed initially. Since reduction does not occur in ethanol heated under reflux unless an excess of triphenylphosphine is present, and since acetone–water mixtures can be used in place of ethanol as a solvent, the triphenylphosphine is, without doubt, the actual reducing agent. The initial product is probably PPh_3Cl_2 which then undergoes solvolysis to form $OPPh_3$; the latter is detectable in the residual solutions. If insufficient ethanol as a solvent is used, an orange crystalline material is at first precipitated, which gives the red complex on continued heating under reflux. This orange complex has an analysis identical with that of the red $RhCl(PPh_3)_3$ and may be a second crystalline form.[16]* The corresponding bromide, prepared by the addition of an excess of lithium bromide to the reaction mixture, can also be isolated in two crystalline forms. The iodide has been prepared similarly, but the conditions of reaction are more critical (see Experimental section).

The above reaction involving triphenylphosphine appears to be unique. By contrast, the interaction of other tertiary aryl alkyl phosphines and arsines with hot ethanolic solutions of rhodium trichloride gives mono- or bi-nuclear rhodium(III) complexes.[17] Although the interaction of rhodium chloride with triphenylphosphine has been reported,[18] stoicheiometric quantities were used in order to obtain $RhCl_3(PPh_3)_3$; we have had some difficulty in reproducing this preparation and although orange products are obtained, they appear to be mixtures which, on repeated crystallisation, give some $RhCl(PPh_3)_3$.

The only compound of a similar type previously reported, appears to be the diphenylphosphine complex,[19] $RhCl(PHPh_2)_3$, obtained by the interaction of $PHPh_2$

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* These compounds were also independently prepared by Bennett and Longstaff (ref. 16).

[8] J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Comm.*, 1965, 17.

[9] J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Comm.*, 1965, 131.

[10] *e.g.*, B.P. 946,062/1964.

[11] L. Vaska and R. E. Rhodes, *J. Amer. Chem. Soc.*, 1965, **87**, 4970.

[12] L. Vaska, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 89.

[13] F. H. Jardine, J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. and Ind.*, 1965, 560.

[14] H. Wakamatsu, *Nippon Kekaku Zasshi*, 1965, **85**, 227 (*Chem. Abs.*, 1964, **61**, 13,173).

[15] *e.g.*, B.P. 801,734/1958; 988,941, 988,942, 988,943, 988,944/1965.

[16] M. A. Bennett and P. A. Longstaff, *Chem. and Ind.*, 1965, 846.

[17] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508.

[18] R. J. Mawby and L. M. Venanzi, *Experimentia Supplementa*, No. 9; "Essays in Coordination Chemistry," Birkhauser, Basel, 1964, p. 240.

[19] R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 301.

with $[(C_2H_4)_2RhCl]_2$. The molecular weight in solution was quoted as normal, in contrast to that of $RhCl(PPh_3)_3$ (see below); no chemical properties were reported. A number of phosphite complexes, *e.g.*, $RhCl[P(OPh)_3]_3$ were obtained[20] from $[(CO)_2RhCl]_2$. These were also stated to have normal molecular weights; it was also specified that tris-tertiary-phosphine complexes could not be obtained from the carbonyl chloride.

It is of some interest that 5-co-ordinate complexes of stoicheiometry $RhXL_4$ seem to be unstable for alkyl or aryl phosphines or phosphites, despite the existence of 5-co-ordinate species such as $Rh(CO)H(PPh_3)_3$,[21] $Rh(C_8H_{10})(SnCl_3)(PPh_3)_2$,[22] and $RhH(PF_3)_4$.[23] It seems reasonable to assume that the difference is due to steric factors. It is pertinent to note that in the triphenylphosphine complexes of ruthenium(II)[24] and palladium(II)[25] an α-hydrogen atom of a phenyl group occupies an axial position of the metal atom in the crystalline complexes. The existence of red and orange forms of $RhCl(PPh_3)_3$ may well be due to differences in such secondary interactions. Furthermore, the formation of the tris-triphenylphosphine derivative, which is stable only in the crystalline state, may be a result of the stabilisation of a sparingly soluble crystalline lattice due to these interactions.

At 25°, the chloride complex is moderately soluble in chloroform or dichloromethane (*ca.* 20 g./l.), slightly soluble in benzene (*ca.* 4 g./l.) or toluene, and considerably less soluble in acetic acid, acetone and other ketones, methanol, ethanol and other alcohols. It is virtually insoluble in light petroleum and cyclohexane. The bromide and iodide are somewhat more soluble in organic solvents. The complexes dissolve and react with donor solvents, (L), such as pyridine, dimethyl sulphoxide, and acetonitrile, to yield complexes of the type $RhCl(PPh_3)_2L$. The solutions in dichloromethane or benzene quite rapidly absorb oxygen to give an oxygen complex[26] * (see later) which is more soluble in organic solvents than is $RhCl(PPh_3)_3$; the higher solubilities reported for $RhCl(PPh_3)_3$[16] may be due to inadequate de-gassing of solvents. It is essential for the determination of molecular weights in solution that air be rigorously excluded; there are difficulties in ensuring this when the Mechrolab Osmometer is used, but freezing-point depression studies are in agreement with the osmometric values (see Experimental section).

The tristriphenylphosphine halides dissociate in solution, *e.g.*,

$$RhCl(PPh_3)_3 \underset{PPh_3}{\overset{\text{solvent}}{\rightleftarrows}} RhCl(PPh_3)_2 + PPh_3 \qquad (1)$$

and the solution species may dimerise:

$$2RhCl(PPh_3)_2 \rightleftarrows [RhCl(PPh_3)_2]_2 \qquad (2)$$

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

On heating benzene solutions of the chloride under reflux, the orange-pink complex of stoicheiometry $RhCl(PPh_3)_2$ is obtained; over long periods (>24 hr.) precipitation of the dimer occurs even from cold concentrated solutions in benzene. The dimer is very sparingly soluble in organic solvents but molecular weights of this substance in solution under hydrogen (see later) agree with a dimeric formula. A dimeric halogen-bridged structure is the most likely, bearing in mind the well-established behaviour of closely related rhodium(I) complexes of the type $[RhClL_2]_2$. The dimer can be readily converted to $RhCl(PPh_3)_3$ by heating with a 10 molar excess of triphenylphosphine in ethanol. It may be mentioned here that although $RhCl(PPh_3)_3$ in the solid state, is stable indefinitely in air, the crystalline dimer is not. Oxygen is taken up and the infrared (i.r.) spectrum of the product shows a strong band at *ca.* 1150 cm.$^{-1}$ attributable to triphenylphosphine oxide.

At the present time, we have no information concerning the structure of the dissociated solution species $RhCl(PPh_3)_2$ (A). If we assume that $RhCl(PPh_3)_3$ has the square configuration common for Rh^I, then on consideration of *trans*-effects one would anticipate that one of the *trans*-phosphine groups would be labile. However, it seems unlikely that this can be the sole reason for this ready lability, and steric repulsion due to overcrowding by the phenyl groups is likely to be a strong and probably decisive contributory factor. It seems unlikely that the formally three-co-ordinate species, (A), would retain the square configuration, with the fourth position occupied by solvent, particularly in rather weakly donating solvents such as chloroform or benzene. Furthermore, steric repulsion between the triphenylphosphine groups will tend to widen the P–Rh–P angle, so that the most likely structure for (A) would appear to be one with pyramidally disposed triphenylphosphine, and chloro-groups. The essential point is that (A) has vacant co-ordination sites which can be occupied either by weakly bound solvent molecules or by other ligand atoms. The existence of vacant sites is essential to the catalytic activity of (A) as we shall see.

We note finally that $RhCl(PPh_3)_3$ gives non-conducting solutions in acetone and dimethylformamide.

(b) *Chemical properties.* (i) Reaction with carbon monoxide and aldehydes.—The co-ordinative unsaturation of (A) is demonstrated by its reaction with donor

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* See behaviour of $IrCl(CO)(PPh_3)_2$ (ref. 26).

[20] L. Vallerino, *J. Chem. Soc.*, 1957, 2473.

[21] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

[22] J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 1964, 5176.

[23] Th. Kruck and W. Lang, *Angew. Chem. Internat. Edn.*, 1965, **4**, 870.

[24] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.

[25] N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *Chem. Comm.*, 1965, 237, 296.

[26] L. Vaska, *Science*, 1963, **140**, 809; J. A. Ibers and S. J. La Placa, *ibid.*, 1964, **145**, 920.

molecules to form adducts, as noted above, but in particular by its affinity for carbon monoxide, when the well-known complex *trans*-bis(triphenylphosphine) carbonyl chlororhodium(I) is formed. Thus, on saturation of benzene or chloroform solutions of (A) with carbon monoxide, an immediate and quantitative reaction occurs, the solution changing in colour from red to yellow:

$$\mathrm{RhCl(PPh_3)_2 + CO \longrightarrow \mathit{trans}\text{-}RhCl(CO)(PPh_3)_2} \qquad (3)$$

It appears to be impossible to reverse this reaction and even the action of molten triphenylphosphine at 100° on the carbonyl complex does not displace carbon monoxide.

The high affinity of (A) for carbon monoxide is also shown by its rapid reaction with aldehydes under mild conditions, when carbon monoxide is abstracted. Thus a solution of (A) in benzene reacts with n-heptaldehyde or valeraldehyde in the cold, or more rapidly on warming, to give quantitative yields of *trans*-$RhCl(CO)(PPh_3)_2$. From heptaldehyde, gas–liquid chromatography (g.l.c.) shows that the other products are *ca.* 80% n-hexane and *ca.* 20% hexenes. Benzaldehyde gives only the complex and benzene. The latter reactions may be regarded as a reverse of the hydroformylation reaction. More detailed studies of the kinetics and mechanism of the reaction have been made[27] and will be reported separately. During our studies, similar reactions of aldehydes with the complex have been briefly described;[28] the reaction with carbon monoxide and abstraction reactions with allyl alcohol and acetate ion have also been noted.[16] We have also demonstrated carbon monoxide abstraction reactions with dimethylformamide on warming, and with dioxan in the presence of an excess of triphenylphosphine on warming. In the latter case, if an excess of triphenylphosphine is not present, heating gives only crystals of the dimer. Methyl ethyl ketone also gives only the dimer and other ketones appear to be unreactive towards carbon monoxide abstraction.

It may be noted that the interaction of rhodium trichloride hydrate in the presence of an excess of triphenylphosphine in solvents such as dioxan and dimethylformamide gives $RhCl(CO)(PPh_3)_2$[29], and (A) may be an intermediate in such reactions. A similar reaction is that of $RhCl_3(PEt_3)_3$ with allyl alcohol or ethanolic potassium hydroxide, which again gives the carbonyl complex.[30]

Finally, an adaptation[27] of the aldehyde reaction employing aqueous formaldehyde as both a reducing agent and a source of carbon monoxide, provides the most rapid and economical preparation of *trans*-$RhCl(CO)(PPh_3)_2$ directly from $RhCl_3,3H_2O$.

(ii) Interaction with ethylene. Ethylene, like carbon monoxide, reacts rapidly with solutions of (A) in benzene or chloroform and the bright yellow, crystalline complex, bis(triphenylphosphine)ethylenechlororhodium(I), $RhCl(PPh_3)_2(C_2H_4)$, can be readily isolated. Although dipole moment measurements cannot be made, it seems that this square complex has *trans*-triphenylphosphine groups like the corresponding carbonyl complex; the ^{19}F n.m.r. spectra of the corresponding tetrafluoroethylene complex[31] show that the tetrafluoroethyl-group is *trans* to chlorine and *cis* to two mutually *trans*-triphenylphosphine groups.

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

$$\mathrm{RhCl(PPh_3)_2 + C_2H_4 \overset{K_2}{\rightleftharpoons} RhCl(PPh_3)_2(C_2H_4)} \qquad (4)$$

The n.m.r. spectrum of the ethylene chloro-complex has been measured in deuterochloroform solution in the presence of varying amounts of ethylene (Table 1).

TABLE 1

Nuclear magnetic resonance spectra of $RhCl(PPh_3)_2(C_2H_4)$ in chloroform at 25°

$\frac{C_2H_4\ (\text{free})}{C_2H_4\ (\text{co-ord.})}$	Line * position	Approximate half-width
0	262	25
0·5	282	20
1·5	300	5
3·0	300	5
∞ †	300	5

* c./sec. on low field side of Me_4Si. † Free C_2H_4 value τ 4·69 in $CHCl_3$.

The spectra show only a single line due to ethylene, whose position depends on the ethylene–rhodium concentration ratio. At low ethylene concentrations the peak is broad, half-width *ca.* 25 c./sec., and even on cooling to −50°, no sharpening or splitting was observed, although a slight downfield shift (*ca.* 7 c./sec.) occurs due to the greater solubility of ethylene at lower temperatures. With increasing ethylene concentration, the line sharpens and moves downfield towards the position of resonance for unco-ordinated ethylene in the solvent. As in other ethylene complexes, it is clear that a rapid exchange between free and co-ordinated ethylene occurs in solution, even at −50°. A mean lifetime for residence of ethylene on the metal atom can be estimated as less than *ca.* 10^{-2} sec., a value comparable to those found by Cramer.[32]

By contrast, ^{19}F n.m.r. spectra show that at 25° there is no ligand exchange with the corresponding complex of tetrafluoroethylene.[31]

The ethylene addition reaction (equation 4) can also be followed spectrophotometrically. De-gassed solutions of $RhCl(PPh_3)_3$ in benzene show a band at 360 mμ (ε ~6000) as a shoulder on a much stronger band present in the ultraviolet (u.v.) spectrum. On passing

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[27] M. Baird, J. A. Osborn, and G. Wilkinson, unpublished results.

[28] J. Tsuji and K. Ohno, *Tetrahedron Letters*, 1965, 3969.

[29] A. Rusina and A. A. Vlček, *Nature*, 1965, **206**, 295.

[30] J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931.

[31] M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, 1965, 6629.

[32] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217; *Inorg. Chem.*, 1965, **4**, 445.

ethylene through the solution, or on dissolving the crystals of $RhCl(PPh_3)_2(C_2H_4)$ in benzene saturated with ethylene, a new band at 416 mμ (ε ~3000) appears at the expense of the 360 mμ band. This change is reversed on passing oxygen-free nitrogen through the solution. The occurrence of isosbestic points at 434 and 402 mμ shows that only two species are involved in this reversible process. The relative concentrations of the two species were estimated by subtracting the extrapolated background resulting from a strongly intensifying band further in the u.v. Thus, for *ca.* 4×10^{-4}M-solutions saturated with ethylene at 1 atmosphere, the ratio of the ethylene complex to the uncomplexed $RhCl(PPh_3)_2$ is *ca.* 20 : 1. Using the solubility of ethylene in benzene at 25° and 1 atmosphere (3·403 ml./ml.), the approximate equilibrium constant for reaction (4) is $K_2 \sim 100$ mole^{-1} l.

The same procedure was used for propylene except that the solution of the ethylene complex in benzene was swept with propylene at 1 atmosphere for 60 min. during which time the spectrum was followed. The band at 416 mμ soon decreased in intensity at the expense of the band at 360 mμ. When an equilibrium had been reached, as indicated by constancy of the spectrum, no measurable intensity above the background could be detected at 416 mμ, while the band at 360 mμ had an intensity virtually that found for the solution of $RhCl(PPh_3)_2$ alone. Hence the ratio of the propylene complex to that of uncomplexed $RhCl(PPh_3)_2$ must be less than the error in measuring the band intensities, say 5%. A similar result was found for hept-1-ene.

Hence the complex constant for the formation of the propylene complex, bearing in mind the greater solubility of propylene in benzene (*ca.* 17 ml./ml.) is at least 2000 times smaller than that for ethylene; thus $K_2 < 0{\cdot}05$ mole^{-1} l. Using $RhBr(PPh_3)_3$ the complexity constant for ethylene is lower by approximately a factor of five. We have been unable to isolate an iodo-complex and the constant is presumably much smaller still. The decrease in ethylene complex forming ability, Cl > Br > I, would be expected, considering the increase in the *trans*-effect of the halide if the halide is *trans* to ethylene.

There is relatively little information in the literature concerning values for the complexity constants except for ethylene [33,34a] and substituted styrenes [34b] with Pd^{II} or Pt^{II}. However, Cramer, in his work on ethylene dimerisation [35] quotes unpublished results on complexes of the type $[RhCl_2(olefin)(solvent)]^-$, stating that ethylene is favoured by a factor of about 10^3 over but-1-ene. Similarly, in studies on olefin oxidation by palladium(II) solutions, it appears qualitatively that, the equilibrium concentrations of the olefin complexes are lower for propylene and but-1-ene than for ethylene.[36]

Since quite bulky substituents can evidently be present on the olefin, at least, in certain complexes,[34b] it would appear that the main factor may be an electronic one. It seems most reasonable to assume that when alkyl groups replace hydrogen in ethylene, hyperconjugation and/or inductive effects lead to a reduction in the π-acidity of the carbon anti-bonding orbitals; this in turn will lead to weaker metal ⟶ olefin π-bonding. Furthermore, for substituted ethylenes there must be, of necessity, asymmetry in the metal to C=C bond, the axis of which is doubtless at some angle to the molecular plane other than the 90° found in ethylene complexes. Such distortion is likely to introduce steric factors particularly when, as in the present case, there are bulky ligands in positions *cis* to that occupied by the olefin. That electronic factors are very important, however, is clear from the high stability and low lability of the tetrafluoroethylene complex.

Despite this low complexing ability of mono-olefins other than ethylene, isolable complexes are easily obtained with chelating diolefins,[16] hexafluorobut-2-yne,[31] and diphenylacetylene.[37]

Finally, an important point concerning the interaction of olefins with (A) is that, in contrast to a number of well-established cases with other complexes of rhodium, as well as with complexes of palladium and other metals, there is no evidence for olefin isomerisation. For example, there was no *cis*–*trans* isomerisation of a 1 : 1 mixture of *cis*- and *trans*-hex-2-enes or isomerisation of hex-1-ene at 25° over periods up to 24 hr. Slight isomerisation occurred when hydrogen was present.

(iii) Reaction with molecular hydrogen; dihydrido-complexes. (*a*) When saturated solutions of (A) in solvents such as benzene, chloroform, ethyl acetate, or glacial acetic acid are shaken with molecular hydrogen, the colour changes from red to pale yellow. Manometric studies indicate that in all of these solvents 1 mole of hydrogen is absorbed per mole of rhodium complex. In chloroform and benzene the dihydrido-species is more soluble than $RhCl(PPh_3)_3$; the dihydrido-species in glacial acetic acid and ethyl acetate have about the same low solubility as $RhCl(PPh_3)_3$. Hence, depending on the concentration, pale yellow or white crystals of the dihydrido-complex may separate as the hydrogen uptake proceeds. N.m.r. spectra of these solutions, which contain one equivalent of displaced phosphine show three high-field lines due to hydrogen atoms bound to rhodium. On sweeping the solutions with nitrogen, the high-field lines disappear and the solution regains its initial red colour. Re-saturation with hydrogen restores the yellow colour and the n.m.r. signals. The cycle can be repeated, apparently indefinitely, showing a reversible equilibrium of the type:

$$RhCl(PPh_3)_2 + H_2 \overset{K_1}{\rightleftharpoons} RhCl(PPh_3)_2H_2 \qquad (5)$$

Analogous behaviour was observed for solutions of $RhBr(PPh_3)_3$ and $RhI(PPh_3)_3$.

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[33] P. M. Henry, *J. Amer. Chem. Soc.*, 1964, **86**, 3246, and references therein.

[34] (*a*) S. I. Shupack and M. Orchin, *J. Amer. Chem. Soc.*, 1963, **85**, 902; (*b*) *ibid.*, 1964, **86**, 586.

[35] R. D. Cramer, *J. Amer. Chem. Soc.*, 1965, **87**, 4717.

[36] J. Smidt, *Chem. and Ind.*, 1962, 54.

[37] D. N. Lawson, J. A. Osborn, and G. Wilkinson, following Paper.

Absorption of molecular hydrogen has not been previously reported for a rhodium complex, but the uptake of hydrogen at normal pressure by the iridium complex $IrCl(CO)(PPh_3)_2$ is well known.[38] The solubility of this hydrido-species was too low for n.m.r. study, but the corresponding bromide and iodide have been stated[39] to be sufficiently soluble as to yield n.m.r. spectra which are consistent with an octahedral species with *cis*-hydrido-groups, a result in confirmation of i.r. data. It has been reported[40] that the dihydrido-derivatives of the corresponding rhodium and cobalt complexes could not be obtained. The uptake of hydrogen by the carbonyl species and their ability to act as hydrogenation catalysts is discussed at a later stage.

(*b*) The nature, spectra, and structure of dihydrido-species. There is no change in the non-conductance of acetone solutions of the chloro- and bromo-complexes $RhX(PPh_3)_3$, (X = Cl or Br), when they are saturated with hydrogen; this indicates that the halide ion remains co-ordinated, a result further confirmed by the analysis of the isolated solids. Although crystalline solids can be obtained fairly readily from hydrogen-saturated solutions, their characterisation has not been easy, due both to the ease of aerial oxidation of, and ready loss of hydrogen from, the solutions.

The microcrystalline white solid isolated from hydrogen saturated chloroform solutions of (A) analyses for $RhCl(PPh_3)_2H_2$; the molecular weight under hydrogen is normal. The species may possibly be 5-co-ordinate in the solid, but in solution 6-co-ordination with solvation by chloroform is most likely. The formation of solvates with chlorinated hydrocarbons is confirmed by the isolation from dichloromethane solutions of a stable yellow crystalline complex $[RhCl(PPh_3)_2H_2]_2,CH_2Cl_2$, which apparently contains quite firmly held and, we propose, co-ordinated, bridging dichloromethane. Using ethyl acetate, glacial acetic acid and dimethylformamide as solvents for $RhCl(PPh_3)_3$, white solids may again be isolated. The analyses, whilst not entirely satisfactory, show that two triphenylphosphine ligands are present for each rhodium atom, and that co-ordinated solvent is present. The latter is also clearly shown by the presence of co-ordinated solvent bands in the i.r. spectra of the complexes. Dissolution of these solvated complexes (which are very sparingly soluble in the parent solvent) in deuterochloroform gives an n.m.r. spectrum identical with that given by hydrogenation of $RhCl(PPh_3)_3$ in deuterochloroform. Hence these solvates appear to have the same basic stereochemistry as the 5-co-ordinate species in chloroform solution.

The high-field n.m.r. spectra (Figure 1 and Table 2) at 56·4 Mc./sec. consist of three peaks (a weak shoulder may occasionally be observed on the highest field line—this is due to the tetrahydrido-complex of the dimer discussed later). The peaks A,A′ are of intensities which are equal and half that of peak B. At 40 Mc./sec., the A,A′ separation remained constant, showing that these lines are attributable to the spin–spin interaction of H with ^{31}P. Additional confirmation that this is so, comes from a study of the corresponding triphenylarsine complex,[41] which has only two lines of equal intensity in

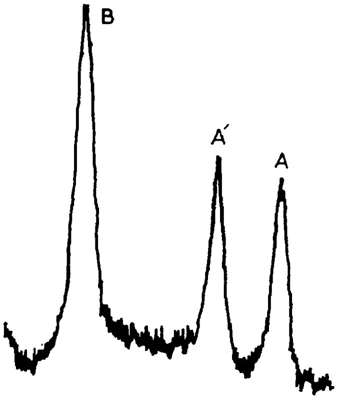

FIGURE 1 Nuclear magnetic resonance spectra at 56·4 Mc./sec. in chloroform solution at 25° of $RhCl(PPh_3)_2H_2$

TABLE 2

N.m.r. and i.r. data on dihydrido-complexes of $RhX(PPh_3)_3$, X = Cl, Br, or I: high-field lines and Rh–H modes only. N.m.r. relative intensities in parentheses

		ν cm.⁻¹	
Solvent	τ[a]	Solution[b]	Solids[c] Rh–H str.; Rh–H bend
Chloride			
$CDCl_3$	28·2(2), 21·5(1), 18·8(1)	2095m, 2050m	2078m, 2013m; 785m
C_6H_6	26·5(2), 20·4(1), 17·8(1)	2066sh, 2035m	2066sh, 2051m; 805m
C_5H_5N	28·6(1), 27·7(1)[d]	2078sh, 2052m	2143m, 2075m;[e] 838m, 812m
CH_2Cl_2	—	—	2099m,[f] 2065m;[e] 845s
$MeCO_2Et$	28·2(2), 21·5(1) 18·8(1)	—	2075m, 2088m;[e] 840m, 775m
MeNCHO	28·2(2), 21·5(1), 18·8(1)	—	2137m, 2081m;[e] —
Bromide			
$CDCl_3$	28·2(2), 21·5(1), 18·8(1)	2177sh, 2057m	— —
C_6H_6	26·5(2), 20·4(1), 17·8(1)	2066sh, 2035m	— —
C_5H_5N	29·2(1), 28·4(1)[d]	2081sh, 2049m	2144m, 2099m;[e] 845m, 830m
CH_2Cl_2	—	—	2103m, 2068m;[e] 847m, 838m
Iodide			
$CDCl_3$	26·2(2), 23·1(1), 20·5(1)		

[a] Measured in $CDCl_3$ except where indicated; values relative to Me_4Si as internal reference. [b] Measured in parent solvent. [c] Spectra taken in Nujol mulls. [d] In pure pyridine: for both chloride and bromide, τ 28·1(1), 27·8(1). [e] Bands due to co-ordinated solvent are also present. [f] For deuteride, 1507 cm.⁻¹.

Note: The n.m.r. spectra of highly concentrated solutions may show lines due to $[RhX(PPh_3)_2H_2]_2$. For the Cl: in $CDCl_3$ τ27·4; in C_6H_6 τ 28·9. For the Br: in $CDCl_3$ τ 29·1; in C_6H_6 τ 25·6.

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[38] L. Vaska and J. W. Di Luzio, *J. Amer. Chem. Soc.*, 1961, **83**, 1262; 1962, **84**, 679.

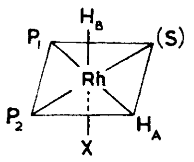
[39] L. Vaska, quoted by A. P. Ginsberg, *Adv. Trans. Met. Chem.*, 1965, **1**, 111; cf. also refs. 11, 12.

[40] See R. S. Nyholm, ref. 1(*b*).

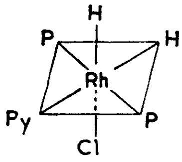
[41] J. T. Mague and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1736.

positions similar to those in the phosphine complex. The absence of fine structure on the lines is discussed below.

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



(I)



(II)

P, P_1, and P_2 = PPh_3; X = halide; S = solvent; Py = pyridine

For a number of octahedral hydride-phosphine complexes it has been found that H–^{31}P coupling constants are of the order 80—150 c./sec. for H *trans* to P, while the couplings for H *cis* to P are *ca.* 15 c./sec. Furthermore, the τ values for H *trans* to P are generally lower than those when H is *trans* to a halide or a similar ligand.[42] The observed spectrum is consistant therefore with (I); a similar spectrum would result if X and S in (I) were interchanged and at present we cannot be certain of the exact dispositions (see later discussion, however).

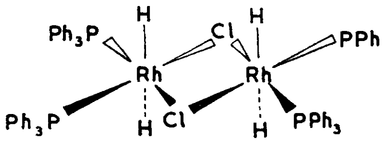
It is possible that in chloroform or benzene solution, there is an unsolvated 5-co-ordinate species which could have a spectrum very similar to that of solvated species, however, we believe that solvent occupation of the vacant site always occurs in solution. The solution species are in any case likely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

The pyridine solutions of (A) after hydrogenation, the isolated dihydro-pyridine complex, and the tetrahydrido-pyridine cleavage product of the dihydrido-dimeric species discussed below, all have an identical spectrum consisting of two rather broad lines. This is consistent with *trans*-phosphines and *cis*-dihydrides as in (II); the τ values are in the region for *cis*-H–P groups, in agreement with i.r. data. Although we have not isolated an acetonitrile complex, the n.m.r. spectra of hydrogenated acetonitrile solutions of (A) are identical with those of the pyridine complex. It is of interest that the reorganisation of the hydrido-complexes in chloroform solution on addition of pyridine or acetonitrile can be followed *via* the growth and decay of the respective high-field lines.

The infrared spectra (Table 2) of the various species in both the solid state in mulls and in solution generally show two broad Rh–H stretching frequencies in the normal region, *ca.* 2000 cm.$^{-1}$ for transition-metal and hydrogen bonds. This is to be expected for *cis*-dihydrido-groups. The dideutero-complex, $[RhCl(PPh_3)_2D_2]_2,CH_2Cl_2$ obtained from dichloromethane solution shows only one Rh–D stretching frequency (ν_{Rh-D} = 1507 cm.$^{-1}$; ν_H/ν_D = 1·39), the other being obscured, presumably, by triphenylphosphine absorption.

(*c*) Broad nature of the high-field n.m.r. lines. The high-field lines of the *cis*-dihydro-species are rather broad (*ca.* 45—70 c./sec.). Fine structure would have been expected to arise (1) from H–^{103}Rh coupling (*ca.* 20—30 c./sec.),[43] (2) from H_A–H_B coupling and (3) from additional *cis* ^{31}P coupling. Although such couplings will appear under the envelope of the broad high-field lines, no resolution could be obtained. This behaviour is in striking contrast to the situation with the hydrido-species obtained from the dimer.

The dimer $[RhCl(PPh_3)_2]_2$ when dissolved in dichloromethane saturated with hydrogen takes up exactly two moles of hydrogen per mole of complex. The hydrido-species is reasonably stable, even in air, and the molecular weight is that for the dimer, showing that no cleavage has occurred on hydrogenation. The n.m.r. spectrum shows a well-defined fine structure of overlapping, resolved, double triplets centred at about τ 26·6. This spectrum results from the interaction of H with ^{103}Rh to give a doublet (splitting 20 c./sec.), which is further split into a triplet by two equivalent ^{31}P nuclei (splitting 15 c./sec.); it is consistent with a structure involving octahedral rhodium(III) with *trans*-hydrogen atoms as in (III). The n.m.r. signal due to this species is occasionally observed in concentrated hydrogenated solutions of $RhCl(PPh_3)_2$, especially when benzene is used as solvent. On the addition of pyridine or triphenylphosphine to solutions of the dimer in the cold under hydrogen, cleavage occurs and the process can be followed by changes in the high-field n.m.r. spectrum.



(III)

Since *trans*-dihydrido-groups on the rhodium atom gave the expected fine structure, it seemed likely, originally, that some exchange process could be occurring in the *cis*-dihydrido-systems which could lead to line broadening. However, there was no detectable change in the appearance of the lines (1) on cooling to −70° or (2) on exerting a pressure of *ca.* 100 atmospheres of hydrogen on the solution in an n.m.r. tube. In these solutions under pressure the proton resonance of dissolved molecular hydrogen[44] at τ 5·57 was readily observed in addition to all three high-field lines, which

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[42] J. Powell and B. L. Shaw, *J. Chem. Soc.*, **1965**, 3879, and references therein.

[43] J. A. Osborn, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, **1964**, 3168.

[44] D. F. Evans and J. P. Maher, *Chem. and Ind.*, **1961**, 1960.

were unchanged in position. From this fact the mean lifetime of a hydrogen molecule on the hydrido-complexes can be estimated as greater than *ca.* 10^{-3} sec.

On the addition of an excess of PPh_3, the line breadth is apparently reduced suggesting, either some inhibition of ligand-dissociation and exchange, or reduction of the concentration of the paramagnetic impurity discussed below. That ligand exchange *can* occur, however, has been shown [41] by the addition of triphenylphosphine to solutions of $RhCl(AsPh_3)_2H_2$, when the changes in the n.m.r. spectrum can be followed.

The main and unexpected cause of line broadening in the *cis*-dihydrido-species is due to the presence of trace quantities of a paramagnetic species in the starting material $RhCl(PPh_3)_3$ even when this is prepared under nitrogen.

(*d*) Electron spin resonance measurements. Solutions of $RhCl(PPh_3)_3$ in de-gassed dichloromethane at 25° show a weak electron spin resonance (e.s.r.) signal. The two lines at $g = 2{\cdot}19$ and $g = 2{\cdot}05$ form a clear doublet structure centred on $g = 2{\cdot}12$, splitting 190 gauss, with an average line width, $\Delta H_{\frac{1}{2}}$ ~60 gauss. This signal is retained on hydrogenation of the sample. Further details of these and related studies will be reported separately. It is clear, however, that the broadening of the n.m.r. high-field lines can be attributed to the shortening of the relaxation time of all the nuclei in the sample by the direct effect of the electron dipole. Further broadening could, of course, result from chemical (including electron) exchange between the diamagnetic species and a small concentration of a paramagnetic rhodium(II) species. The concentration of the latter is estimated as 1 in 10^4.

Since the original rhodium source material, $RhCl_3,3H_2O$ shows only a very feeble e.s.r. signal, the paramagnetic species, perhaps $RhCl_2(PPh_3)_2$, must be produced in the reduction process and collected with the crystalline $RhCl(PPh_3)_3$. There is a possibility that the extraneous paramagnetic impurity in $RhCl_3,3H_2O$ is being selectively complexed; however, this seems unlikely, first because of the nature of the e.s.r. signal and secondly because $RhCl_3,3H_2O$ is believed to be free from transition-metal salts other than perhaps a trace of iridium.

Since the dimer hydride has sharp n.m.r. lines, the dimerisation process in hot benzene must leave the Rh^{II} species in solution. However, on reconversion of the dimer to the monomer by heating the dimer with an excess of triphenylphosphine in ethanol under reflux, the paramagnetic impurity is regenerated. We have so far failed to obtain a sample of $RhCl(PPh_3)_3$ which is free from paramagnetic contamination.

(iv) Other reactions. Tris(triphenylphosphine)chlororhodium or its solutions interact with a great variety of ligands. Thus, they add various molecules [45] in a way similar to the reactions of square complexes. Methyl iodide gives the complex $RhClI(CH_3)(PPh_3)_2ICH_3$ where CH_3I acts as a donor. Allyl chloride adds to give allylic complexes of stoicheiometry, $RhCl_2(PPh_3)_2(C_3H_5)$, while hydrogen chloride gives $RhCl_2(PPh_3)_2H$. It may be noted also that, in solution both $RhCl(PPh_3)_3$ and the corresponding arsine complex take up 1 mole of oxygen and that solid adducts can be isolated. These and other reactions will be described separately.

(B) *Catalytic Hydrogenation of Olefins and Acetylenes.*—(a) *General remarks.* In benzene or similar solvents, the tris(triphenylphosphine)halogenorhodium(I) complexes are extremely efficient catalysts for the homogeneous hydrogenation of non-conjugated olefins and acetylenes at ambient temperature and pressures of 1 atmosphere or below. Functional groups such as keto-, hydroxy-, cyano-, nitro-, chloro-, azo-, ether, ester or carboxylic acid are not reduced under these conditions. Although in the present Paper we are concerned with quantitative measurements on hept-1-ene, cyclohexene and hex-1-yne, a wide variety of unsaturated compounds containing olefinic and acetylenic bonds have been studied. Details will be given separately; however, it appears that; (1) terminal olefins (including non-conjugated, non-chelating diolefins such as octa-1,7-diene) are reduced more rapidly than internal olefins, *e.g.*, hex-1-ene > hex-2-ene; (2) *cis*-olefins are reduced faster than *trans*-olefins, *e.g.*, *cis*-hex-2-ene > *trans*-hex-2-ene; (3) conjugated olefins, such as butadiene or cyclohexa-1,3-diene are not hydrogenated at 1 atmosphere, although they may be reduced at higher pressures (*ca.* 60 atmospheres); (4) chelating non-conjugated diolefins, *e.g.*, cyclo-octa-1,5-diene, which may, and in some cases, do, displace the phosphine ligands from the complex, nevertheless, may be hydrogenated very slowly at 1 atmosphere but again rapidly under pressure; (5) in contrast to some other homogeneous catalytic systems, ethylene is *not* hydrogenated (see Discussion section), although propene, butenes, and higher olefins are effectively hydrogenated at 1 atmosphere pressure.

The rates of reduction compare favourably with those obtained by heterogeneous catalysts such as Raney nickel or Adams catalyst. A comparison of the rates of hydrogenation of cyclohexene under normal operating conditions by $RhBr(PPh_3)_3$ and Adams catalyst (equimolar amounts of the metal) is shown in Figure 2.

Using 10^{-3} M-solutions of the catalyst in benzene with hydrogen pressures of *ca.* 1 atmosphere, the hydrogenation of olefins may be so rapid that the temperature of the solution is raised to the boiling point. For example 10^{-4} moles of $RhCl(PPh_3)_3$ in benzene (80 ml.) containing cyclohexene (16 g.) absorbed hydrogen at *ca.* 30 ml./min. at 25°, which corresponds to the generation of *ca.* 40 cal./min. in the solution. Under identical conditions the bromide and iodide had absorption rates approximately two and three times as fast, respectively.

In the kinetic studies, which were made at constant volume, it was necessary not only to have thermal control of the reaction vessel, but also to ensure that the reactions were not diffusion controlled due to inadequate saturation with hydrogen. Details of the apparatus and the procedure used are given in the Experimental section.

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[45] M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Comm.*, 1966, 129.

The solid catalyst was added to the hydrogen-saturated solution, before the addition of olefin. This procedure was found to be desirable since the solid dissolves rather slowly in benzene whereas the dihydro-complex is more soluble, thus assisting dissolution; it also prevents any appreciable prior dimerisation of $RhCl(PPh_3)_2$ in the more concentrated solutions at temperatures above 25°. Furthermore, since the hydrido-species is a very pale yellow, the presence of undissolved catalyst is readily detected, whereas this is sometimes difficult to ascertain in the deep red solution given by the catalyst in benzene alone. The addition of olefin (without stirring) causes immediate darkening of the pale yellow solution to deep red-brown; on rapid stirring in of hydrogen the colour lightens to a clear yellow-orange. If the stirring is stopped, over a period (*ca.* 30 sec. under normal conditions), this yellow-orange deepens again to the deep red-brown. The reasons for this sequence of changes will be discussed later.

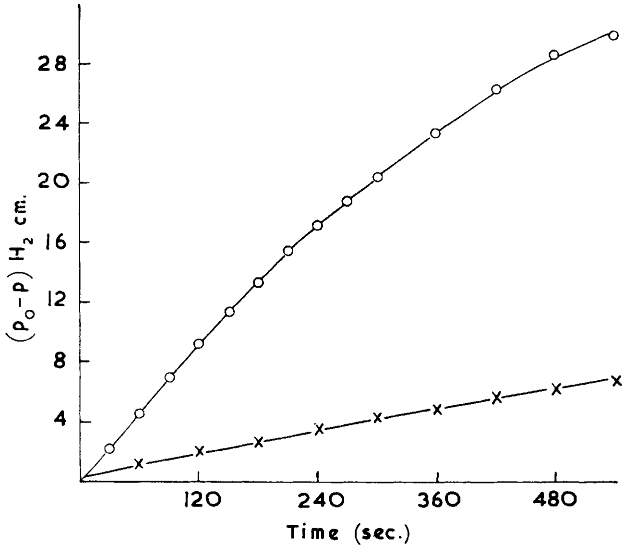


FIGURE 2 Qualitative comparison of the rates of homogeneous and heterogeneous catalysis, (○) 10^{-4} moles of $RhBr(PPh_3)_3$ in 1 : 1 benzene–ethanol, (×) 10^{-4} moles of Adams' catalyst in glacial acetic acid. Solvent volume, 50 ml. with 10 ml. cyclohexene at 25°. There is no detectable uptake of hydrogen under these concentration conditions and on this time scale using either $RhCl(CO)(PPh_3)_2$ or $IrCl(CO)(PPh_3)_2$. The latter shows very slow uptake at 40° using hex-1-ene

Although the trace quantities of hydroperoxides present in cleaned and dried olefins after storage do not appreciably inhibit catalytic hydrogenation, nevertheless, at high olefin concentrations some fall off from maximum rates is observed if the hydrocarbons are not freshly purified. In the quantitative work presented here, the olefins were distilled under nitrogen or *in vacuo* into a burette attached to the reaction flask before use.

(b) *Quantitative measurements.* The overall rates of hydrogenation of hept-1-ene, cyclohexene and hex-1-yne have been measured and the dependence on temperature, pressure, substrate concentration, catalyst concentration, catalyst nature and co-solvents and/or poisons investigated.

The rate of hydrogen uptake was obtained from the tangent to the plot of hydrogen pressure against time in a closed system. The standard hydrogen pressure used was 50 cm., and conversion to the rate of consumption of substrate (S) in mole $l.^{-1}$ $sec.^{-1}$ was made using the stoicheiometric relationship $-d[H_2]/dt = -d[S]/dt$. The solubility of hydrogen was considered constant from run to run and was assumed to obey Henry's Law; partial pressure of benzene and olefins were taken from standard tables. The amount of substrate consumed at the time of measurement (at a pressure of 50 cm.) is less than 1% and is considered negligible. The results shown graphically are generally the average of at least two determinations and are reproducible to ±5%; two independent sets of apparatus were used, one in which the olefin was distilled in nitrogen, the other *in vacuo*. There was no evidence of any heterogeneous reaction, and identical results were obtained when glass helices were added to the reaction flask.

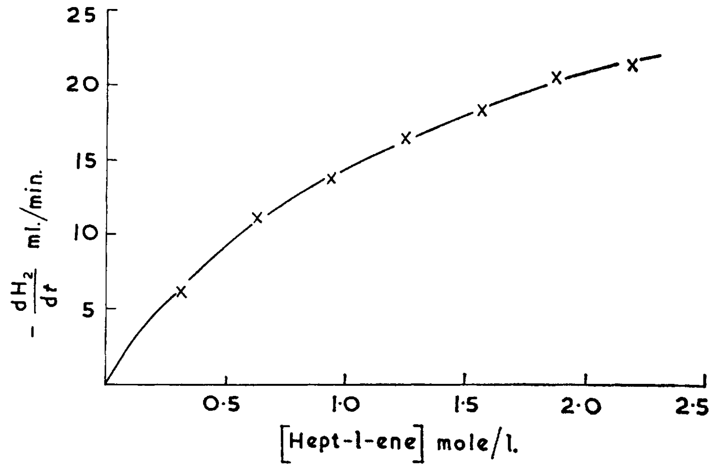


FIGURE 3 Variation of rate of hydrogenation of hept-1-ene with concentration of the olefin in benzene at 25°, with 1·25 mM-$RhCl(PPh_3)_3$

(i) Dependence on substrate concentration. A typical plot showing the rate of hydrogen consumption against hept-1-ene concentration is shown in Figure 3. The rate does not increase linearly with increasing olefin concentration but approaches an asymptotic value. The plot of the reciprocal of this rate (in mole^{-1} l. sec.) against the reciprocal of the olefin concentration (Figure 4) is linear with a positive intercept on the y-axis. Figure 4 also gives comparable data for cyclohexene. The reciprocal of this intercept gives the maximum rate possible under the specified condition, *i.e.*, the asymptotic value in Figure 3. Similar results for hex-1-yne are given in Figure 5.

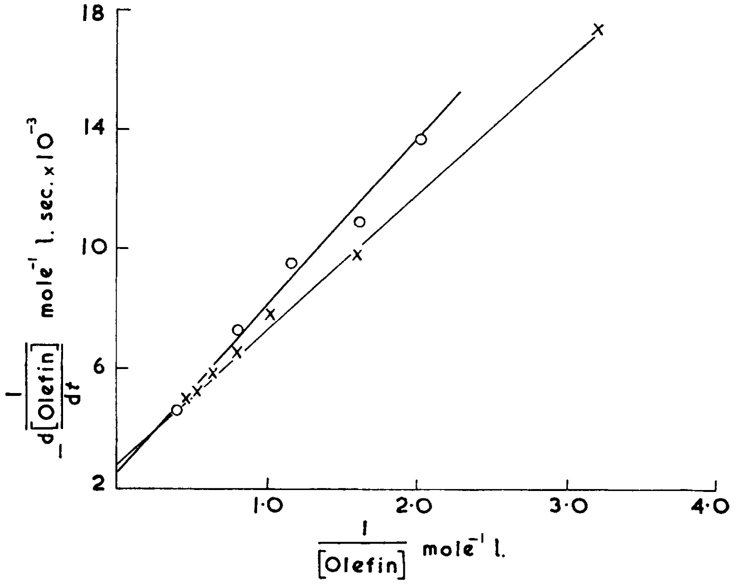


FIGURE 4 Plot of reciprocal of rate of hydrogenation of hept-1-ene (×) and of cyclohexene (○) against the reciprocal of the olefin concentration in benzene at 25° with 1·25 mM-$RhCl(PPh_3)_3$

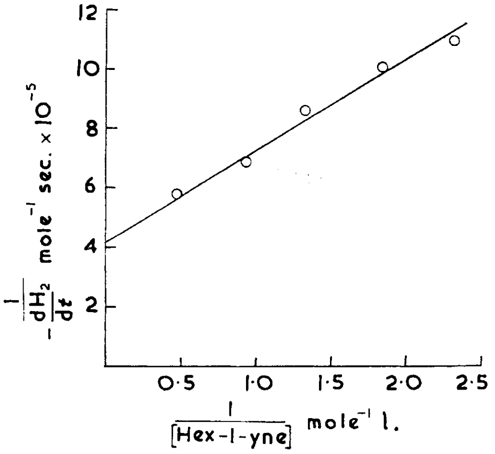


FIGURE 5 Plot of reciprocal of the rate of hydrogen consumption by hex-1-yne against the reciprocal of acetylene concentration in benzene at 25° with 1·25 mM-$RhCl(PPh_3)_3$

From these results it can be seen that the rate (R) is related to the substrate concentration [S] by the relationship $1/R = C(1/[S]) + C'$.

(ii) Dependence on hydrogen pressure. The qualitative dependence of the rate on hydrogen pressure can be seen from Figure 2. From results under standard conditions, the reciprocal of the rate against the reciprocal of the pressure (Figure 6) is a linear plot. Values for two catalyst concentrations are given. Thus, assuming Henry's Law is obeyed, $1/R = \alpha(1/p') + \beta$ where p' is the hydrogen pressure and α and β are constants. From the plots we obtain the following data: 1·25 mM catalyst: $\alpha = 2{\cdot}04 \times 10^{-2}$ ml. cm. min.$^{-1}$, $\beta = 2{\cdot}4$ ml.$^{-1}$ min. 2·50 mM. catalyst: $\alpha = 1{\cdot}52 \times 10^{-2}$ ml. cm. min.$^{-1}$, $\beta = 1{\cdot}2$ ml.$^{-1}$ min.

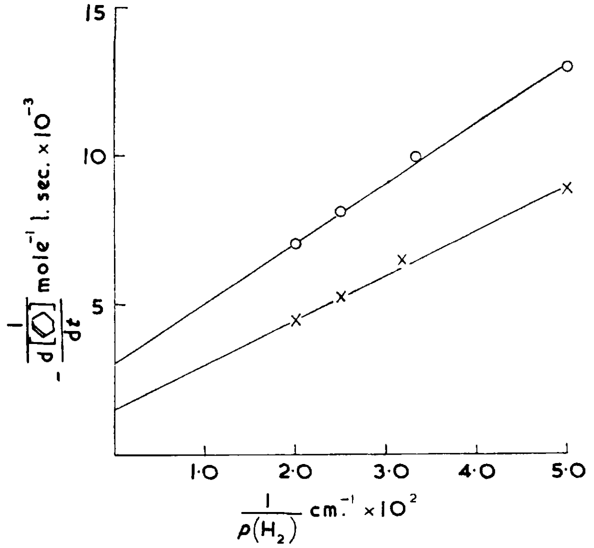


FIGURE 6 Dependence of rate of hydrogenation of cyclohexene with hydrogen pressure in benzene at 25°; 2·50 mM-concentrations of $RhCl(PPh_3)_3$ (○), 1·25 mM (×)

(iii) Dependence on catalyst concentration. A plot of the reciprocal of the rate against the reciprocal of the olefin concentration as in (1) for three catalyst concentrations is shown in Figure 7. The intercepts on the y-axis and the gradients are given in Table 3 together with rate constants derived from them as discussed later. The dependence of the rate of reduction on catalyst concentration for various concentrations of cyclohexene is shown in Figure 8; in the absence of catalyst no hydrogen uptake was detectable. The data suggest pseudo first-order behaviour, but there is evidently a small intercept on the rate axis, which is discussed later.

TABLE 3

Data derived from plot of reciprocal of rate *vs.* reciprocal of cyclohexene concentration for different values of catalyst concentration; 25°, $RhCl(PPh_3)_3$

Catalyst conc. mM/l.	Intercept mole^{-1} l. sec. × 10^{-3}	Gradient sec. × 10^{-3}	Ratio * Intercept/gradient	Rate Constant k' mole^{-1} sec.$^{-1}$ l.†
0·625	4·25	8·50	0·50	0·18
1·25	3·00	5·25	0·57	0·15
1·875	2·25	4·00	0·56	0·13

* Assumes concentration of dissolved hydrogen at 50 cm. pressure, 25° approximately 2·5 × 10^{-3} mole l.$^{-1}$ (see M. W. Cook, University of California, Radiation Laboratory Report No. 2459). † Calculation assumes that the concentration of the hydrido species is the same as that of the catalyst.

(iv) Dependence on temperature. Rates were measured at four temperatures ranging from 15—30° for three cyclohexene concentrations. From the plots of the reciprocal of the rate against the reciprocal of the olefin concentration, which remain linear throughout the temperature range, the gradients given in Table 4 can

TABLE 4

Data derived from the plot of the reciprocal of the rate *vs.* the reciprocal of cyclohexene concentration for varying temperatures

T° K	Gradient sec. × 10^{-3}	Rate constant k', mole^{-1} sec.$^{-1}$ l. × 10^2	$\log_{10} k'$
288	20·7	3·9	−1·409
293	10·6	7·5	−1·125
298	5·4	14·8	−0·830
303	2·6	30·8	−0·512

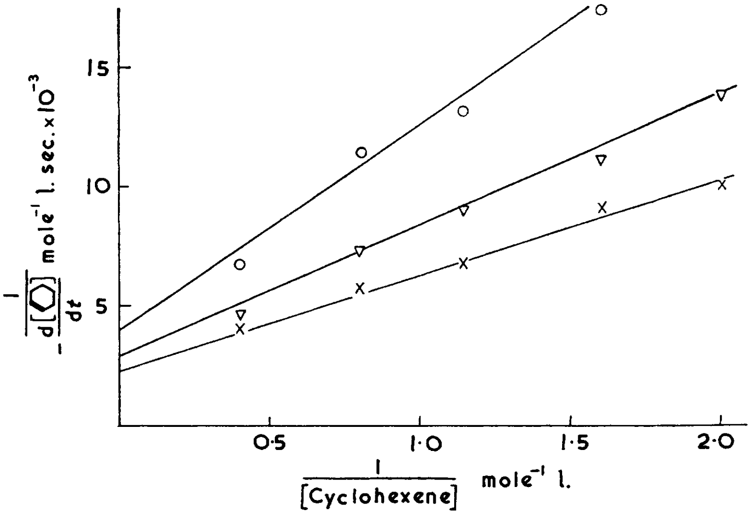


FIGURE 7 Plot of the reciprocal of the rate of hydrogenation of cyclohexene *vs.* the reciprocal of olefin concentration for catalyst concentrations of (○) 0·625, (▽) 1·25, (×) 1·875 mM-$RhCl(PPh_3)_3$ in benzene at 25°

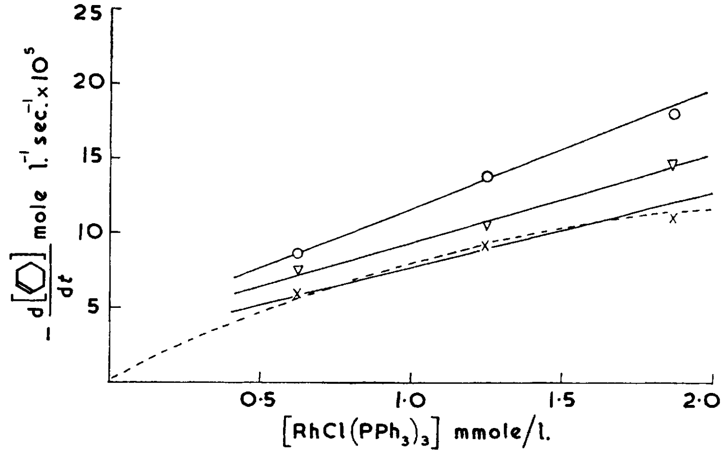


FIGURE 8 Rate of hydrogenation of cyclohexene as a function of catalyst concentration in benzene at 25° with $RhCl(PPh_3)_3$; cyclohexene (○) 2·49M, (▽) 1·245M, (×) 0·87M

be obtained. The calculated rate constant, k' (see later) is also given, and a plot of $\log_{10}k'$ against 1/T × 10^3 is shown in Figure 9. A good linear plot is obtained, indicating that the kinetics of the system are not complicated.

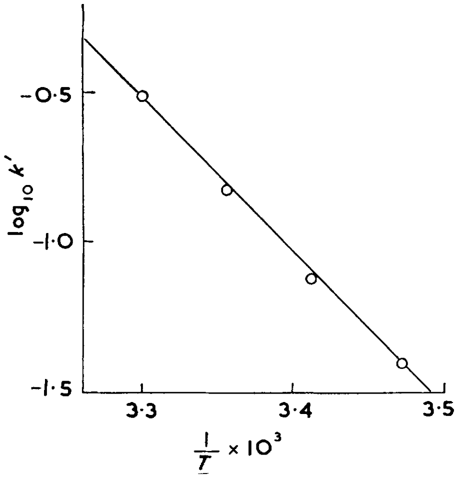


FIGURE 9 Plot of $\log_{10} k'$ *vs* $(1/T°\text{K}) \times 10^3$ from data given in Table 4

The effect on the kinetics of the small differences in solubility of hydrogen over this temperature range can be neglected.

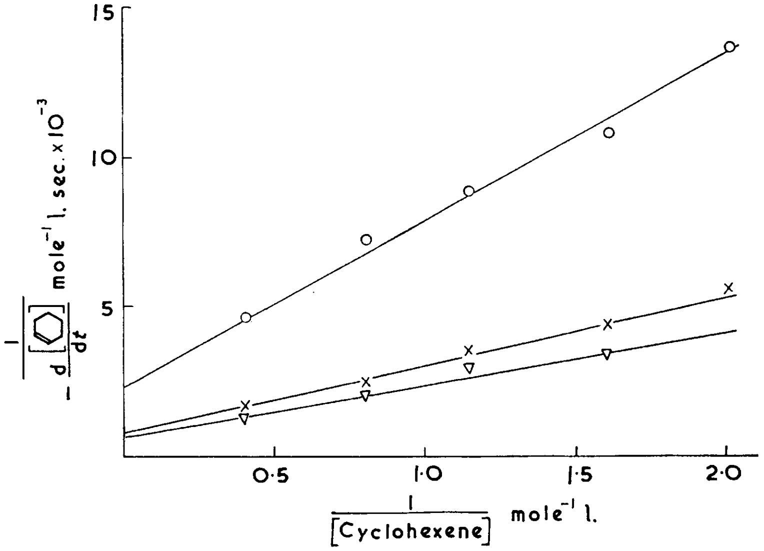


FIGURE 10 Dependence of rate of hydrogenation of cyclohexene on the nature of the catalyst in benzene at 25°. 1·25 mM-Catalyst (○) $RhCl(PPh_3)_3$, (×) $RhBr(PPh_3)_3$, (▽) $RhI(PPh_3)_3$

From Figure 9, a value for the activation energy, E_a, of 22·9 kcal. mole^{-1} is obtained; $\Delta H^‡$ is 22·3 kcal. mole^{-1} and $\Delta S^‡$ is +12·9 e.u.

(v) Dependence on the halide. The relative rates for $RhX(PPh_3)_3$, (X = Cl, Br, or I) under identical conditions and using equimolar quantities of the complexes is shown in Figure 10. The lines have been drawn so that the ratio of the intercept to the gradient is constant. This is necessary for a valid comparison of the rates for the three halides and assumes that the ratio of the rates is constant for all olefin concentrations.

(vi) Effect of co-solvents. The addition of polar solvents such as alcohols or ketones to the benzene solutions normally employed gave a substantial increase in the rate of hydrogenation of the substrates. Figure 11 gives relative rates under otherwise identical conditions for benzene, 1 : 1 benzene–ethanol and 1 : 1 benzene–methy lethyl ketone; as for Figure 10, the ratios of the intercepts to the gradients are constant. The overall rate is approximately doubled using co-solvent. There is no correlation of the rate increase with dielectric constant of the co-solvent. The solubility of hydrogen is not significantly different in the different solvent mixtures. Other co-solvents that can be used are, methanol, t-butyl alcohol, isopropanol, phenol, glacial acetic acid, ethyl acetate, dimethylformamide, dioxan and dimethyl sulphoxide. Some of these solvents may be used alone, although the low solubility of the catalyst in them reduces the effectiveness. Using pure alcohols, slow abstraction of carbon monoxide may occur over a period of time (several hours at 25°) leading to deactivation of the catalyst. More strongly co-ordinating substances inhibit the rate of hydrogenation and in high concentrations totally prevent reduction at 25° and 1 atmosphere. Such materials are: triphenylphosphine, thiophen, 8-hydroxyquinoline, pyridine and acetonitrile. Ethylene, conjugated diolefins and oxygen also poison the low pressure activity but hydrogenation at higher pressures is readily effected.

(c) *Discussion of kinetic results*. The experiments discussed under Section (A) (b) show that in solution, the dissociated catalyst species, $RhX(PPh_3)_2$, can rapidly attain equilibrium with dissolved hydrogen and/or olefin to give a complex. For the hydrido-complex there is a vacant co-ordination site and for the olefin complex, two. Thus in the transfer of hydrogen molecules in solution to the olefin in solution *via* a catalyst complex species, the rate determining step can be either one or both of two possible paths: (1) attack of uncomplexed olefin on the dihydrido-complex at the vacant site to give a transition state in which both hydrogen and olefin are bound to the metal; (2) attack of molecular hydrogen on the olefin complex, $RhX(PPh_3)_2$(olefin), to give the same transition state as in Scheme 1.

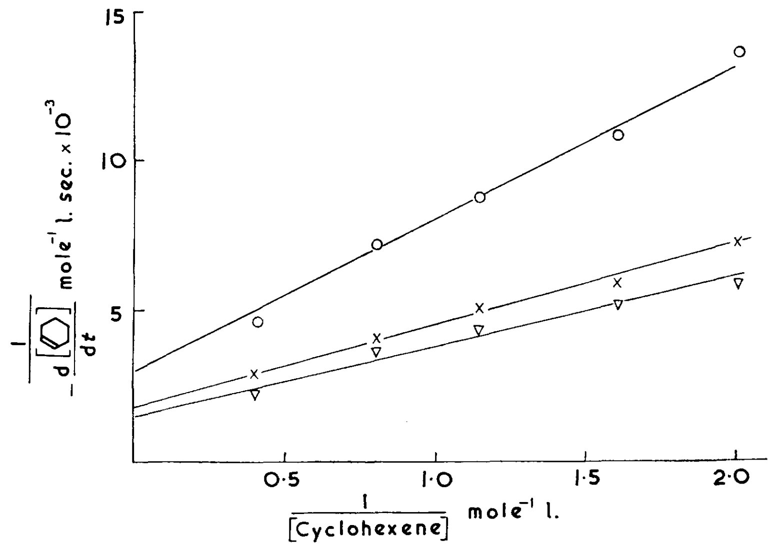
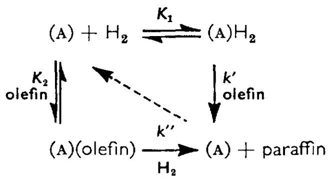


FIGURE 11 Dependence of rate of hydrogenation of cyclohexene with co-solvent (1 : 1 with benzene) at 25°; 1·25 mM-$RhCl(PPh_3)_3$. (○) Pure benzene, (×) methyl ethyl ketone, (▽) ethanol

From the overall rates of hydrogenation measured, these paths are indistinguishable and are kinetically equivalent if it is assumed that the equilibria are set up quickly. Although, from other experiments described later it appears that (1) is the preferred path, we shall write the formal scheme [(A) = $RhX(PPh_3)_2$]:



Scheme I

The colours of the reacting solutions noted earlier give some indication of the competition between the rapidly established equilibria K_1 and K_2. Thus $(A)H_2$ is pale yellow, (A) + (A)(olefin) deep red-brown (except for ethylene as noted before), while the reacting solutions are normally orange, although at high olefin concentrations or low hydrogen pressures they darken towards red-brown.

If K_1 and K_2 are the equilibrium constants and k' and k'' the rate constants for the reactions as shown in the Scheme, p is the concentration of hydrogen in solution and [S] and [A] are the substrate and catalyst concentrations, respectively, then the rate, R, is:

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

This rate expression assumes the same form if $k'' = 0$ and there is good reason to believe, as outlined later, that this is so, *i.e.*, the attack of hydrogen on the olefin complex does not occur. The rate expression then reduces to:

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

This expression is found to reasonably accommodate most of the experimental data described earlier.

(i) The dependence of the rate on substrate concentration is:

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

which is identical in form to that obtained in Section (B) (b) (i) with

$$C = \frac{1 + K_1 p}{k'K_1 p[A]} \text{ and } C' = \frac{K_2}{k'K_1 p[A]}$$

Thus for effective catalytic reduction of a substrate, k' must be large and K_2 small; however, it is necessary to the form of the results that K_2 should have a finite value.

For ethylene, which of all simple mono-olefins has by far the largest value of K_2, catalytic reduction does not occur, even although, as discussed later, transfer of hydrogen from the dihydrido-species to ethylene is rapid.

It is appropriate at this point to discuss competitive experiments involving ethylene and *trans*-stilbene.

If ethylene (*ca.* 25 cm. pressure) is admitted to the benzene solutions of $RhCl(PPh_3)_3$ the bright yellow complex is formed immediately, as discussed earlier. Admission now of hydrogen (*ca.* 25 cm. pressure) produces no change in colour, nor is any gas absorbed. This is in striking contrast to the behaviour of propylene and but-1-ene under identical conditions, where rapid hydrogenation takes place. Furthermore, if cyclohexene is added to the bright-yellow complex solution under ethylene–hydrogen (1 : 1, total pressure *ca.* 50/cm.) no hydrogenation occurs—ethylene is thus an effective poison for the hydrogenation of other olefins. When the initial procedure was reversed and the dihydrido-species were prepared first, admission of ethylene was followed by a small rapid absorption which rapidly ceased; the solution again assumes the yellow colour (and has the absorption spectrum) characteristic for $RhCl(PPh_3)_2(C_2H_4)$. We can thus conclude that this complex cannot activate molecular hydrogen. The possibility that it can activate molecular hydrogen but that the transfer step to co-ordinated ethylene cannot occur can be dismissed, since a transition state or intermediate complex would have to be identical to that formed in the reaction of the dihydrido-species and ethylene. Furthermore, at high concentrations, n.m.r. studies of the ethylene complex under hydrogen show no high-field lines. The implication is clear that in the kinetic mechanism proposed, we can eliminate the path involving hydrogen attack on the olefin (or acetylene) complex. It might be expected from the *trans*-effects of halide on the ethylene complex formation constant [Section (A) (b) (ii)] that for the bromide and especially iodide, the higher concentration of uncomplexed species might allow hydrogenation to proceed. For the iodide only, very slow hydrogenation of ethylene does occur (initial absorption rate 0·5 ml./min.) with a 1 : 1 ratio of hydrogen and ethylene at a total pressure of *ca.* 50 cm.

The low reactivity of *trans*-stilbene towards hydrogenation provides evidence for the requirement that the substrate as well as molecular hydrogen, be activated by complexing, *i.e.*, that the vacant co-ordination site on the *cis*-dihydrido-species is essential to the efficiency of the system. In benzene at 25° and 1 atmosphere of hydrogen, *trans*-stilbene is only very slowly reduced (hours). However, if cyclohexene is added, immediate rapid hydrogen absorption occurs at the rate normal for cyclohexene alone, while the rate of stilbene reduction continues unaffected. The stilbene is clearly unable to occupy the vacant site readily for steric reasons.

(ii) The dependence on pressure is of similar form, *viz.*,

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

This agrees with the results in Section (B) (b) (ii) with the values:

$$\alpha = \frac{1 + K_2[\mathrm{S}]}{k'K_1[\mathrm{S}][\mathrm{A}]} \text{ and } \beta = \frac{1}{k'[\mathrm{S}][\mathrm{A}]}$$

Thus both α and β should be proportional to 1/[A] and it can be seen from the values given in (B) (b) (ii) that this is approximately correct.

(iii) From the above section (i) it can be seen that the gradient of the plot of $1/R$ *vs.* 1/[S] (Figure 7) becomes, $1/k'[\mathrm{A}]$ if $K_1\mathrm{p}$ is $\gg 1$. The latter is evidently so from the measurements of the electronic spectrum of the catalysing solutions, which is that of the pure hydrido-species.

Using this relationship, from the data in Table 3, we obtain the rate constant k' for the rate-determining step; the values of k' are also listed in Table 3 and the average value 0·153 was used in calculations. The rate constants used in the Arrhenius plots are derived similarly from Figure 7.

The intercepts and gradients should be proportional to 1/[A] and from Table 3 it appears that this dependence does hold approximately. Moreover, it can also be seen that ratio of the intercept to the gradient for the plot (Table 3) is equal to $K_2/K_1\mathrm{p}$, which gives K_2/K_1 approximately $1{\cdot}6 \times 10^{-3}$ mole^{-1} l. This value, although quantitatively rather smaller than expected, assuming reasonable values for K_1 and K_2, is, nevertheless, of the right order of magnitude.

The dependence of the rate on the catalyst concentration should be linear:

$$\mathrm{R} = \frac{k'K_1\mathrm{p}[\mathrm{S}]}{1 + K_1\mathrm{p} + K_2[\mathrm{S}]} \cdot [\mathrm{A}]$$

However, although a linear dependence was observed in Figure 8, the line does not pass through the origin as required by this equation. This divergence could be due to some dimerisation or reassociation of the catalyst at the higher concentrations, thus effectively decreasing the rate values and consequently shifting the plots away from the origin but still maintaining the approximately linear dependence. For a small association or dimerisation of the catalyst species the rate expression approximates to

$$R = k[\mathrm{A}] - k'[\mathrm{A}]^2$$

where $k \gg k'$; it is assumed that the undissociated monomer and dimer are inactive catalytically. Thus a curve of this form shown as a dotted line in Figure 8 could result. At higher concentrations of catalyst, of course, greater divergence from linearity would occur, unfortunately, the low solubility of the complex precludes study in this region. Molecular weight studies should indicate any appreciable dimerisation but we have not been able to determine them under the conditions used catalytically. However, at higher concentrations in benzene dimerisation plainly occurs. The molecular weight studies would in any case not reliably detect dimerisation to the extent of 5—10% which is all that would be required. Any dimer present would be hydrogenated and as we show in Section (C) the dimer hydride does not transfer hydrogen to olefins.

(iv) The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from these studies may be compared with those quoted by Halpern [1] for the homogeneous reduction of iron(III) by hydrogen using tetrachloropalladate(II), $\Delta H^{\ddagger} = 20$ kcal. mole^{-1}, $\Delta S^{\ddagger} = -6{\cdot}8$ e.u. and for the reduction of fumaric acid by hydrogen in the presence of ruthenium(II) were $\Delta H^{\ddagger} = 18$ kcal. mole^{-1}, $\Delta S^{\ddagger} = -8$ e.u.

The overall rate expression can hence be formulated as

$$k' = 1{\cdot}1 \times 10^{16}\, e^{-22{,}900/RT}\ \text{l. mole}^{-1}\ \text{sec.}^{-1}$$

(v) The increase in the catalytic activity of $RhX(PPh_3)_3$, $X = Cl < Br < I$, can be due to two factors. First, the equilibrium constant, K_2 is decreased due to the *trans*-effect increase $Cl < Br < I$ [cf. Section (A) (b) (ii)] and hence according to the rate equation the rate of reduction should increase. Secondly, the increasing *trans*-effect of the halide could increase the lability of one of the hydrogen atoms in the *cis*-dihydrido-species $RhX(PPh_3)_2H_2$(solvent); this would be most likely if the halide were *trans* to the hydride as in (I). However, as noted earlier, we cannot unequivocally confirm this orientation although the *trans*-position for X seems reasonable since it leaves the solvent occupied site available for olefin competition mutually *cis* to both hydrogen atoms.

The *trans*-effect argument has to be used with caution. For example, the complex $Rh(SnCl_3)(PPh_3)_3$ [22] has catalytic activity well below that of $RhCl(PPh_3)_3$ despite the prediction based on the known [46] large *trans*-effect of $SnCl_3^-$ that the rate would be very fast. Very small changes in electronic effects can significantly alter the thermodynamic entities involved. An active intermediate must have a rather well-defined thermodynamic stability yet must be sufficiently labile to allow fast transformations to occur.

(vi) The increase in rate achieved by use of polar solvents suggests that the rate determining step involves the formation of an activated complex which has a greater dipole moment than the reacting species. That is, some charge separation is occurring in the formation of the intermediate. This may result from either one of the hydrogen atoms in $RhCl(PPh_3)_2H_2$(solvent) becoming increasingly positive with respect to the other, possibly due to differences in solvation of the halide ions *trans* to hydrogen. It is shown in Section (C) that the co-solvent plays no part in the actual hydrogen transfer mechanism.

(C) *Direct Hydrogen Transfer to Olefins; Deuterium Studies.*—(a) *Hydrogen transfer.* Since the implications are clear that the catalytic reactions involve transfer of hydrogen to an olefin *via* a metal *cis*-dihydrido-species of the type characterised by n.m.r., we have studied the direct transfer of hydrogen, necessarily using high concentrations of the dihydrido-species, by n.m.r. methods.

A hydrogen-saturated deuterochloroform solution of (A) in an n.m.r. tube was frozen and a suitable quantity of ethylene condensed. On allowing the tube to warm up slowly in a low temperature probe, both the high-field lines of $(A)H_2$ and the line due to *unco-ordinated* ethylene were readily observable at $-50°$. At about 0°, the intensities of both lines decreased, while a new line at $\tau \sim 9{\cdot}69$, due to ethane, appeared. No sign of lines due to an intermediate containing a $Rh{-}C_2H_5$ group produced by ethylene insertion into the Rh–H bond was observed.

Similar direct transfer experiments were carried out in benzene solutions of $(A)H_2$ with ethylene and liquid olefins, *e.g.*, hex-1-ene. The direct transfers are also indicated by colour changes in the solutions, the yellow $(A)H_2$ colour being replaced by the red-brown of (A) (or an (A)–olefin complex) as was observed in the catalytic experiments described earlier. Due to the low concentrations of (A) in the latter, it is impossible to demonstrate a standing concentration of $(A)H_2$ by either n.m.r. or i.r. methods. However, the electronic absorption spectra of these solutions are identical with that of the dihydrido-species. Similar experiments were made adding hex-1-ene to solutions of the pyridine hydrido-complex, $RhCl(PPh_3)_2\,py\,H_2$, and the dimeric hydride $[RhCl(PPh_3)_2H_2]_2$ and in both cases the high-field lines remained unchanged.

(b) *Lack of exchange with deuterium.* Solutions of $RhCl(PPh_3)_3$, in the absence of olefin, were exposed to deuterium gas under catalytic conditions, for periods up to 4 days. Samples for mass spectrometric analysis were withdrawn periodically. After making a small correction for exchange of deuterium with traces of water, etc., in the system in absence of catalyst in the solution, as determined by separate experiment, it appeared that there was *no exchange of* deuterium with *any* component of the catalyst system. Experiments were made using pure benzene, benzene–hexane, 1 : 1 benzene–ethanol, and similar solutions containing up to 3M-concentrations of triphenylphosphine. No HD other than normal contamination was evident in any case.

In a similar experiment, a small quantity of catalyst (*ca.* 10^{-4} moles) in solution was exposed to two separate amounts of deuterium for periods of 4 days: there was no evidence from infrared measurement of any incorporation of deuterium in the recovered catalyst.

From these studies it is clear that the α-hydrogen atom of the phenyl groups in co-ordinated triphenylphosphine are not involved in the catalyst system despite the possibility *in crystals* of short distances [24,25] between the metal and the α-hydrogen atoms.

(c) $H_2{-}D_2$ *exchange: reduction of hex-1-ene by* $H_2{-}D_2$ *mixtures.* The kinetic data show that only one catalyst molecule is involved in the transfer of hydrogen to the olefin. Provided the $H_2{-}D_2$ exchange process on the catalyst can be minimised, it should be possible to confirm this since reduction of hex-1-ene with $H_2{-}D_2$ mixtures should only yield dihydrido- and dideutero-paraffin.

(i) $H_2{-}D_2$ exchange. Benzene solutions of $RhCl(PPh_3)_3$ were stirred under 1 : 1 $H_2{-}D_2$ mixtures (total pressure $\sim$60 cm.) and gas samples withdrawn for mass spectrometric analysis after 1½ hr. Using 1·25- and 2·50-mM solutions, the increase of HD in the gaseous phase was

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[46] See F. A. Cotton and G. Wilkinson, " Advanced Inorganic Chemistry," 2nd edn., Interscience, Wiley, 1966, p. 1029, 1034.

0·9 and 3·7%, respectively. Thus, the rate of exchange as demonstrated by the appearance of HD in the gaseous phase appears to be slow compared with the rate of reduction under identical conditions. Moreover, the rate of exchange at zero time seems to have approximately a second-order dependence on the catalyst concentration, suggesting that the exchange process occurs by a bimolecular collision process.*

(ii) Reduction of hex-1-ene by H_2–D_2 mixtures. It is seen from the above Section that in order to minimise the effect of the inter-molecular exchange process during reduction, the standing concentration of the dihydro- or dideutero-species in solution must be kept to a convenient but small value. Hence, low concentrations of $RhCl(PPh_3)_3$ and low total gas pressure, but large concentrations of olefin were used. The gas pressure was maintained *ca.* 15 cm. by carefully adding equal quantities of hydrogen and deuterium when required. The same experiments were repeated at total pressure of *ca.* 60 cm. The results are shown in Table 5. The peak at $m/e = 87$ was corrected for: (*a*) the natural HD contamination in the hydrogen and deuterium used and for the natural abundance of ^{13}C and D in the n-hexane which result in $C_6H_{13}D$ as contaminant, and (*b*) the presence of ions such as $C_6H_{11}D_2^+$ resulting from cracking in the ionisation chamber. This correction was obtained from a sample of hex-1-ene which had been catalytically deuterated.

TABLE 5

Mass spectrometric analysis of n-hexanes obtained by reduction of hex-1-ene with hydrogen, deuterium and *ca.* 1 : 1 mixtures of hydrogen and deuterium in benzene at 25°

Mole l.$^{-1}$ hexene	Gas	P_{av} cm.	m/e * 86	87	88
0·728	H_2	30 †	20	0·8	—
0·728	D_2	30 †	—	0·9	23·0
0·728	$H_2 + D_2$	60 †	32·7	24	35·5
1·845	$H_2 + D_2$	15 ‡	20·5	4·0	18·0

* Average uncorrected data for two runs. † 1·82 mM $RhCl(PPh_3)_3$. ‡ 1·54 mM $RhCl(PPh_3)_3$.

From the data in Table 5 after these corrections have been made, at the average gas pressure 15 cm. the products of the reduction are C_6H_{14}, 50%; $C_6H_{13}D$, 6·1%; $C_6H_{12}D_2$, 43·9%. Thus, there is a 93·9% addition of hydrogen and deuterium separately which is in agreement with the kinetic data showing a first order dependence on catalyst concentration. However, at an average pressure of 60 cm. the products are C_6H_{14}, 36·6%; $C_6H_{13}D$, 23·7%; $C_6H_{12}D_2$, 39·7%; this is a considerable increase on the yield of H–D product expected to result from the H_2–D_2 exchange process. It is probable that the results in (i) are misleading since the appearance of HD in the gaseous phase may well fail to reflect the actual concentration of HD in solution *in an equilibrium system*, where diffusion is the only driving force to overcome surface barrier effects.

(d) *Deuteration and stereochemistry of addition to olefins.* In view of the above results deuterium reduction can be used to determine the stereochemistry of the reaction using maleic and fumaric acids since the corresponding dideuterosuccinic acids have been characterised.[47] From maleic acid, the succinic acid product had a strong band at 1192 cm.$^{-1}$, but only a very weak band at 1215 cm.$^{-1}$, confirming that the major component was *meso*-1,2-dideuterosuccinic acid. This indicates that predominantly *cis*-deuteration of the double bond has occurred. Confirmation was obtained from the fumaric acid which had been similarly deuterated, and where the product had bands in the region 1220—1170 cm.$^{-1}$ corresponding to DL-sym-1,2-dideuterosuccinic acid.

Yet further evidence that the addition of hydrogen or deuterium by the complex is *cis* is obtained from the reduction of hex-2-yne. Although the reduction of this acetylene is slow at 1 atmosphere, it is rapid at 50 atmospheres and 20°. If the reaction is stopped before the hex-2-yne is fully reduced and the products analysed by gas–liquid chromatography (g.l.c.) it is found that not only is n-hexane present but also hex-2-enes. A two stage reduction of the acetylene is hence involved in which free olefin is formed as intermediate. Analysis of the hexene fraction shows that the *cis*-product is >20 times more abundant than the *trans*-isomer. Furthermore, since *cis*-olefins appear to be more rapidly reduced than their *trans*-isomers, this must be a minimum value for the *cis*–*trans* ratio.

(e) *Kinetic isotope effect.* The rates of uptake of hydrogen and deuterium by cyclohexene using $RhCl(PPh_3)_3$ under identical conditions are plotted as the reciprocals against the reciprocal of the olefin concentration in Figure 12. The lines have been drawn such that the gradients are in the same ratio as the intercepts on the *y*-axis. The ratio of the rate of reduction using hydrogen to that of deuterium approximates to 0·9. The significance and implications of this value are referred to in the Discussion section.

DISCUSSION

The mechanism of catalytic hydrogenation of unsaturated substrates can conveniently be regarded as one involving three steps: (1) hydrogen activation, (2) substrate activation, (3) hydrogen transfer. We shall discuss these steps separately since, if effective reduction of a substrate is to occur, all three conditions must be met. Although many metal complexes have been shown to activate hydrogen molecules, very few have been able to reduce olefins or acetylenes either because the latter have not been activated on the metal complex, or because transfer of activated hydrogen was kinetically or thermodynamically impossible. The interplay of the

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* Rapid exchange could occur if both hydrogen and deuterium molecules were simultaneously activated by one metal atom. This would involve the formation of four, mutually *cis* M–H (or D) bonds and, since promotion of the metal to Rh^V, as well as possibly an increase in the co-ordination number, would be required, this seems highly unlikely [cf. Section (A) of the Discussion section].

[47] C. R. Childs and K. Bloch, *J. Org. Chem.*, 1961, **26**, 1630.

various factors involved is extremely critical for all three steps to be successfully achieved.

(A) *The Hydrogen Activation Process.*—The ability of a metal ion or complex to induce fission of molecular hydrogen to form one or, as in our present case, two metal–hydrogen bonds depends on a number of factors which cannot readily be divorced from each other. Some of these factors have been discussed especially by Halpern and by Nyholm.[1]

For a d^8 complex to be oxidised by hydrogen to give a d^6 species:

$$H_2 + ML_4 \longrightarrow H_2ML_4$$

it would appear that $2E_{M-H} > E_{H-H} + P$, where E_{M-H} is the energy of formation of the metal–hydrogen bond, E_{H-H} is the bond strength for molecular hydrogen and P is the promotional energy of the metal in the complex. Clearly, if the hydrogen activation reaction is to be reversible then $2E_{M-H}$ must be approximately equal to $E_{H-H} + P$. The electronic and ligational conditions for a reversible system to be formed are very critical. For the present system this can be seen by considering the species $RhCl(PPh_3)_2L$. When L is a ligand of low π-acidic nature, *e.g.*, chloroform, benzene, acetic acid, ethyl acetate, pyridine, or acetonitrile, activation proceeds readily. If, however, L is a strong π-acid, *viz.*, carbon monoxide, tetrafluorethylene, ethylene or perfluorobut-2-yne no activation occurs at atmospheric pressure (although activation may occur at elevated pressures it is not necessarily the same type as at 1 atmosphere since ligand displacement may occur). Since E_{H-H} remains constant and E_{M-H} is not significantly changed * the principal factor is the promotional energy, including energies of re-orientation of ligands. Thus, any ligand which withdraws electron density from the metal increases the promotional energy and reduces the ability of the species to activate molecular hydrogen.

The primary interaction of molecular hydrogen in solution with a metal species must, we believe, involve the feeding-in of electron density in filled metal orbitals to an acceptor orbital on one hydrogen atom of the hydrogen molecule. The tentative suggestion has been made by Nyholm [1] that an anti-bonding orbital could be used as an acceptor. On the other hand, Halpern [1] has suggested that the bonding electrons of hydrogen could attack a vacant metal orbital. The former concept seems most likely, especially since hydrogen activators are in general electron-rich systems. The precise mode of operation is, however, speculative although the hydrogen *p* orbitals with their greater spacial extension could act as acceptors even though they are of higher energy. The main point is, however, that the charge separation induced in the H–H bond by such electron flow will, in the proximity of the metal atom, lead to bond weakening, lengthening, and synchronous formation of two metal–hydrogen bonds; initially at least, these should be mutually *cis* but, depending on the nature of the metal species, rearrangement may occur. Thus, if the configuration of the complex is such that no *cis* site is immediately available, which is the case for $IrCl(CO)(PPh_3)_2$ or $(Ph_3P)_2RhCl_2Rh(PPh_3)_2$, then some type of reorganisation, *e.g.*, by edge-displacement, and/or dissociation is required; *trans*-dihydrides could then result depending on the nature of the metal and its ligands. Alternatively, in other cases, solvation by polar solvents could remove the more positively charged atom so that heterolytic fission

$$M + H_2 = MH + H^+$$

occurs. This is doubtless what happens when octahedral species, *e.g.*, py_3RhCl_3, activate hydrogen;

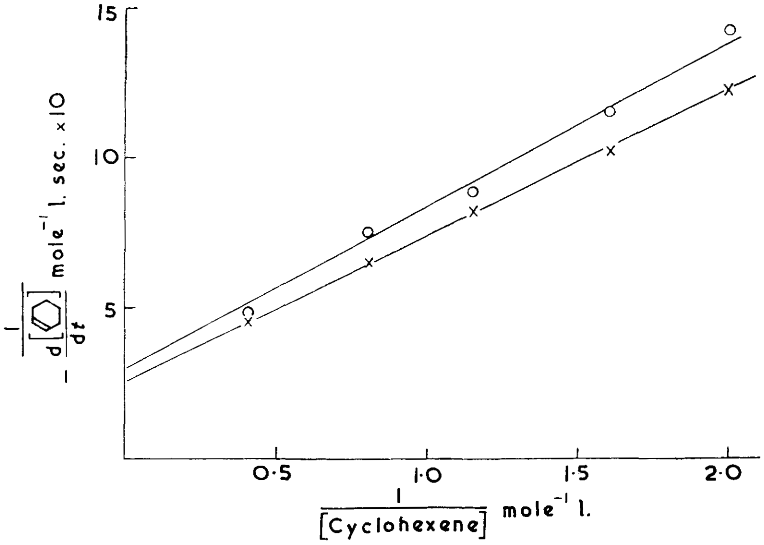

FIGURE 12 Kinetic isotope in the hydrogenation of cyclohexene in benzene at 25° with 1·25 mM-$RhCl(PPh_3)_3$. (○) Hydrogen, (×) deuterium

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* The i.r. M–H stretching frequencies in *cis*-$H_2IrCl(CO)(PPh_3)_2$ obtained from the activator $IrCl(CO)(PPh_3)_2$ are 2190 and 2100 cm.$^{-1}$ whilst those in, say, *cis*-$H_2RhCl(py)(PPh_3)_2$ are 2143 and 2075 cm.$^{-1}$.

hydrogen chloride is in fact eliminated with the formation of py$_3$ RhCl$_2$H.[41]

The failure of RhCl(CO)(PPh$_3$)$_2$ to activate hydrogen is in contrast to the ability of the iridium analogue to give reversible hydrogen activation and a *cis*-dihydride.* The difference can be ascribed to the greater special extent of non-bonding *d* electron density and the lower promotion energy in the large third transition series atoms and partly to the somewhat increased strength of the Ir–H bonds compared to Rh–H.

The failure of the square phosphite complex, RhCl[P(OPh)$_3$]$_3$ to activate hydrogen at 1 atmosphere may be attributed in part to the higher π-acidity of triphenylphosphite compared to triphenylphosphine,[48] † which lowers the non-bonding electron density on the metal. However, the main difference is that the phosphite complex does not dissociate in solution thereby providing a vacant site. In view of the higher π-acidity of P(OPh)$_3$ a greater tendency to dissociation would have been expected on the grounds of *trans*-competition. It appears, therefore, that the main factor causing dissociation in the triphenylphosphine complex is the greater steric hindrance between the triphenylphosphine ligands; the steric hindrance between *cis*-P(OPh)$_3$ ligands appears to be small.

Finally, the unexpected inability of RhCl(PPh$_3$)$_2$(S) to *catalytically* hydrogenate ethylene has an explanation entirely analogous to that for the effect of carbon monoxide in RhCl(CO)(PPh$_3$)$_2$. It is known from the *trans*-effect and other studies that ethylene stands high in the π-acid and *trans*-effect sequence and is indeed comparable to carbon monoxide as a π-acid ligand. Thus RhCl(C$_2$H$_4$)(PPh$_3$)$_2$ cannot be expected to activate hydrogen at 1 atmosphere. There is of course no conflict here with the experiments demonstrating direct transfer to ethylene of hydrogen by RhCl(PPh$_3$)$_2$H$_2$; it is merely that once the ethylene complex is formed, hydrogen activation ceases.

The problem of why propylene and higher olefins *can* be catalytically hydrogenated—or, reformulating, why such olefins do not inhibit hydrogen activation—is clearly due to the enormously reduced complexity constants for these olefins, as discussed in Section (A) (b) (ii). From the rate equation derived in the kinetic section, if K_2 is small the rate may be large (in the absence of steric factors), and *vice versa*.

(B) *The Substrate Activation Step.*—Whether there is an actual intermediate species, RhCl(PPh$_3$)$_2$H$_2$ (olefin), cannot be readily ascertained. It may be noted, however, that the lifetime of the hydrido-species is evidently quite long and thus, together with evidence discussed earlier, indicates strongly that the olefin attacks the hydrido-species. The alternative pathway has a further contra-indication since we should not expect an olefin complex to be even able to activate molecular hydrogen.

It seems clear that there must be an intermediate species, or at least an activated complex, in which both molecular hydrogen (as *cis*-MH$_2$) and an olefin are co-ordinated to the metal atom. The poisoning and competitive experiments indicate that a vacant site *on the hydrido-species*, at which the substrate olefin can be activated, is necessary for efficient catalysis. Those substrates which cannot approach the activating site because of steric factors are not readily reduced. In view of the very rapid and stereospecific *cis*-reduction, it is reasonable also to assume that the vacant site is *cis* to the two M–H bonds as in (I).

It is now clear why certain species, even though they can activate molecular hydrogen quite rapidly and reversibly, *e.g.*, IrCl(CO)(PPh$_3$)$_2$, RhCl(PPh$_3$)$_2$ in pyridine or acetonitrile, are either unable to catalytically hydrogenate olefins at 25° and 1 atmosphere or do so only very slowly. On the dihydrido-species there is no vacant site for olefin co-ordination—*i.e.*, they are co-ordinatively saturated. The very slow hydrogenation of olefins by the iridium species IrCl(CO)(PPh$_3$)$_2$H$_2$ at elevated temperatures is best attributed to thermal dissociation of the phosphine ligands ‡ which would then competitively provide a co-ordination site. A less likely explanation would be direct attack of olefins on the hydrido-species.

(C) *The Transfer Step.*—All the evidence is in agreement with the initial formation of RhCl(PPh$_3$)$_2$H$_2$(solvent), displacement of solvent competitively by olefin, and stereospecific *cis*-transfer of bound hydrogen to the olefin in an actual intermediate or in an activated complex. Diffusion of the saturated substrate away from the transfer site leaves the complex again ready to activate dissolved hydrogen molecules. As to the precise manner in which the two hydrogen atoms are transferred to the olefin, it is our view, though this is not unequivocally proven, that essentially simultaneous transfer occurs without the formation of an alkyl intermediate. We have no evidence so far from chemical studies that it is possible to attack one hydrogen atom in RhCl(PPh$_3$)$_2$H$_2$ without the involvement of the other—either *both* hydrogens react as in olefin hydrogenation, or both hydrogens are evolved as molecular hydrogen. The principal difference between the present system and the very few cases in complexes

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* [*Note added in Proof.*—P. B. Chock and J. Halpern (*J. Amer. Chem. Soc.*, 1966, **88**, 3511) have now described the kinetics of addition of hydrogen to *trans*-IrX(CO)(PPh$_3$)$_2$. The rate of addition was markedly dependent on the halide X (increasing in the order Cl < Br < I) and also on the solvent used, increasing when more polar solvents replaced benzene. These results are very similar to those found in our studies. The very small deuterium isotope effect also observed ($k_{H_2}/k_{D_2} = 1{\cdot}22$) could mean that bond breaking in the hydrogen molecule was accompanied by a synchronous metal–hydrogen bond formation possibly through a triangular transition state.]

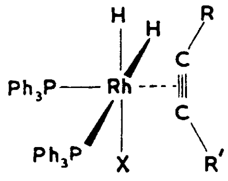
† See also W. Hieber and E. Linder, *Ber.*, 1961, **94**, 1417, for difference in dissociation constants of HCo(CO)$_3$L [L = PPh$_3$ and P(OPh)$_3$].

‡ This would predict that the triphenylphosphine exchange rate should be very slow for IrCl(CO)(PPh$_3$)$_2$H$_2$ [although it is exceedingly rapid for square IrCl(CO)(PPh$_3$)$_2$] and should increase with temperature paralleling the increased catalytic activity.

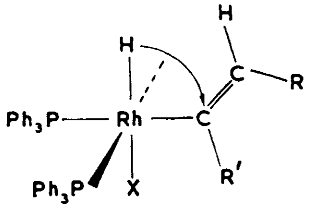
[48] W. D. Horrocks, jun., and R. C. Taylor, *Inorg. Chem.*, 1963, **2**, 723.

where an unsaturated hydrocarbon (usually ethylene) is known to attack an M–H bond is that in the latter there *is* only one M–H bond and the attack of olefin is best regarded as an *insertion reaction* into the M–H bond. In view of the appreciable stability of the rhodium–ethyl bond (detected by n.m.r.) formed by insertion of ethylene into an Rh–H bond in the dimerisation process for ethylene studied in great detail by Cramer [35] and of the high stability of $C_2H_5RhCl_2(PPh_3)_2$ at 25° in solution,[45] we should have expected our n.m.r. direct transfer studies to ethylene to have shown the presence of an ethyl intermediate. None could be observed.

It might have been thought possible to eliminate an alkyl stage by stereochemical argument, since if an alkyl intermediate had a lifetime long compared to the time of free rotation about the M–C bond, both *cis*- and *trans*-hydrogen addition should occur equally. However, inspection of the stereochemistry shows that the insertion of an olefin such as maleic acid into an M–H bond probably determines itself the overall stereochemistry of the addition process. This is very obvious when acetylenes are considered. Thus when RC≡CR′ co-ordinates or occupies the activation site, the groups R,R′ will be bent slightly away from the metal as in (IVa). Transfer of one hydride to give a metal–carbon bond will thus cause R and R′ to become *cis* to each other as in (IVb). Although we cannot determine *which* hydrogen atom is transferred first, it is likely that it would be the one *trans* to triphenylphosphine; in the iridium hydrido-complex, $IrH_2Cl(PEt_2Ph)_3$, the hydrogen *trans* to phosphorus is reactive towards dilute mineral acids whereas the hydrogen *trans* to chloride is not.[49] The transfer of the second hydride will then retain the *cis*-configuration of the product.

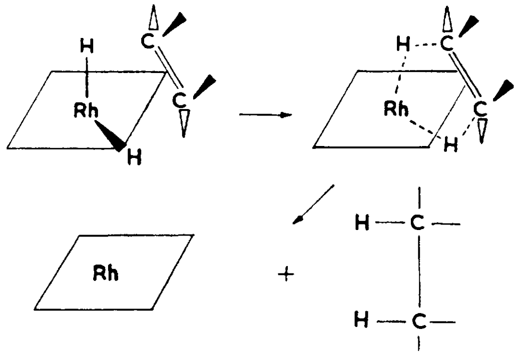


(IVa)



(IVb)

A deeper insight into the mechanism of the transfer process is provided by the very low value for the overall kinetic isotope effect [Section (C)] where the ratio of the rates (H)/(D) is about 0·9. It is well known [50] that the kinetic isotope effect results from changes in the activation energy of the process caused by differences in the zero-point energy when the reactants are converted to an activated complex. Complete loss of a Rh–H stretching vibration (ν_{Rh-H} ~2100 cm.$^{-1}$) in the transition state at 25° would lead to a value of (rate H)/(rate D) ~4, the zero-point energy difference of Rh–H and Rh–D being *ca.* 0·86 kcal./mole. However, it has been proposed that in certain hydride transfer reactions in organic systems, *e.g.*, those in the Cannizaro reaction,[51] the alkaline cleavage of triphenylsilane,[52] and the hydrolysis of pyridine diphenylborane,[53] where low (rate H)/(rate D) values are found, a complete rupture of the X–H bond does not occur; the bond is bent so that the hydrogen atom can attach itself to another part of the molecule leading to a three-centre transition state in which the lengthening of the X–H bond occurs synchronously with the formation of, say, a C–H bond. This concept can be applied in the present case for a Rh–H bond and such a mechanism would significantly reduce the (rate H)/(rate D) value; indeed, the inverse size of this effect indicates that zero-point energy is actually gained in the transition state. Thus a "tightening up" may occur in the activated complex whereby zero-point energy lost by the bending and lengthening of the Rh–H bond is more than compensated for by the zero-point energy gained by the formation of a C–H bond since the zero-point energy of a C–H bond is greater than that of the Rh–H bond by ~1·43 kcal./mole. Moreover, if the olefin complex occupies a position *cis* to both Rh–H bonds it is possible that by suitable alignment of the double bond about this position, both hydrides may be transferred simultaneously, each by a three-centre transition state as in Scheme 2. It seems quite likely that all insertion mechanisms of this type proceed *via* such triangular transition states. It is pertinent to note in this connection that appreciable interaction between a transition metal and C–H bonds of a bound ligand has been clearly demonstrated in several cases [54] and indeed in one case,[55] that of $Ru(Me_2PCH_2CH_2PMe_2)_2$, there is evidently an equilibrium between two forms, one with co-ordinated phosphine and the other with a Ru–H plus a Ru–CH_2 bond. Furthermore, there is a close



Scheme 2

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[49] J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7393.

[50] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.

[51] K. B. Wiberg, *J. Amer. Chem. Soc.*, 1954, **76**, 5371.

[52] S. L. Kaplan and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1955, **77**, 1300.

[53] M. F. Hawthorne and E. S. Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 4296.

[54] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1960, 989, 3753; R. B. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1922.

[55] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843.

analogy between the transition state postulated here and that proposed in hydrogenations using di-imide.[56]

EXPERIMENTAL

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

N.m.r. spectra were obtained using a Varian Associates model 43100 spectrometer at 56·45 and 40 Mc./sec., and e.s.r. spectra on a Varian Associates V-4502-15 spectrometer.

Melting points (uncorrected) were determined on a Kofler hot-stage microscope. G.l.c. measurements were made using a Perkin-Elmer model F-11 chromatograph with flame ionisation detector and 2 m. columns. The stationary phase was squalene for low boiling hydrocarbons or silver nitrate–diethyleneglycol where better resolution was required; calibrations were made using standard samples. Infrared spectra were taken on a Grubb–Parsons grating "Spectromaster" and electronic spectra on a Perkin-Elmer model 350 spectrometer. Mass spectra were obtained using an A.E.I. MS-9 spectrometer.

Materials.—The rhodium chloride, $RhCl_3,3H_2O$ was from Johnson Matthey Ltd.; the only transition-metal impurity is believed to be possibly a trace of iridium.[57] Triphenylphosphine (Albright and Wilson Ltd.) was recrystallised from benzene–ethanol before use.

Hydrogen (British Oxygen Co.) was passed through an Engelhard "Deoxo" catalyst tube and through a silica gel drying tube before admission to the vacuum system. Cylinder deuterium gas (Matheson Lecture bottle, 99·5%) was used without treatment; after equilibration in the system the gas was analysed mass spectrometrically for each run.

Ethylene, *cis*- and *trans*-but-2-ene (Matheson Lecture bottle), and propylene (I.C.I.) were used without purification. Hex-1-ene, hept-1-ene, and cyclohexene (Koch–Light) were freed from peroxides by acid ferrous sulphate washes, dried over $CaCl_2$, and were stored under nitrogen and protected from light. They were freshly distilled in nitrogen or *in vacuo* for each run, directly into a burette attached to the reaction vessel. Purity was checked by g.l.c. Hex-1-yne (Koch–Light) was passed through an activated alumina column under nitrogen and immediately distilled into the burette.

All other solvents were of reagent-grade quality and were dried and de-gassed before use. All experiments were normally carried out under nitrogen, hydrogen or *in vacuo*.

(A) *Preparations and Reactions*.—(a) *Tris(triphenylphosphine)chlororhodium*(I). To a solution of freshly recrystallised PPh_3 (12·0 g. 6M excess), in hot ethanol (350 ml.), was added a solution of rhodium trichloride trihydrate (2 g.) in hot ethanol (70 ml.) and the solution was heated under reflux (30 min.). The hot solution was filtered and the burgundy-red crystals of the *complex* were washed with degassed ether (50 ml.) and dried *in vacuo*. Yield 6·25 g. (88% based on Rh), m. p. 157—158° [Found: C, 70·1; H, 4·9; Cl, 3·9; O, 0·0. $C_{54}H_{45}ClP_3Rh$ requires C, 70·1; H, 4·9; Cl, 3·8; O, 0·0%]. The molecular weight data is given in Table 6.

If more concentrated solutions are used, *i.e.*, using a total of 200 ml. or less of ethanol, orange crystals of the complex are obtained after 5 min. heating under reflux; these often mixed with a small quantity of the above-mentioned red complex (Found: C, 69·7; H, 4·9; Cl, 4·4%). On continued heating under reflux, gradual conversion of these orange crystals to the deep red form occurs.

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

TABLE 6

Molecular weight data for $RhCl(PPh_3)_3$ (*M*, required 924·9). Mechrolab osmometer at 37°

Solvent	Concentration (g./l.)	*M*	Solvent	Concentration (g./l.)	*M*
$CHCl_3$ ...	5·654	471	C_6H_6 * ...	2·783	480
	13·856	440		4·025	473
	18·044	462		4·550	492
	23·534	461			

* Above 4·6 g./l. variable results are obtained but these are generally above 600. Cryoscopic values in benzene: 2·575 g./l., *M*, 458; 2·321 g./l., *M*, 457.

The preparation of the complex can also be carried out in aqueous acetone. Thus, $RhCl_3,3H_2O$(0·1 g.) in water (5 ml.) is added to a hot solution of PPh_3 (0·6 g.) in acetone (25 ml.) and heated under reflux. Orange crystals of the complex are deposited after a few minutes (Found: C, 69·6; H, 4·6%).

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

(b) *Tris(triphenylphosphine)bromorhodium*(I). To a solution of PPh_3 (12 g., 6M excess) in hot ethanol (250 ml.) was added a solution of $RhCl_3,3H_2O$ (2 g.) in warm ethanol (70 ml.). After heating under reflux until the solution begins to lighten in colour (5 min.), LiBr (8 g.) in hot ethanol (50 ml.) was added and the mixture heated under reflux for 1 hr. Orange prisms of the *complex* were collected from the warm solution, washed with de-gassed ether (50 ml.) and dried *in vacuo*. Yield 5·1 g. (64%), m. p., 133—134° (Found: C, 66·8; H, 4·9; Br, 8·2. $C_{54}H_{45}BrP_3Rh$ requires C, 66·9; H, 4·7; Br, 8·2%).

A second form of the bromide can be prepared as follows. To a solution of $RhCl_3,3H_2O$ (0·5 g.) in warm ethanol (75 ml.) was added LiBr (2 g.). After heating under reflux (5 min.), hot ethanol (75 ml.) containing PPh_3 (3 g.) was added and the mixture heated under reflux for 30 min. Deep brown crystals of the *complex* were collected from the warm solution, washed with de-gassed ether (25 ml.) and dried *in vacuo*. Yield, 1·3 g. (69%), m. p. 129—130° (Found: C, 66·7; H, 4·7; Br, 8·3%).

Again, no differences were found in the i.r. spectra of the two forms from 4000—600 cm.$^{-1}$ and their chemical properties are identical.

(c) *Tris(triphenylphosphine)iodorhodium*(I). To a solution of PPh_3 (6·0 g., 6M excess freshly recrystallised from ethanol) in hot ethanol (200 ml.) was added a solution of $RhCl_3,3H_2O$ (1·0 g.) in warm ethanol (60 ml.) and the mixture brought to the boil. When lightening of the colour of the solution occurred and orange crystals began to be deposited (*ca.* 5—10 min.), a solution of LiI (4 g.) in hot ethanol (80 ml.) was added quickly dropwise, and the

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[56] S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem. Internat. Edn.*, 1965, **4**, 271.

[57] Dr. F. M. Lever, personal communication.

solution stirred. The mixture heated under reflux for 3—4 hr. and brown crystals collected from the warm solution. These were often contaminated with a material of higher iodine content, probably the dimeric species $[RhI(PPh_3)_2]_2$. The product was therefore dissolved in the minimum quantity of hot benzene containing an excess of PPh_3, the solution filtered and allowed to stand for several hours under nitrogen. Deep red prisms of the *complex* were collected, washed with ether and dried *in vacuo*. m. p. 118—120° (decomp.) (Found: C, 64·1; H, 4·8; I, 12·3. $C_{54}H_{45}IP_3Rh$ requires C, 63·8; H, 4·4; I, 12·5%).

(d) *Tetrakis(triphenylphosphine)-μμ'-dichlorodirhodium*(I). Saturated solutions or suspensions of $RhCl(PPh_3)_3$ in benzene, toluene or preferably methyl ethyl ketone when heated under reflux under nitrogen, give salmon-pink crystals of the *complex* in essentially quantitative yield. The collected material was washed with de-gassed ethanol and dried *in vacuo* (Found: C, 65·4; H, 4·8; Cl, 5·3. $C_{72}H_{60}Cl_2P_4Rh_2$ requires C, 65·1; H, 4·5; Cl, 5·4%).

The complex slowly absorbs oxygen from the air in the solid state but more rapidly as a suspension in organic solvents in which it is sparingly soluble. Storage should be *in vacuo*. The molecular weight (in chloroform, saturated with hydrogen) is that for a dimer: *M* (found), 1263, *M* (calc.), 1324. If molecular weight measurements are carried out under aerobic conditions, low values are obtained, presumably because of the formation of the soluble oxygeno-complex, $RhCl(PPh_3)_2O_2$. The dimer in suspension undergoes cleavage with carbon monoxide at 25°, to give $RhClCO(PPh_3)_2$, identified by comparison of its i.r. spectrum with an authentic sample. Crystallisation from benzene solution containing an excess of triphenylphosphine gives $RhCl(PPh_3)_3$.

(e) *Interaction of the complexes with carbon monoxide.* When carbon monoxide is passed through a solution of $RhCl(PPh_3)_3$ (0·05 g.) in benzene (10 ml.) the solution rapidly turns yellow and after removal of solvent, crystals of $RhClCO(PPh_3)_2$ are obtained in essentially quantitative yield. The product was identical (i.r.) with the authentic material prepared from $[Rh(CO)_2Cl]_2$ (Found: C, 64·3; H, 4·3; Cl, 5·3. Calc. for $C_{37}H_{30}ClOP_2Rh$, C, 64·4; H, 4·4; Cl, 5·1%).

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

(f) *Interactions of the complexes with aldehydes.* A suspension of $RhCl(PPh_3)_3$ (0·5 g.) in benzene (10 ml.) was warmed (40°) and n-heptaldehyde added (0·5 ml.). The solution rapidly turned pale yellow, and on cooling, crystals of $RhClCO(PPh_3)_2$ were deposited from the solution (identified by i.r.). Analysis of the residual solution by g.l.c. shows the following yields of products: n-hexane, 80%; hex-1-ene, 10%; *cis*-hex-2-ene, 5%; *trans*-hex-2-ene, 5%.

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

The corresponding bromide and iodide were found to behave similarly, $RhBrCO(PPh_3)_2$ and $RhICO(PPh_3)_2$ being identified as the products.

(g) *Bis(triphenylphosphine)ethylene chlororhodium*(I). On bubbling ethylene through a solution of $RhCl(PPh_3)_3$ (0·1 g.) in de-gassed chloroform (10 ml.), the red colour rapidly changes to yellow and on concentration of the solution under an ethylene atmosphere, yellow crystals of the *complex* were obtained. They were collected rapidly, washed with a little ethylene-saturated chloroform and dried in air. Yield, *ca.* 70% (Found: C, 65·5; H, 5·0; Cl, 4·9. $C_{38}H_{34}ClP_2Rh$ requires C, 66·0; H, 4·8; Cl, 5·1%).

The corresponding bromide *complex* is made in an identical way from $RhBr(PPh_3)_3$ (Found: C, 62·3; H, 4·7; Br, 10·5. $C_{38}H_{34}BrP_2Rh$ requires C, 62·0; H, 4·6; Br, 10·9%).

The complexes are readily soluble in benzene, chloroform and dichloromethane. The solutions lose ethylene rapidly but regeneration is complete in the presence of an excess of ethylene.

(h) *Absorption of hydrogen by* $RhCl(PPh_3)_3$ *and* $[RhCl(PPh_3)_2]_2$. In a standard micro-hydrogenation apparatus, 5 ml. of solvent (benzene, ethyl acetate, glacial acetic acid) were saturated with hydrogen at 1 atmosphere pressure. Then $RhCl(PPh_3)_3$ (*ca.* 40—45 mg.) were tipped into the solvent from a bucket and the additional hydrogen uptake measured. The rate of uptake varied with each solvent, but no useful data could be obtained because of the differing solubilities of the complex and the dihydride product in each of the solvents. Generally, uptake was complete after 1 hr. In all cases the absorption was found to correspond to 1 mole of hydrogen per mole of $RhCl(PPh_3)_3$. The dimer (37·45 mg.) in dichloromethane absorbed 1·30 ml. hydrogen at s.t.p. ($\equiv$2·05 moles hydrogen per mole).

(i) *Bis(triphenylphosphine)dihydridochlororhodium*(III). On passing hydrogen through a solution of $RhCl(PPh_3)_3$ (0·5 g.) in de-gassed chloroform (10 ml.) for a few minutes, the solution turned pale yellow. On concentrating the solution under hydrogen to a small volume ($\sim$2 ml.) or by the addition of a little de-gassed ether, pale yellow crystals of the *complex* were obtained. These were quickly collected, washed with a little hydrogen-saturated ether and dried *in vacuo* (Found: C, 65·2; H, 5·1; Cl, 6·2. $C_{36}H_{32}ClP_2Rh$ requires C, 65·0; H, 4·8; Cl, 5·3%). The molecular weight in $CHCl_3$ under hydrogen is 700 (required 665).

The yellow crystals, even after storing *in vacuo* for several days, smell faintly of chloroform and the high chloride analysis reflects the retention of some weakly bonded chloroform. $[RhCl(PPh_3)_2(H_2),CHCl_3$ requires Cl, 18·1%].

(j) *Di[bis(triphenylphosphine)dihydrochlororhodium*(III)] *dichloromethane*. This was prepared in the same manner as the possibly five co-ordinate species above except using dichloromethane as solvent. Yellow crystals of the *complex* were obtained on concentrating the solution under hydrogen; they were filtered, washed with a little de-gassed ether and dried *in vacuo* for several days (Found: C, 61·8; H, 5·0; Cl, 9·5. $C_{13}H_{66}Cl_4P_4Rh_2$ requires C, 62·0; H, 4·7; Cl, 10·0%).

The i.r. spectrum (mull) shows bands due to the presence of dichloromethane. The corresponding dideutero-complex was made in an analogous way.

(k) *Bis(triphenylphosphine)pyridinedihydridochlororhodium*(III). On passing hydrogen through a solution of $RhCl(PPh_3)_3$ (0·25 g.) in pyridine (10 ml.) for 20 min., the solution gradually turned pale yellow. On concentration under hydrogen to *ca.* 2 ml., crystals of the *complex* were obtained. These appeared to be yellow but after washing with ether (5 ml.) were white. Yield *ca.* 90% (Found: C, 66·6; H, 5·1; Cl, 4·8. $C_{41}H_{37}ClNP_2Rh$ requires C, 66·2; H, 5·0; Cl, 4·8%).

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

The corresponding *bromide* can be obtained in an analogous way from $RhBr(PPh_3)_3$ (Found: C, 62·4; H, 4·7; Br, 10·3. $C_{41}H_{37}BrNP_2Rh$ requires C, 62·4; H, 4·7; Br, 10·2%).

As well as Rh–H frequencies i.r. spectra of both compounds show bands due to both PPh_3 and pyridine.

(l) *Other solvent hydrido-complexes.* Repetition of the preceding experiments using benzene, ethyl acetate, glacial acetic acid or dimethylformamide gave pale yellow solutions, from which almost white crystals were obtained directly or by precipitation upon concentration of the solution in a stream of hydrogen. However, the solids were rather unstable, losing hydrogen. In addition to Rh–H bands (Table 2), i.r. spectra of the ethyl acetate and dimethylformamide products had frequencies assignable to co-ordinated solvent at 1734m and 1639m cm.$^{-1}$, respectively.

(B) *N.m.r. Studies.*—(a) *Ethylene complex.* Deuterochloroform (0·5 ml.) containing $RhCl(PPh_3)_2(C_2H_4)$ (0·05 g.) and one drop of $SiMe_4$ in an n.m.r. tube was attached to a vacuum line, frozen in liquid nitrogen, evacuated, and an appropriate measured amount of ethylene condensed into it. After sealing, the tube was placed in a Varian low temperature probe for the 40 Mc./sec. spectrometer and the spectrum measured over the range −50—25°. Repetition with varying quantities of ethylene led to the results given in Table 1.

(b) *Hydrogen pressure studies.* A deuterochloroform (0·5 ml.) solution of $RhCl(PPh_3)_3$ (0·1 g.) containing one drop of $SiMe_4$ was saturated with hydrogen and transferred to a thick-walled n.m.r. tube. The latter was sealed in to a brass adaptor by Ciba Araldite epoxy resin (type AY/HY111). The adaptor was connected to stainless steel pressure tubing (1 mm. outside diam.) terminating in a needle valve and connection to pressure gauge and cylinder. The system was flushed with hydrogen and thereafter the pressure slowly increased to *ca.* 100 atmospheres. After a few minutes to allow equilibration (and for safety reasons) the tube arrangement was disconnected from the cylinder and the n.m.r. tube inserted in the spectrometer.

(c) *Hydrogen transfer to olefins.* A solution of $RhCl(PPh_3)_3$ (*ca.* 0·1 g.) in $CDCl_3$ (3·0 ml.) in an n.m.r. tube sealed to a vacuum line, was saturated with hydrogen until yellow; after addition of a little $SiMe_4$, ethylene was condensed onto it. After sealing, the n.m.r. spectrum was followed from −70°—25°.

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

(C) *Catalytic Experiments.*—The reaction vessel was a 250 ml. flask with an outer jacket which was flattened on one side to accommodate a magnetic stirrer. It was attached *via* a condenser to a vacuum system with storage bulbs, manometers, sampling tubes, etc.

Water from a thermostat bath was rapidly pumped (*ca.* 2 l./min.) through the jacket and the temperature of hydrogenating solutions could be maintained to ±0·25°, as checked by the direct measurement of temperature of these solutions.

The stirrer was a Teflon coated magnet fitted with two Teflon flange discs and was driven by the external motor so that it operated at the gas–liquid interface. This gives very efficient stirring in of hydrogen, and hydrogen absorption rates of up to *ca.* 250 ml./min. have been observed with $RhI(PPh_3)_3$ without any apparent limitation due to hydrogen starvation or diffusion control. In kinetic runs the initial uptake rates were customarily well below 90 ml./min. so that there is little likelihood of hydrogen starvation in solution.

The catalyst (10^{-4} moles, in general) was weighed into a small glass bucket, suspended from a side-arm, which on rotation dropped the bucket into the solution.

The standard solvent in kinetic runs was benzene (50 ml.) plus petroleum [(30-*n*) ml.] (hexane fraction, Hopkin and Williams " Spectrosol " for u.v. spectroscopy), where *n* is the volume of substrate used. The total volume was hence constant throughout the series of runs; this procedure was adopted to minimise any effect of dielectric constant changes.

The solvent was de-gassed by careful evacuation and the system flushed three times with hydrogen. The catalyst was added and the solution stirred until the solid had dissolved giving a pale yellow solution. The stirring was then stopped and freshly distilled substrate run in from the burette; the colour of the solution became deep brown but absorption of hydrogen did not occur until stirring had begun. The hydrogen was evacuated, the system allowed to equilibrate (2—3 min.) and the vapour pressure measured (the values were reproducible to *ca.* 0·3 cm.). Hydrogen was then re-admitted to a total pressure of *ca.* 60 cm.; this pressure was adjusted so that the critical readings at the standard 50 cm. partial pressure of hydrogen occurred at least 2—3 min. after initiation of the reaction by starting the stirrer; this period was sufficient to allow the setting up of a steady state. During this reaction time only *ca.* <1% of the substrate was consumed. Where small quantities of substrate were used, the total volume of the system was reduced to *ca.* 0·5 l. by isolation of the storage bulb, so that smaller amounts of substrate are consumed for a larger pressure change.

(D) *Deuteration Studies.*—(a) *Reduction of maleic and fumaric acids.* To 1 : 1 benzene–ethanol (50 ml.) containing $RhCl(PPh_3)_3$ (2×10^{-4} moles) was added the acid (0·0424 moles). Deuterium (600 ml.) was admitted and after complete absorption (*ca.* 20 hr.) the solution was filtered, concentrated *in vacuo* and the crystals of succinic acid so obtained collected and crystallised from acetonitrile: the i.r. spectra were measured in Nujol mulls.

(b) *Hydro-deuteration of hex*-1-*ene.* After exposure to the mixed gases for 60 min. the solution was fractionally distilled and the fraction between 64—70° collected. This fraction, enriched in n-hexane, was analysed directly mass spectrometrically. The data is collected in Table 5.

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