SUMMARY

The thesis comprises of four main chapters, each of which is again subdivided into several parts. The first part of Chapter I describes the general characteristics of the metal atoms, the ligands and the complexes required to get good catalysts. General review of different homogeneous catalytic processes i.e. hydrogenation, hydroformylation, polymerization, isomerization and oligomerization, etc. has been presented in the second part. Different phenomena such as hydrogen activation by oxidative addition and heterolytic cleavage, ligand dissociation, substrate activation etc. have been discussed and some well known reduction mechanisms have been included. Reductions of organic nitro-compounds by various reducing agents also form a part of this chapter. Proposed reduction mechanisms and the rate equations based mainly on the isolation of catalytic intermediates and the observed kinetics have been presented.

General experimental set up for carrying the hydrogenation of alkenes and nitroarenes under both normal and high pressure conditions have been discussed in Chapter IIA. Chapter IIB describes the dihydrogen reduction of various nitroarenes with trans-PdL_2X_2 (L = pyridine or its alkylderivatives and X = Cl, Br or I). Among trans-$Pdpy_2X_2$, the chloro-complex is most active while the iodo-complex is almost ineffective. The chloro-complex can reduce the various mono- and dinitroarenes but not nitroalkanes, $> C = C <$, $> C = O$ or —CHO groups in

alcohol medium. Basic ethanolic medium was necessary for efficient reduction of p-halonitrobenzenes and 1-nitronaphthalene. The catalyst is sparingly soluble in alcohol and is decomposed to Pd^o in hydrogen without substrate. The solubility of the complex is greatly increased in presence of nitroarene and the resulting solution is stable towards hydrogen. Highest rate of reduction was found at room temperature (30^oC).

The passage of hydrogen through the solution of the substrate and the complex catalyst produced a dark green precipitate (A) which dissolved quite rapidly to produce a catalytically active light green solution (B). Highest rate of reduction was observed only after the complete dissolution of (A). The rate of hydrogen absorption decreased slowly during the progress of the reaction and the reduction stopped at the end with simultaneous discharge of the green colour of the solution. Induction periods ranging from (5-30) minutes were observed in all cases except nitrobenzene, o-nitroaniline and p-nitrotoluene. A catalytically active light green compound isolated from the final reaction mixture could be reused for nitroarene reduction. Addition of fresh nitroarene to the final reaction mixture revived the green colour and the hydrogen absorption started again.

Only the chloro-complex can survive the high pressure reduction conditions. The solution mixture at the end was light brown and too sensitive to air and moisture and can be reused.

The effect of (catalyst : substrate) mole ratio, solvent, temperature, reaction time, pH, hydrogen pressure, etc. on the

nature and yields of the final products have been studied and the optimum conditions have been determined. The results are presented in the Table-1.

The deep green precipitate (A) isolated only with nitrobenzene and o-nitroaniline are suggested to have the following structure :
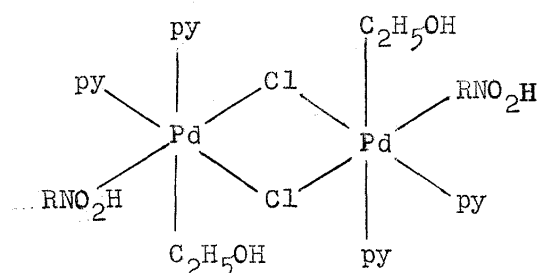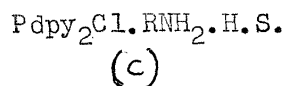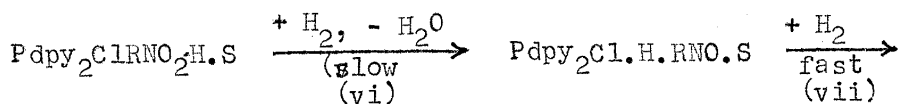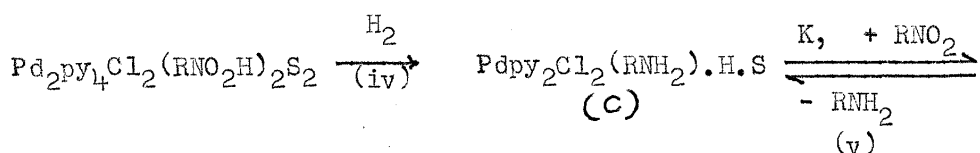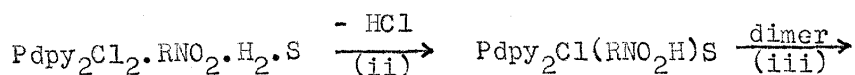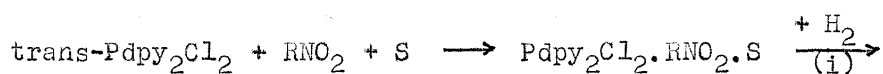

The presence of extra ligands such as pyridine, picoline, dipyridyl, 1,10-phenenthroline etc. either decreased or inhibited the reduction. The presences of dilute alkali or acid had no appreciable effect on the reduction process. Phenylhydroxyl-amine or p-nitrophenol was not detected at any stage.

The liberation of HCl at the initial stage was detected chemically. Some proton acceptors should be present for the reaction to proceed. Alcohol or aniline formed at later stage probably behaved as proton acceptors.

Sequential and preferential reductions of dinitroarenes and mixture of various nitroarenes have been studied. In case of dinitroarenes, formation of diamines started after more than 80%.

formation of mononitroanilines. Preferential reduction of nitro-
benzene or p-nitrotoluene took place when any one of them was
present along with any other nitroarenes. In case of p-nitro-
benzaldehyde, a polymeric schiff base compound of composition
$\angle^{-}$-HC $=$ NC_6H_4-$\angle$$_n$ was isolated.

Kinetic studies have been made with nitrobenzene, o-nitro-
toluene and o-chloronitrobenzene. The initial rate of aniline
formation obeys a first order dependence with respect to catalyst
concentrations and hydrogen pressures (from 200 mm to 1000 mm
of Hg) and independent on nitroarene concentrations. The plot of
1/rate vs. initial concentration of added aniline produces a
straight line with a positive intercept on the 1/rate axis. Based
on these facts, the following mechanism has been proposed :

$$\text{trans-}Pdpy_2Cl_2 + RNO_2 + S \longrightarrow Pdpy_2Cl_2.RNO_2.S \xrightarrow[\text{(i)}]{+ H_2}$$

$$Pdpy_2Cl_2.RNO_2.H_2.S \xrightarrow[\text{(ii)}]{- HCl} Pdpy_2Cl(RNO_2H)S \xrightarrow[\text{(iii)}]{dimer}$$

$$Pd_2py_4Cl_2(RNO_2H)_2S_2 \xrightarrow[\text{(iv)}]{H_2} Pdpy_2Cl_2(RNH_2).H.S \underset{- RNH_2}{\overset{K, + RNO_2}{\rightleftharpoons}}$$
$$(c) \qquad (v)$$

$$Pdpy_2ClRNO_2H.S \xrightarrow[\text{(slow} \atop \text{(vi)}]{+ H_2, - H_2O} Pdpy_2Cl.H.RNO.S \xrightarrow[\text{fast} \atop \text{(vii)}]{+ H_2}$$

$$Pdpy_2Cl.RNH_2.H.S.$$
$$(c)$$

Considering the step (vii) to be fast, a rate equation of the type,

$$\text{rate} = \frac{kK[CAT]_T [NB][PH_2]}{[AN] + K[NB]}$$

can be derived where, $[CAT]_T$, $[NB]$, $[PH_2]$ and $[AN]$ are initial catalyst concentration, nitrobenzene concentration, hydrogen pressure and aniline concentration respectively. Assuming $K \gg 1$, the equation reduces to,

$$\text{initial rate} = k[CAT]_T[PH_2], \qquad \text{at } t = 0.$$

Again,

$$\frac{1}{\text{rate}} = \frac{1}{kK[CAT]_T[NB][PH_2]} [AN] + \frac{1}{K[CAT]_T[PH_2]}$$

from the slope and intercept of the plot of 1/initial rate vs. $[AN]$, k and K were found to be $0.461 \times 10^3 mol^{-1}$ lit min and 14.484 respectively. The assumption $K \gg 1$ was found correct. For o-nitrotoluene the values of k and K are $0.769 \times 10^3 mol^{-1}$ lit min and 13.35 respectively.

The catalytic activities of trans-PdL_2Cl_2 ($L = \alpha$, β or γ-picoline, 2,4- or 2,6-lutidine) towards nitroarene reductions have been studied and the results were almost comparable to those of trans-$Pdpy_2Cl_2$. In these cases, higher induction periods were in general observed for any substrate. The higher

is the electron density on the metal atom centre and lower is the complex sterically hindered, more is the catalytic activity. Comparing the catalytic activities of different complexes, the ligands can be arranged in the following order,

2,4-lutidine > γ-picoline > β-picoline $\approx$ α-picoline >> 2,6-lutidine.

Considering the rate of reduction, 2,4-lutidine complex was found to be better catalyst than trans-Pdpy$_2$Cl$_2$. But this complex always required much higher induction periods.

Chapter III deals with the use of palladium(II) complexes with poly-4-vinylpyridine for the reduction of nitroarenes and aromatic aldehydes. A brief review of the different polymer bound transition metal complexes used in the hydrogenation and polymerization of alkenes, unsaturated oils and oxidation of some organic compounds have been presented at the begining of this chapter.

Four polymers, P_1, P_2, P_3 and P_4 of average molecular weights 4,000; 10,000; 30,000 and 80,000 respectively were prepared using POCl$_3$ and copper acetate as initiators. The complexes may be represented as $(C_5H_4NCHCH_2)_nPdCl_2$, where n = 3.05; 3.5; 3.76 and 6 for P_1, P_2, P_3 and P_4 complexes respectively. The presence of five coordinate palladium(II), with trigonal bipyramidal configuration containing three pyridine moieties and two chlorines coordinated to metal atom centre has been suggested in all of them.

These complexes reduce nitroarenes and aromatic aldehydes to the corresponding anilines and alcohol respectively in ethanol medium. Pretreatment of the catalyst with hydrogen for 40 to 70 minutes (activation period) depending on the nature of the substrate and the complex was essential. The yellow catalyst changes to dark green during this period. The rate of hydrogen absorption remained almost constant during the catalytic run and only the corresponding anilines were detected at any stage during reduction. In case of P_1-$PdCl_2$, a part of the catalyst dissolved producing a light green solution which was found to be catalytically active.

The pH and conductances of the solution changed during the activation period indicating the liberation of HCl.

Effects of temperature, pH, extra ligand, solvent, etc. on the reduction rate and nature and yields of the products have been studied and the results are presented in Table-2. The compounds can reduce azoxybenzene and nitrosobenzene but cannot reduce azobenzene. The deep green catalyst is stable to air and moisture in the dry solid state and can be used repeatedly for these reductions.

In case of dinitroaromatics, sequential reduction was observed while with mixture of nitroarenes, the compounds offering least steric hindrance was reduced preferentially. With p-nitro-benzaldehyde, a polymeric schiff base product, nonisolable from the catalyst was produced. Hence nitro-group was reduced at a faster rate than the aldehyde group.

The kinetic studies have been done with the polymer complexes and also with the light green solution formed using P_1-$PdCl_2$. The rate depends linearly on (a) the amount of polymer complex or on the palladium(II) content in the green solution, (b) on the hydrogen pressures and (c) not on the substrate concentrations. The initial rate did not depend on the concentrations of the initially added aniline.

Formation of phenylhydroxylamine, p-nitrophenol or nitroso-benzene could not be detected at any stage during reduction. From these observations a reduction mechanism has been proposed. A rate equation; Initial rate = $k'[CAT]_T[PH_2]$, based on the reduction mechanism and in accordance to the observed kinetics has been derived.

The dihydrogen reduction and isomerization of olefins by $PdCl(acac)PPh_3$ forms the subject matter of Chapter IV. The purity of the complex was checked by chemical analysis and spectral studies. The passage of hydrogen through the catalyst solution in benzene methanol (1:4) slowly changed the colour from light yellow to deep red within 45 minutes (activation period). Addition of substrate did not change the colour of the solution in most cases but rate of hydrogen absorption increased to maximum only after 15 to 45 minutes. The red solution remained almost unchanged upto the end. Addition of isoprene discharged the deep red colour of the solution and the hydrogenation proceeds smoothly. Evaporation of the red solution mixture at the end left a red

precipitate which can be reused with almost full efficiency. The optimum reduction conditions together with yields of various products are given in Table-3. It has generally been observed that the linear olefins are reduced more quickly than the cyclic ones. The highest and lowest rate of reduction was observed with styrene and cyclohexene respectively.

Experiments showed the red precipitate to be a mixture of $PdCl(acac)PPh_3$ and $Pd(acac)PPh_3.H$. The formation of free HCl during the passage of hydrogen through $PdCl(acac)PPh_3$ solution has been confirmed. Addition of dilute alkali reduces the activation period but leads to the decomposition of the catalyst at later stages.

Hydrogenation and isomerization of 1-alkene proceeds simulteneously and the catalyst is ineffective towards 2-alkenes. In case of isoprene, the nmr spectra of the solid isolated at the end indicates the formation of a palladium σ-alkyl compound.

The rate of reduction was found to be first order dependent on catalyst concentration and hydrogen pressure and the plot of 1/rate vs. 1/substrate concentration gives a straight line passing through the origin. Based on these facts a rate equation,

$$r = \frac{k''[A]_T[Olefin][PH_2]}{1 + K_1K_2[Olefin]} \text{ ,}$$

where $[A]_T$ = total catalyst concentration, $k'' = kk'K_2K_3$ and k = rate constant.

has been derived. On the basis of kinetic data and the experimental observations, a tentative mechanism for this process has been proposed.
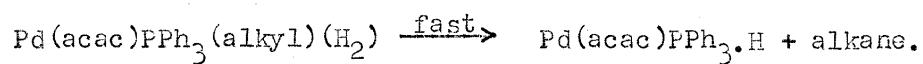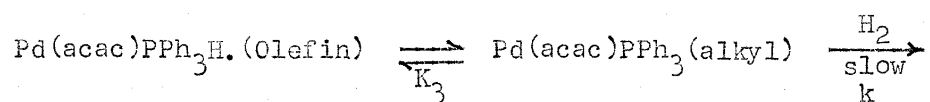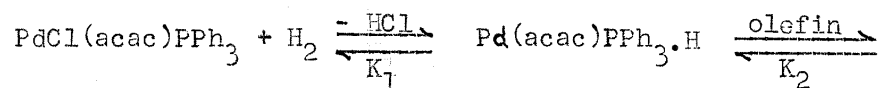
$$PdCl(acac)PPh_3 + H_2 \xrightleftharpoons[K_1]{- HCl} Pd(acac)PPh_3 \cdot H \xrightleftharpoons[K_2]{olefin}$$

$$Pd(acac)PPh_3H \cdot (Olefin) \xrightleftharpoons[K_3]{} Pd(acac)PPh_3(alkyl) \xrightarrow[slow \atop k]{H_2}$$

$$Pd(acac)PPh_3(alkyl)(H_2) \xrightarrow{fast} Pd(acac)PPh_3 \cdot H + alkane.$$

Table-1

Optimum conditions and the reduction products for various substrates

with trans-Pdpy$_2$Cl$_2$ as catalyst

Substrate	Substrate concentration (C)	Catalyst : substrate mole ratio (r)	Reaction time (in hours) (t)	Nature and yields of products (on the basis of mol (%) of the substrate fed)
1	2	3	4	5
Nitrobenzene	1M	2 x 10^{-3} : 1	8	Aniline-94 Azobenzene-4
o-Chloronitrobenzene	0.5M	10 x 10^{-3} : 1	6	o-Chloroaniline-95
o-Nitrotoluene	1M	15 x 10^{-3} : 1	6	o-Toluidine-95 o-Azotoluene- 3
#p-Chloronitrobenzene	0.25M (10^{-3}M)	4 x 10^{-3} : 1	10	p-Chloroaniline-60 4-4'-Dichloroazoxybenzene-20
#p-Bromonitrobenzene	0.25M (10^{-3}M)	5 x 10^{-3} : 1	10	p-Bromoaniline-60
p-Dinitrobenzene	0.2M	8 x 10^{-3} : 1	6	p-Phenylenediamine-60 p-Nitroaniline-35

Table-1 (Contd.)

1	2	3	4	5
p-Nitroaniline	0.25M	4×10^{-3} : 1	2.5	p-Phenylenediamine-60
p-Nitrotoluene	1M	4×10^{-3} : 1	6	p-Toluidine-95
p-Nitrobenzaldehyde	0.25M	8×10^{-3} : 1	4	Polymeric Schiff base 96
m-Dinitrobenzene	0.2M	8×10^{-3} : 1	6	m-Phenylenediamine-90
m-Nitroaniline	0.2M	6×10^{-3} : 1	4	m-Phenylenediamine-90
#1-Nitronaphthalene	0.25M (10^{-3}M)	6×10^{-3} : 1	8	1-Aminonaphthalene-98

Reductions were carried out at 30°C in dry ethanol medium under normal pressure of hydrogen.

Basic ethanol medium was used, figures in parenthesis indicate the concentration of NaOH in the reaction medium.

Table-2

Reduction of different nitro compounds with products using P_1-PdCl$_2$ as catalyst

Substrate	Concentration of the substrate	Wight of the catalyst	% of products at different temperatures (mole % as per substrate fed)		
			30°C	40°C	50°C
Nitrobenzene	1M	30 mg	Aniline-96	Aniline-98	Aniline-95
o-Chloronitrobenzene	0.25M	do	Very very slow rate	o-Chloroaniline-95	o-Chloroaniline-90
o-Nitrotoluene	0.5M	do	do	o-Toluidine-96	o-Toluidine-94
p-Chloronitrobenzene	0.25M	do	p-Chloroaniline-90		
p-Nitrotoluene	0.25M	do	p-Toluidine-90		
m-Dinitrobenzene	0.25M	do	m-Phenylene-diamine-95 m-Nitroaniline-4		
p-Dinitrobenzene	0.25M	do	p-Phenylenediamine-95 p-Nitroaniline- 3-4		
1-Nitronaphthalene	0.25M	do	1-Aminonapthalene-98		
Benzaldehyde	1M	do	Benzylalcohol-98		

Table-3

Reduction of various olefins with products using Pd(acac)(PPh$_3$)Cl as catalyst

Substrate	Substrate concentration	Catalyst concentration	% of products (on the basis of mol (%.) of the substrate fed)
1-Hexene	1M	10^{-3}M	Hexane-55 + 2-Hexene-45
1-Pentene	1M	do	Pentane-60 + 2-Pentene-40
1-Heptene	1M	do	Heptane-52 + 2-Heptene-48
Styrene	1.5M	do	Ethylbenzene-100
Cyclohexene	0.5M	do (10^{-3}M NaOH)	Cyclohexane-100
Acrylonitrile	1M	10^{-3}M	Ethylnitrile-100
Isoprene	1M	do	2-Methyl-1-butene-100
Cinnamic acid	0.5M	do	3-Phenylpropionic acid-90
Fumaric acid	0.5M	do	Succinic acid-90