HOMOGENEOUS HYDROGENATION OF CYCLOHEXENE CATALYZED BY COMPLEXES OF RHODIUM AND IRIDIUM

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Summary

The synthesis and characterization of $RhClHN(CH_2CH_2PPh_2)_2$ and $IrClHN(CH_2CH_2PPh_2)_2$ and their catalytic activity in the homogeneous hydrogenation of cyclohexene over the temperature range 20 - 50 °C and 0.4 - 1 atm H₂ partial pressure have been investigated. The dependence of the rate of hydrogenation on factors such as the catalyst concentration, the substrate concentration, H₂ pressure and the temperature is reported. A mechanism has been proposed in which the catalysts activate molecular hydrogen by forming dihydrido species of the type $MClL(H)_2$ [M = Rh(I), Ir(I) and L = HN(CH_2CH_2PPh_2)_2] followed by transfer of hydrogen to the olefin to form the saturated product. The experimental data are in accordance with a rate expression of the form:

Rate = $\frac{k'K_1[H_2][S][C]}{\{1 + K_1[H_2]\}\{1 + K_2[S]\}}$

where [H₂], [S] and [C] are the concentration of H₂, substrate and catalyst, respectively. The activation parameters of the reaction, ΔH^{\dagger} and ΔS^{\dagger} , have also been evaluated.

Introduction

The catalytic activity of Rh(I) and Ir(I) tertiary arsine and phosphine complexes has been studied in a variety of catalytic reactions [1 - 3]. The use of some of the binuclear complexes of rhodium(I) and iridium(I) with mixed arsine and phosphine ligands as hydrogenation catalysts for olefins has also been reported [4]. In the present work, we report the synthesis of MClHN(CH₂CH₂PPh₂)₂ where M = Rh(I), Ir(I) and abbreviated as MClL, and the homogeneous hydrogenation of cyclohexene catalyzed by MClL. The

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square-planar complexes of Rh(I) and Ir(I) with bis(diphenylphosphinoethylamine) are of special interest as the catalysts involve a tridentate ligand with mixed donor N and P atoms.

Experimental

The elemental analyses of the complexes reported were undertaken at Galberts Laboratory in the U.S.A. and at CSIRO, Australia. The conductivity measurements were made on a Digisum model Digital conductivity meter. The IR spectra of the solids were recorded on a Beckman IR-12 spectrophotometer and the NMR spectra for $CDCl_3$ solutions were obtained using a Varian A-60 I model instrument. The electronic spectra were recorded on a Beckman DB model spectrophotometer. Melting points were obtained through the use of a Biochem melting point apparatus having an automatic heating control.

Cyclohexene was prepared by a known procedure [7] and freed from peroxide by washing with acidified ferrous sulphate, dried over calcium chloride, distilled under nitrogen and kept in the dark. Ethanol was purified and distilled twice over magnesium and iodine. Hydrogen gas from a cylinder was purified by passing first through a saturated potassium permanganate solution to remove contaminated olefins and finally through concentrated sulphuric acid before entry into the vacuum system. All the solvents used were of reagent grade and were dried and degassed before use.

The cyclooctene dimer $[MCl(C_8H_{14})_2]_2$ [M = Rh(I), Ir(I)] was synthesized using the published procedure [5]. The ligand bis(diphenylphosphinoethylamine) was synthesized by adopting the procedure reported by Sacconi and Morassi [6].

Preparation of the complexes

Complexes (1) and (2) were prepared in a nitrogen atmosphere.

Bis(diphenylphosphinoethylamine)chloroiridium(I) (1)

To a solution of $[IrCl(C_8H_{14})_2]_2$ (0.2 g) in hot benzene (20 ml) was added a solution of $Cl^-H_2N^+(CH_2CH_2PPh_2)_2$ (0.230 g) in warm benzene (10 ml). The colour of the solution of the bis[cyclooctenechloroiridium(I)] complex turned to light greenish brown a few minutes after the addition of the ligand. The resulting solution was refluxed for 1 h, the complex filtered, washed with benzene and dried *in vacuo* (yield 61%). M.p. 234 °C (dec.). Anal. calcd. for $C_{28}H_{29}NP_2IrCl$: C, 50.4; H, 4.09; N, 2.13; Cl, 5.31. Found: C, 50.2; H, 4.33; N, 2.09; Cl, 5.30.

Bis(diphenylphosphinoethylamine)chlororhodium(I) (2)

To a solution of $[RhCl(C_8H_{14})_2]_2$ (0.240 g) in hot benzene (20 ml) was added a solution of $Cl^-H_2N^+(CH_2CH_2PPh_2)_2$ (0.321 g) in warm benzene (10 ml). The dark orange solution of the rhodium cyclooctene complex in benzene instantaneously changed its colour to yellowish brown on addition of the bis(diphenylphosphinoethylamine) salt solution. The resulting solution was refluxed for 20 - 30 min until no further changes in the colour of the solution occurred. A yellowish green precipitate was obtained which was filtered, washed with warm benzene and dried *in vacuo* (yield 70%). M.p. 230 °C (dec.). Anal. calcd. for $C_{28}H_{29}NP_2RhCl: C, 58.1; H, 5.01; N, 2.39; Cl,$ 6.22. Found: C, 58.0; H, 5.10; N, 2.41; Cl, 6.12.

Reactions of MClL with hydrogen

Hydrogen was passed through a concentrated solution of MClL in ethyl acetate which was stirred vigorously. After 2 - 4 h the solution became pale in colour and finally a very light yellow precipitate was obtained which was filtered and washed with benzene (m.p., 260 $^{\circ}$ C (dec.)).

Kinetic studies

The rate of absorption of hydrogen was measured using a glass manometric apparatus which was provided with leak-proof Springham stopcocks. High vacuum silicon grease was applied to the stopcocks to keep the system airtight. The temperature of the reaction was maintained constant by circulating water at a particular temperature through a water jacketted glass cell. The standard pressure of H₂ employed was 0.4 - 1 atm in conjunction with an ethanolic solution of the catalyst.

A known weight of the catalyst was introduced into the reaction cell and the air completely displaced by repeating the process of evacuating and flushing with hydrogen at a particular partial pressure several times. A known concentration of the alkene was prepared in ethanol and then introduced into the cell. Sufficient time was allowed for the solution to equilibrate with hydrogen and to completely dissolve the catalyst. In order to minimize the effect of solvent vapour, a blank was run simultaneously under the same conditions of temperature, pressure and volume. The absorption of hydrogen was measured manometrically by noting the change in the levels of the indicator solution in the measuring burette at suitable intervals of time. The stirrer was operated at the gas-liquid interface in such a manner that the rate of dissolution of hydrogen was much faster than its rate of absorption by the catalyst and there was no limitation due diffusion control. The catalyst concentration was in the range 0.4 - 1.8×10^{-5} M, the concentration range of cyclohexene was 0.5 - 2.5 M and the H₂ pressure was in the range 0.4 - 1 atm. The solubility of hydrogen in ethanol was calculated [8] and was considered to be constant for every run at a particular temperature. It was assumed that Henry's Law was obeyed by the system, an assumption which was approximately valid since there is a slight variation in the Henry's Law constant with temperature.

Spectrophotometric studies

The equilibrium constant K_2 (see later) for the formation of cyclohexene complex was also calculated spectrophotometrically. Ethanolic solutions of MClL gave UV spectra characterized by bands at 310 and 320 nm ($\epsilon = 3424, 3562$) for the Rh(I) and Ir(I) complexes respectively. On addition of cyclohexene to solutions of the complexes two new peaks appeared at 408 and 412 nm ($\epsilon = 1998$ and 1836) for the Rh(I) and Ir(I) complexes respectively. These peaks correspond to the formation of the cyclohexene complexes MClL(S) in the solutions. On saturation with the olefin, solutions of MClL contain a very high ratio of complexed species, *i.e.* MClL(S), relative to the uncomplexed species MClL. On extrapolation, the relative concentrations of the two species may be calculated and the value of K_2 determined. At 30 °C, the values of K_2 for the Ir(I) and Rh(I) complexes were found to be 0.423 and 0.63 M⁻¹, respectively.

Results

Cleavage of the chloride bridge in the cyclooctene complex [MCl- $(C_8H_{14})_2$]₂ by the Lewis base L = HN(CH₂CH₂PPh₂)₂ results in the formation of the monomeric complexes MClL [M = Rh(I), Ir(I)]. The IR spectra of these phosphine complexes exhibit absorption bands at 360 and 365 cm⁻¹ [ν (M—Cl)], at 530 and 550 cm⁻¹ [ν (M—P)] and at 480 and 490 cm⁻¹ [ν (M—N)] for the iridium and rhodium complexes, respectively. The N—H stretching vibration occurred at 3150 cm⁻¹ while the C—H stretching frequency was observed at 3000 cm⁻¹. The absorption peak at 1640 cm⁻¹ was assigned to the skeletal vibration of the phenyl ring. The M—H stretching frequency for the dihydrido complex was observed as two peaks at *ca*. 1950 - 2000 cm⁻¹ for both the iridium and rhodium complexes.

The NMR spectrum of the ligand shows two peaks at 2.3 δ and 3.1 δ , respectively, reflecting the different electronic environments around the methylene groups. A very broad peak at *ca.* 8.3 - 9.8 δ was assigned to the N-H proton. A peak at 7.2 δ corresponded to the phenyl protons. On complexation, the methylene peaks were shifted by 0.8 - 1 δ while the amine proton peak occurred in the same region as those for the ligand. Integration of the peaks gave the correct number of protons present in the complexes.

Conductivity measurements on the complexes (1) and (2) in ethanol showed that they are both non-electrolytes. Based on the elemental analyses, conductivity data, NMR and IR spectra, the structure of the complexes is proposed as being square-planar.

Catalytic hydrogenation

The hydrogenation reaction was carried out in pure dried ethanol. The maximum absorption of H_2 was attained after the reaction had proceeded for *ca.* 25 min.

The rate of absorption of hydrogen was obtained from the tangent of the plot of the number of moles of hydrogen absorbed *versus* the time at constant temperature, hydrogen pressure, catalyst and olefin concentration. Conversion to the rate of consumption of the substrate, S, was obtained from the stoichiometric relationship: At the end of each reaction, the volume of hydrogen absorbed was found and the moles of H_2 absorbed calculated.

Dependence of the rate on the cyclohexene concentration

The plot of the rate of hydrogen consumption as a function of the concentration of cyclohexene at constant concentration of the catalyst, $MClHN(CH_2CH_2PPh_2)_2$, was non-linear, indicating that the reaction is not first order with respect to the substrate. When the reciprocal of the rate was plotted *versus* the reciprocal of the cyclohexene concentration at a constant catalyst concentration [MClL] (where M = Rh(I), Ir(I)) and temperature was drawn, a linear plot was obtained with a positive intercept on the ordinate (Fig. 1) irrespective of the nature of M in the catalyst. The reciprocal of the intercept gave the maximum rate possible under these conditions. Similar plots were obtained for reactions undertaken at 30, 40 and 50 °C, respectively, although it was found that the rates of homogeneous hydrogenation of cyclohexene increased with an increase in the temperature. These results indicate that the rate of hydrogenation of cyclohexene *R* is related to [S] by the relationship

 $1/R = a/[S] + b \tag{2}$

Dependence of the rate on the catalyst concentration

Figure 2 shows a plot of the rate of hydrogenation of cyclohexene at constant cyclohexene concentration as a function of the concentration of



Fig. 1. Plot of the reciprocal of the rate of homogeneous hydrogenation of cyclohexene versus the reciprocal of the olefin concentration catalyzed by $IrClHN(CH_2CH_2PPh_2)_2$ in ethanol at 20 °C and 1 atm H₂ pressure.



Fig. 2. Plot of the rate of homogeneous hydrogenation of cyclohexene as a function of IrClHN(CH₂CH₂PPh₂)₂ concentration in ethanol at 20 °C and 1 atm H₂ pressure.

the catalyst $IrClHN(CH_2CH_2PPh_2)_2$. Similar results were obtained for the catalyst $RhClHN(CH_2CH_2PPh_2)_2$. The data fit a pseudo first order plot. At higher concentration of the catalyst the rates do not increase linearly. In the absence of the catalyst no hydrogen absorption occurred. At higher catalyst concentrations the rates levelled off in all the cases, either because of dimerization of the catalyst or because of the formation of a catalytically inactive species.

Dependence of the rate on the H_2 concentration

Figure 3 illustrates the dependence of the rate of hydrogenation of cyclohexene on the hydrogen concentration at 20 °C at a constant cyclohexene and catalyst concentration. The plot of the reciprocal of the rate against the reciprocal of $[H_2]$ is linear. Assuming that Henry's Law is obeyed, it follows that:

$$1/R = A/[H_2] + B$$
 (3)

where A and B are defined in eqn. (9).

The rate of hydrogenation of cyclohexene was measured over the temperature range 20 - 50 °C for cyclohexene concentrations in the range 0.5 -2.5 M at four different H₂ partial pressures. The rate constants presented in Table 1 were calculated from the slope of the plot of the reciprocal of rate versus the reciprocal of the cyclohexene concentration.

Dependence of the rate on the temperature

Figure 4 shows a plot of $\log_{10} k'$ versus 1/T for the catalyst IrClHN-(CH₂CH₂PPh₂)₂. The effect on the kinetics due to the small difference in the solubility of hydrogen over this temperature range is negligible. From Fig. 4, a value for the activation energy, E_a , of 9.66 kcal mol⁻¹ was obtained. A similar plot was obtained for the catalyst RhClHN(CH₂CH₂PPh₂)₂ where the activation energy, E_a , was 7.82 kcal mol⁻¹. The ΔH^{\pm} and ΔS^{\pm} values calculated for both catalysts are listed in Table 1.



Fig. 3. Plot of the reciprocal of the rate of homogeneous hydrogenation of cyclohexene versus $1/[H_2]$ in ethanol at 20 °C and two concentrations of $IrClHN(CH_2CH_2PPh_2)_2$.

TABLE 1

Data obtained for the homogeneous hydrogenation of cyclohexene catalyzed by IrClHN- $(CH_2CH_2PPh_2)_2$ and RhClHN $(CH_2CH_2PPh_2)_2$ respectively

Catalyst	Temp. (°C)	Rate constant k' (M ⁻¹ min ⁻¹)	$\log(k'+1)$	ΔH^{\ddagger} (kcal mol ⁻¹)	ΔS^{\ddagger} (e.u.)
IrClHN(CH ₂ CH ₂ PPh ₂) ₂	20 30 40 50	0.242 0.389 0.540 0.920	0.384 0.579 0.740 0.964	9 }	-31
RhClHN(CH ₂ CH ₂ PPh ₂) ₂	20 30 40 50	0.33 0.48 0.68 1.05	0.52 0.68 0.83 1.01	7 }	-36

Discussion

A mechanism for the hydrogenation of the olefin which best fits the rate data is:



Fig. 4. Plot of $\log_{10} k$ versus 1/T for the homogeneous hydrogenation of cyclohexene using IrClHN(CH₂CH₂PPh₂)₂ in ethanol as the catalyst at 1 atm H₂ pressure.

$$LMCl + H_{2} \stackrel{K_{1}}{\longleftrightarrow} LMCl(H)_{2}$$

$$LMCl + (S) \stackrel{K_{2}}{\longleftrightarrow} LMCl(S)$$

$$LMCl(H)_{2} + (S) \stackrel{k'}{slow} LMCl(H)_{2}(S)$$

$$LMCl(S) + H_{2} \stackrel{k''}{slow} LMCl(H)_{2}(S)$$

$$LMCl(H)_{2}(S) \stackrel{fast}{\longrightarrow} LMCl + paraffin$$

In the above mechanism, K_1 and K_2 are the equilibrium constants and k' and k'' are the rate constants for the reactions. As the metal olefin complex MClL(S) is an inactive species [9], the rate constant k'' is assumed to be

zero. Under these conditions the rate law is given by eqn. (3) where $[H_2]$, [C] and [S] refer to the hydrogen concentration in the solution, the catalyst and the substrate concentrations, respectively.

Rate (R) =
$$\frac{k'K_1[H_2][S][C]}{\{1 + K_1[H_2]\}\{1 + K_2[S]\}}$$
(4)

From eqn. (4) we obtain:

$$\frac{1}{R} = \frac{1 + K_1[H_2]}{k'K_1[H_2][C]} \times \frac{1}{[S]} + \frac{1 + K_1[H_2]}{k'K_1[H_2][C]} \times K_2$$
(5)

Equation (5) agrees with the experimental results. A plot of the reciprocal of the rate *versus* the reciprocal of the cyclohexene concentration is linear with a slope (a) and intercept (b) which may be expressed as in eqn. (6).

$$a = \frac{1 + K_1[H_2]}{k'K_1[H_2][C]}; \ b = \frac{1 + K_1[H_2]}{k'K_1[H_2][C]} \times K_2$$
(6)

From the slope of the plot of 1/R versus 1/[S] (Fig. 1), the rate constant k' for the rate-determining step may be calculated using the known values of K_1 , $[H_2]$ and [C]. The rate constants k' used in the Arrhenius plot are derived similarly and are listed in Table 1.

The equilibrium constant K_2 was calculated using the slope and intercept of the similar plots. The K_2 values lie in the range 0.4 - 0.85 and 0.65 -0.98 M⁻¹ for the Ir(I) and Rh(I) complexes respectively, over the temperature range 20 - 50 °C. The value of K_2 , *i.e.* the equilibrium constant for the formation of the species MClL(S), obtained spectrophotometrically was virtually equal to the kinetically derived value within 1 - 2% error.

The dependence of the rate on the catalyst concentration should be linear as shown by the rate equation, *i.e.*

$$R = \frac{k'K_{1}[H_{2}][S]}{\{1 + K_{1}[H_{2}]\}\{1 + K_{2}[S]\}} \times [C]$$

As seen from Fig. 2, a linear dependence is observed experimentally but the plot does not pass through the origin as required by the above equation. A similar trend has been observed by Osborn and coworkers [9] in the reduction of olefins by H_2 in the presence of RhCl(PPh₃)₃. The existence of a small intercept could be due to dimerization or to the formation of a catalytically inactive species at higher concentrations, causing a decrease in the rate values and thereby shifting the plots away from the origin although still maintaining an approximate linearity. Taking this deviation into account, the calculated rate expression becomes

$$R = k'[C] - k^{0}[C]^{2}$$
(7)

where $k' \gg k^0$; it is assumed that the dimer formed is catalytically inactive.

From such an equation, the type of curve shown as the dotted line in the Fig. 2 could result. At higher concentrations the deviation is expected to be large.

The dependence of the rate on $[H_2]$ in solution (Fig. 3) is of the form:

$$\frac{1}{R} = \frac{1 + K_2[S]}{k'K_1[S][C]} \times \frac{1}{[H_2]} + \frac{1 + K_2[S]}{k'[S][C]}$$
(8)

Equation (8) agrees with the results of Fig. 3, *i.e.* a plot of 1/R versus $1/[H_2]$ gave a straight line with slope A and intercept B where

$$A = \frac{1 + K_2[S]}{k'K_1[S][C]}; B = \frac{1 + K_2[S]}{k'[S][C]}$$
(9)

The equilibrium constant K_1 was calculated using the slope and the intercept of such plots; the values obtained lie in the range of $0.2 \times 10^3 - 1.8 \times 10^3$ M^{-1} and $0.88 \times 10^3 - 4.1 \times 10^3$ M^{-1} for Ir(I) and Rh(I) catalysts respectively over the temperature range 20 - 40 °C.

The order of the reaction with respect to the catalyst concentration is pseudo first order and that with respect to the substrate concentration and hydrogen concentration respectively is fractional.

There have been numerous reports [3, 9 - 11] regarding the catalytic activity of the tertiary phosphine and arsine complexes of Rh(I) and Ir(I) in the homogeneous hydrogenation of olefins. The catalysts used in the present investigation are square-planar complexes where three of the coordination sites are occupied by the tridentate ligand bis(diphenylphosphinoethylamine) and the fourth by the chloride. It is found that these complexes of Rh(I) and Ir(I) with bis(diphenylphosphinoethylamine) are quite efficient in the homogeneous catalytic hydrogenation of cyclohexene in solution.

The MClHN($CH_2CH_2PPh_2$)₂ catalysts function by reversibly coordinating to the reacting molecules and orienting them in suitable positions in the coordination sphere of the metal ions so as to facilitate their reaction in the catalytic cycle which involves the making and breaking of bonds. The catalysts $IrClHN(CH_2CH_3PPh_2)_2$ (1.002 mol) and $RhClHN(CH_2CH_2PPh_2)_2$ (1.001 mol) have been shown to absorb 1 mol H_2 per mole of catalyst. At low concentrations of the ethanolic solutions of the catalyst $(10^{-4} - 10^{-6} \text{ M})$, these complexes are effective catalysts for the homogeneous hydrogenation of olefins. The activation of molecular hydrogen by these catalysts is usually a one-step process in which the hydrogen molecule adds onto the metal ion through an oxidative addition mechanism. The rate-determining step of the reaction is the formation of the dihydrido-olefin mixed ligand complex $MClL(H)_2(S)$. Wilkinson *et al.* [9] have also proposed the formation of a similar hydrido-olefin mixed ligand complex as a slow step in the hydrogenation of cyclohexene catalyzed by RhCl(PPh₃)₃. The hydrides are then transferred to the coordinated olefin in a fast step to form the saturated product.

Another equally probable mechanism for the hydrogenation of olefins by these complexes may involve the equilibrium formation of a mixed ligand metal-olefin complex MClL(S) followed by formation of $MClL(S)(H)_2$. Although there is no conclusive evidence in favour of either pathway, that involving the formation of the dihydrido species $MClL(H)_2$ followed by the dihydrido-olefin mixed ligand complex of the type $MClL(H)_2(S)$ is preferred [9] on the basis of the low activity of rhodium(I)-olefin complexes in the activation of molecular hydrogen.

The activation parameters, ΔH^{\dagger} and ΔS^{\dagger} , for the catalysts IrClHN-(CH₂CH₂PPh₂)₂ and RhClHN(CH₂CH₂PPh₂)₂ are presented in Table 1. The higher value for ΔH^{\dagger} in the case of iridium may be due to its size and probably to the greater stability of the iridium dihydrido intermediate with respect to dissociation of the hydride groups for the formation of the cyclohexane. The difference could also be due to Rh(III) being more labile than Ir(III), allowing faster substrate coordination thereby favouring the ΔH^{\dagger} value for the rhodium catalyst.

The activation parameters for the homogeneous hydrogenation of cyclohexene catalyzed by RhCl(PPh₃)₃ in benzene are $\Delta H^{\dagger} = 18.6$ kcal mol⁻¹ and $\Delta S^{\dagger} = 1.1$ e.u. respectively [12]. However, with methyl cyclohexene steric hindrance becomes more prominent and is reflected in the negative entropy value, *i.e.* $\Delta S^{\dagger} = -26$ e.u.; ΔH^{\dagger} is however positive (12.7 kcal mol⁻¹) for this reaction. The unfavourable ΔS^{\dagger} values for the investigated reactions may be due to steric hindrance of the bulky phenyl groups. It is thus seen that steric factors have a marked influence on the entropy of activation.

References

- 1 B. R. James and D. Mahajan, Can. J. Chem., 57 (1979) 180.
- 2 J. Halpern, A. S. C. Chan, D. P. Riley and J. J. Pluth, Adv. Chem. Ser., 173 (1979) 16 - 25.
- 3 H. Van Gaal, H. G. A. M. Cuppers and A. Van Der Ent, Chem. Commun., (1970) 1694.
- 4 M. M. Taqui Khan, Mehreen Ahmed and B. Swamy, Indian J. Chem., 20A (1981) 359.
- 5 A. Van Der Ent and A. L. Onderdelinden, Inorg. Synth., 14 (1973) 92.
- 6 L. Sacconi and R. Morassi, J. Chem. Soc. (a), (1968) 2997.
- 7 A. I. Vogel, Practical Organic Chemistry, Longman, Green and Co., London, 1951, p. 245.
- 8 J. Castell-Evans (ed.), *Physicochemical Tables*, Vol. 2, Charles Griffin, London, 1920.
- 9 J. A. Osborn, F. M. Jardine, J. F. Young and G. Wilkinson, J. Chem. Soc. (A), (1966) 1711.
- 10 L. Vaska and R. E. Rhodes, J. Am. Chem. Soc., 84 (1962) 679.
- 11 J. P. Collman, N. W. Hoffman and D. E. Morris, J. Am. Chem. Soc., 91 (1969) 5659.
- 12 F. H. Jardine, J. A. Osborn and G. Wilkinson, J. Chem. Soc. (A), (1967) 1574.