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Synthesis, characterization and catalytic activity of $Rh(PPh_3)_2(en)Cl$ complex

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Ethylenediamine bis(triphenylphosphine) monochlororhodium has been prepared by the interaction of Wilkinson's catalyst and ethylenediamine in benzene. The complex has been isolated and characterized by conventional and spectroscopic methods. The catalytic activity of the complex was investigated for the hydrogenation of 1-octene as a model reaction at a hydrogen pressure of 1 atmosphere (101 kPa) using methanol as a solvent. The influence of various factors such as catalyst, substrate concentrations and temperature have been studied. The hydrido complex has been identified as an intermediate product by IR and NMR studies. The experimental data are in accordance with a rate expression of the form:

$$\text{Rate} = \frac{Kk_1[\text{cat}][\text{H}_2][\text{olefin}]}{k_{-1} + k[\text{olefin}]}$$

Keywords: $Rh(PPh_3)_2(en)Cl$ complex, synthesis, characterization, model hydrogenation reaction

INTRODUCTION

Transition metal catalysis has experienced considerable growth during the past two decades. Industrial uses of homogeneous catalyst systems are increasing. Homogeneous catalysts with tertiary phosphine ligands possess the steric and electronic properties that are necessary for catalytic reactivity and selectivity. The catalytic activity of rhodium–tertiary phosphine complexes has been studied in a variety of catalytic reactions.[1–3] In the present work, we report the synthesis of $Rh(NH_2CH_2CH_2NH_2)(PPh_3)_2Cl$ and the homogeneous hydrogenation of 1-octene catalysed by this complex, which involves a bidentate ligand and mixed donor, nitrogen (N) and phosphorous (P) atoms.

EXPERIMENTAL

Materials

1-Octene (TCI Company, Italy), triphenylphosphine (Fluka AG, Germany). $RhCl_3.3H_2O$ (Sisco, Bombay, India), ethylenediamine (en) (Sarabhai M. Chemicals, India, GR grade) were used as received. The solvents used were freshly distilled and dried.

Elemental analysis was carried out in our laboratory using a Coleman analyser. IR spectra of solids were recorded on a Beckman-IR 12 instrument in KBr. NMR spectra in $CDCl_3$ solutions were obtained using a Perkin–Elmer R-32 (90 MHz) model instrument. Ultraviolet spectra were recorded on a Shimadzu UV-240, DTA/TG data were recorded on Shimadzu DT-30 under a nitrogen atmosphere. Magnetic moments were measured using a Gouy balance. Melting points, were obtained with Gallenkamp (UK) apparatus having an automatic heating control.

Preparation of the complex

The $Rh(PPh_3)_3Cl$ complex (**1**) was prepared as described by Osborn *et al.*[4]

A portion (0.5 g, 0.54 mmol) of **1** was dissolved in 50 cm^3 benzene in a 100 cm^3 round-bottom flask and 0.072 cm^3 (0.93 mmol) of ethylenediamine (en) in 15 cm^3 of benzene was placed in a pressure-equalizing addition funnel fitted to the reaction vessel. The solution of ethylendiamine was added dropwise under vacuum and the mixture stirred at room temperature for seven days under constant vacuum. The detailed procedure is described elsewhere.[5] The brown complex $Rh(en)(PPh_3)_2Cl$ (**2**) precipitated and was separated by filtration, recrystallized from methanol,

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Table 1 IR spectra (cm^{-1}) of the metal complexes[a]

Metal complex	Rh—P (str)	Rh—Cl (str)	Rh—N (str)	N—Rh—N (bending)	N—H (str)
$Rh(PPh_3)_3Cl$	545	360	—	—	—
$Rh(en)(PPh_3)_2Cl$	545	360	450	275	3000

[a] KBr disc

and dried in vacuum; yield 60%, m.p. (charred above 280°C).

Elemental analysis: Found: C, 63.10; H, 5.15; N, 3.90; Cl, 4.87. Calculated: C, 63.13; H, 5.26; N, 3.87; Cl, 4.91%.

The purity of **2** was confirmed by TLC (seen as a single spot), IR and NMR.

Kinetic studies

The kinetics of hydrogenation were studied at atmospheric pressure in a magnetically stirred glass reactor. The rate of uptake of hydrogen was measured using a glass manometric apparatus. The temperature of the reaction and of the glass manometer was maintained constant by circulating water at a particular temperature through a jacket which was wrapped around the apparatus.

A known amount of the catalyst and methanol were introduced into the reaction. The air in the system was completely displaced by repeating the process of evacuating and flushing with hydrogen several times. Finally, an adequate amount of hydrogen gas was stored in the gas burette. The catalyst solution was saturated with hydrogen by starting the stirrer; during this time the brown solution turned to pale yellow indicating the formation of a hydrido species. After 10–15 min, the stirrer was stopped and a known amount of 1-octene was injected into the reaction vessel through a hypodermic syringe. The reaction was initiated by starting the stirrer and the progress of the reaction was monitored by measuring the hydrogen uptake at different time intervals at STP. The stochiometry of the reaction was checked by carrying out a few experiments at a constant temperature and at one atmosphere pressure of hydrogen at various concentrations of 1-octene for longer time intervals. In all these experiments the amount of hydrogen absorbed was stochiometrically proportional to the 1-octene converted (calculation based on the GC analysis of the product). This suggests that there was no formation of side-products. The rate data based on hydrogen uptake measurements were used to study the kinetics of the reaction.

RESULTS AND DISCUSSION

In addition to the elemental analysis, the coordination of the ethylenediamine ligand to the metal atom was confirmed by comparing the infrared spectra of the complex and of Wilkinson catalyst, i.e. of $Rh(PPh_3)_3Cl$, and $Rh(en)(PPh_3)_2Cl$, in the range 250–4000 cm^{-1}. The assignment[6,7] of different frequencies is given in Table 1.

A shift and broadening of the N—H band may be due to coordination of the nitrogen atom in ethylenediamine to the metal atom. Further the coordination of ethylenediamine to the metal atom was shown by the proton NMR spectrum (Fig. 1). A detailed description of the NMR spectra is given in Table 2.

Due to coordination of the ethylenediamine molecule to the metal atom in the $Rh(en)(PPh_3)_2Cl$ complex, the methylene protons were shifted by $\delta 0{\cdot}5$ ppm while the amino protons peak appeared in the same region with multiple splitting (Fig. 1), reflecting the coordination of the ethylenediamine molecule with the metal atom. The UV–VIS spectra in the range 200–300 nm showed a triplet and quartet for $Rh(PPh_3)_3Cl$ and $Rh(en)(PPh_3)_2Cl$ complexes respectively, indicating differences in charge transfer between ligand and metal. Magnetic moment measurement showed that both compounds are diamagnetic, consistent with rhodium(I).

Thermal study

The thermal behaviour of the rhodium complex was studied by DTA and TG methods (Fig. 2). From the figure it was concluded that the complex is thermally stable up to *ca* 110°C; above this temperature the total decomposition of the metal

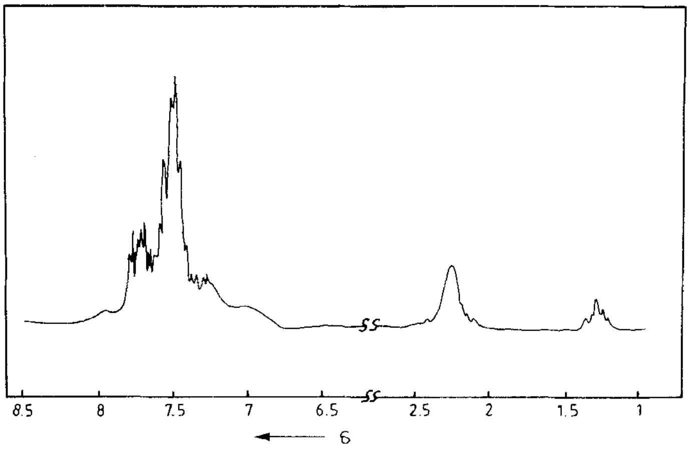

Figure 1 NMR spectrum of $Rh(en)(PPh_3)_2Cl$ in $CDCl_3$.

Table 2 NMR specta (δ, ppm) of ethylenediamine and the metal complexes[a]

Sample	Amino protons	Methylene protons	Aromatic protons
Ethylenediamine	1.3	2.7	—
$Rh(en)(PPh_3)_2Cl$	1.3	2.2	6.9–8.1
$Rh(PPh_3)_3Cl$	—	—	6.9–8.1

[a] $CDCl_3$ solution

complex begins, and it undergoes endothermic reaction in three stages. No attempt was made to identify the sequence of decomposition.

Reaction with molecular hydrogen

IR spectra of $Rh(en)(PPh_3)_2Cl$ saturated with hydrogen in solution showed two broad stretching bands around $2100 \, cm^{-1}$ [(νRh–H)]. When a solution of $Rh(en)(PPh_3)_2Cl$ was shaken with molecular hydrogen the colour changed from brown to pale yellow. Manometric studies showed that 1 mole of hydrogen was absorbed per mole of rhodium complex.

Hydrogenation reaction

In the present investigation the partial pressure of hydrogen and the concentration of hydrogen in solution was kept constant by carrying out the reaction at one atmosphere pressure and using a fixed amount of solvent. The rate of consumption of hydrogen was obtained from the tangent of the plot of the number of moles of hydrogen consumed (at STP) at various intervals of time at constant temperature, hydrogen pressure, catalyst and olefin concentrations. The concentrations of dissolved hydrogen in methanol at the different temperatures studied were taken from solubility data[8,9] reported in the literature. Necessary corrections for the vapour pressure of the solution were applied to the calculations. 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

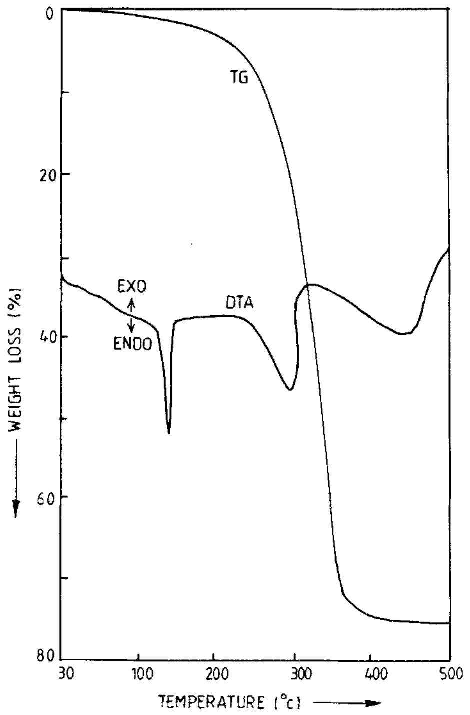

Figure 2 DTA/TG curves for $Rh(en)(PPh_3)_2Cl$ catalyst recorded under a nitrogen atmosphere.

Table 3 Summary of the kinetic data for the hydrogenation of 1-octene at atmospheric pressure with $Rh(en)(PPh_3)_2Cl$ catalyst[a]

Temperature (°C)	Rh present (μmol litre^{-1})	1-Octene (m mol litre^{-1})	Rate of reaction (m mol min^{-1})
25	6.368	3.19	0.44
	6.368	6.38	0.62
	6.368	9.57	1.00
	6.368	12.76	1.25
35	6.368	3.19	0.89
	6.368	6.38	0.97
	6.368	9.57	1.50
	6.368	12.76	1.83
25	1.010	6.38	0.39
	2.020	6.38	0.47
	3.184	6.38	0.57
	6.368	6.38	0.62
	9.550	6.38	0.48
	12.730	6.38	0.39

[a] Solvent used for the reaction: methanol (10 cm^{-3})

catalyst and there was no limitation due to diffusion control. Isomerization products were not detected during the hydrogenation. The results observed under different operating conditions are presented in Tables 3 and 4 and the influence of various parameters is discussed below. The hydrogenation experiments were carried out at least twice to ensure reproducibility of the results. Values for the rate of hydrogenation were taken as an average of these two results.

Effect of 1-octene concentration

The influence of the 1-octene concentration on the rate of the reaction was studied at 25–35°C, under 1 atmospheric pressure of hydrogen using a catalyst concentration of 6.368 μmol Rh litre^{-1} and 1-octene concentrations in the range 3.19–12.76 mmol litre^{-1}. The plot of rate of reaction against concentration of 1-octene was found to be linear (Fig. 3), indicating the first-order behaviour of rate with respect to 1-octene.

Table 4 Effect of temperature on the rate of hydrogenation of 1-octene at atmospheric pressure[a]

Temperature (°C)	Rate of reaction m mol (m min^{-1})	Activation energy (kcal mol^{-1})
25	0.62	17.88
30	1.42	
35	1.83	
45	4.20	

[a] 1-Octene concentration, 6.38 mmol litre^{-1}; rhodium concentration, 6.368 μmol litre^{-1}.

Effect of catalyst concentration

The effect of $Rh(en)(PPh_3)_2Cl$ concentration on the rate of the reaction was studied over the

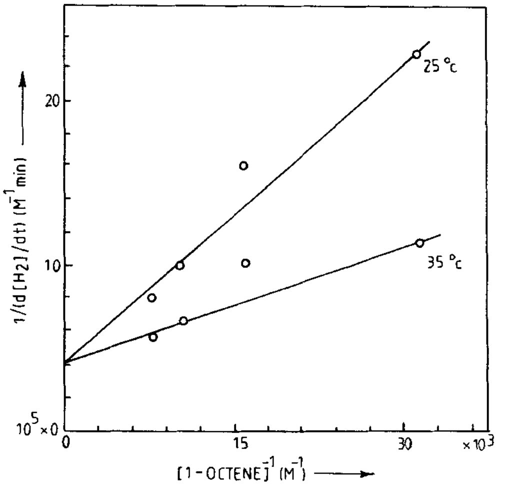

Figure 3 Rate of reaction as a function of [1-octene].

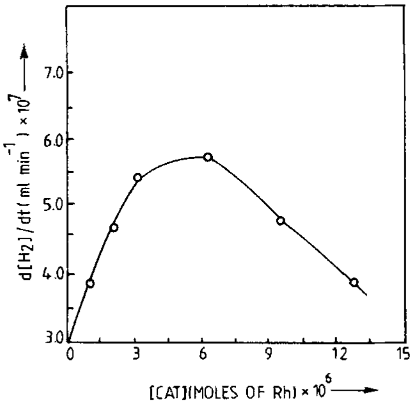

Figure 4 Rate of reaction versus $[Rh(en)(PPh_3)_2Cl]$.

concentration range 1.01–12.03 μmol Rh litre^{-1} at 25°C and 1 atmosphere pressure of hydrogen. The results are shown in Fig. 4. It was found that a plot of the rate of reaction versus the catalyst concentration passes through a maximum, the rate increasing with an increase in catalyst concentration below 6.30 μmol Rh litre^{-1}, while at higher catalyst concentrations the rate was found to decrease with an increase in catalyst concentration. This behaviour is not common and may possibly be attributed either to the dimerization of the catalytic species at higher concentrations or to the formation of catalytically inactive species. Similar observations have been made earlier by Wilkinson and co-workers[4] and Taquikhan *et al.*[10] in homogeneous hydrogenation of olefins using rhodium phosphine (PPh_3) complexes. For the purpose of kinetic studies, only the data at the lower catalyst concentration have been considered. The plot of rate of hydrogenation versus catalyst concentration (Fig. 4) below 6.30 μmol Rh mol litre^{-1} is found to be pseudo-first order. The rate does not vary linearly with increase in concentration of catalyst.

Reaction mechanism

With the above spectroscopic evidence and experimental observations and also from the literature evidence for the formation of rhodium dihydrido complex through the dissociation of $Rh(PPh_3)_2Cl$[11, 12], the following mechanism is proposed (Eqns [1–4]).

$$Rh(en)(PPh_2)_2Cl \overset{K}{\rightleftharpoons} Rh(en)(PPh_3)Cl + PPh_3 \quad [1]$$

$$Rh(en)(PPh_3)Cl + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Rh(en)(PPh_3)(H)_2Cl \quad [2]$$

$$Rh(en)(PPh_3)(H)_2Cl + olefin \underset{slow}{\overset{k}{\rightleftharpoons}} [Rh(en)(PPh_3)(H)_2(olefin)]^+ + Cl^- \ldots. \quad [3]$$

$$[Rh(en)(PPh_3)(H)_2(olefin)]^+ + Cl^- + PPh_3 \rightarrow Rh(en)(PPh_3)_2Cl + alkane \quad [4]$$

An alternative to Eqn [2] would be transition of ethylenediamine from bi-to mono-dentate coordination, with consequent availability of the empty coordination position to attack by hydrogen. On the basis of similar mechanistic conclusions for the Hoechst–Walker process[13] and on the basis of other precedents,[12] we propose the mechanistic route shown in Eqn [2]. It is not however possible to distinguish unrequivocally between the two possibilities on the basis of the present evidence.

The following rate equation [5] may be derived using the above mechanism and applying the steady-state principle to Eqn [4].

$$Rate = \frac{Kk_1[cat]\,[H_2]\,[olefin]}{k_{-1} + k[olefin]} \quad [5]$$

where k_1, k_{-1} and k are rate constants. In the present investigation the concentration of hydrogen was kept constant and the concentration of olefin employed was low; hence Eqn [5] reduces to Eqn [6]:

$$Rate = constant \times [cat]\,[olefin] \quad [6]$$

The observed results are in agreement with Eqn [6].

Effect of temperature

The effect of temperature on the rate of hydrogenation was studied over the range 25–45°C and at a catalyst concentration of 6.37 μmol litre^{-1}, 1-octene concentration of 6.38 mmol and at 1 atmosphere hydrogen pressure (Table 4). The results are shown in Fig. 5 as a plot of log (reaction rate) versus $1/T$. The activation energy for

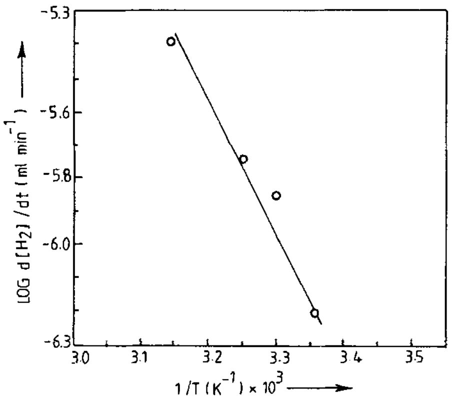

Figure 5 Arrhenius plot for Rh(en)$(PPh_3)_2Cl$ catalyst.

the reaction calculated from the slope of the Arrhenius plot in Fig. 5 is 17.88 kcal mol^{-1}. The lower energy of activation is presumably due to the formation of the dihydrido complex.

CONCLUSION

Introduction of chelating ligand in the rhodium(I) complex (i.e. Wilkinson catalyst) increased the thermal stability of the complex but did not inhibit the dimerization process. This type of complex provides a new route for the anchoring of metal complexes on the polymer matrix through chelating ligands. The new complexes are expected to be more stereoselective in the product distribution of hydrogenation as well as hydroformylation reactions.

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