Hydrogenations and hydro-acylations using homogeneous platinum metal catalysts

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Chapter 1. Introduction

1.1 Precious- and platinum metals

Precious metals like silver and gold are valuable metals that are relatively scarce and chemically rather inert. Gold and silver are not the only precious metals and another important group is formed by the platinum group metals, six elements clustered together in the periodic table consisting of platinum, ruthenium, rhodium, palladium, osmium and iridium. Precious metals are mainly mined in Russia and South Africa, together these two countries contribute to more than half of the world’s precious metals production. Nowadays precious and platinum metals are still used for jewellery and as an alternative investment for global currencies and fixed assets in the financial sector (especially Au). Platinum metals in the industrial sector are mainly used as catalysts. Examples are found in the chemical industry and in the automotive industry, where the metals are the major components in catalysts for exhaust gas cleaning. Other application areas are the glass industry (moulds) and the electronic and electrical industry. As suggested by the name precious and platinum metals are expensive metals. This is illustrated in Table 1.1, where the trade prices (as per 15-05-2009) are given.

Table 1.1 Trade prices of precious metals.5

<table>
<thead>
<tr>
<th></th>
<th>Pt</th>
<th>Au</th>
<th>Ag</th>
<th>Rh</th>
<th>Ru</th>
<th>Pd</th>
<th>Os</th>
<th>Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price ($/oz)</td>
<td>1123.00</td>
<td>926.30</td>
<td>14.02</td>
<td>1250.00</td>
<td>85.00</td>
<td>227.00</td>
<td>380.00</td>
<td>425.00</td>
</tr>
</tbody>
</table>

1.1.1 Platinum metals in catalysis

Precious metals were, despite their supposed inertness, already used in the early days of catalysis. In the beginning of the 19th century a series of discoveries were made involving the use of precious metals. Examples are the catalytic oxidation of coal gas and air by a Pt wire (Sir H. Davy, 1817), the Pt-catalysed oxidation of ethanol to produce acetic acid and water (J. W. Döbereiner, 1822) and the ignition of hydrogen and air by a platinum sponge (J. W. Döbereiner, 1823). In general platinum metals in catalysis are versatile and broadly applicable, active at
milder conditions compared to other metals and show higher selectivities. Nowadays, platinum metals are used to catalyse a broad range of reactions. Examples are hydrogenations, oxidations, dehydrogenations, hydrogenolysis, hydrosilylations, carbon-carbon and carbon-heteroatom coupling, carbonylations and hydroxylations.2

1.1.2 Platinum metals in industrial heterogeneous catalysis

The most important processes in industry involving heterogeneous platinum group metal catalysts in one of the processing steps are given chronologically in Table 1.2.

Table 1.2 The use of platinum group metals in heterogeneous catalysis throughout time.8-11

<table>
<thead>
<tr>
<th>year</th>
<th>process</th>
<th>Catalyst (main component)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1870</td>
<td>SO₂ oxidation</td>
<td>Pt</td>
</tr>
<tr>
<td>1910</td>
<td>NH₃ oxidation to nitric acid</td>
<td>Pt/Rh nets</td>
</tr>
<tr>
<td>1940</td>
<td>Catalytic reforming of hydrocarbons (gasoline)</td>
<td>Pt/Al₂O₃</td>
</tr>
<tr>
<td>1940</td>
<td>Benzene hydrogenation to cyclohexene</td>
<td>Pt</td>
</tr>
<tr>
<td>1960</td>
<td>Xylene hydro-isomerisation</td>
<td>Pt</td>
</tr>
<tr>
<td>1960</td>
<td>Improved hydrocarbons reforming</td>
<td>Pt-Ir on Al₂O₃, Pt-Re on Al₂O₃</td>
</tr>
<tr>
<td>1960</td>
<td>Ethylene oxidation to vinyl acetate</td>
<td>Pd/Cu</td>
</tr>
<tr>
<td>1970</td>
<td>Auto exhaust gas catalysts</td>
<td>Pt, Rh, Pd on oxide</td>
</tr>
<tr>
<td>1970</td>
<td>Hydro-isomerisation</td>
<td>Pt/zeolite</td>
</tr>
<tr>
<td>1980</td>
<td>Vinyl acetate from ethene and acetic acid</td>
<td>Pd</td>
</tr>
<tr>
<td>1980</td>
<td>Hydrotreatment of hydrocarbons</td>
<td>Pt/zeolite</td>
</tr>
<tr>
<td>1980</td>
<td>Vitamin K₄ production (hydro-acetylation)</td>
<td>Pd membrane</td>
</tr>
<tr>
<td>1990</td>
<td>Complete combustion of natural gas</td>
<td>Precious metals and/or mixed oxides</td>
</tr>
</tbody>
</table>

The first real use of a heterogeneous platinum metal in an industrial process was the application of platinum for the oxidation of SO₂ to SO₃ in the production of sulphuric acid. In Germany at the start of the 20th century the need for nitrogen compounds for agriculture and later for weapon production stimulated the development of ammonia production processes and the oxidation of ammonia to produce nitric acid. For the latter purpose, the platinum metals platinum and rhodium were used extensively. Just before and during the second world war in Germany almost all hydrocarbons were produced from coal. Coal was treated in coke ovens to produce
ethylene form acetylene and aromatics, coal was hydrogenated into liquids used in chemical industry and gasified into synthesis gas. Platinum was used in reforming and hydrogenation reactions. In the sixties hydrocarbon reforming processes were greatly improved by using bimetallic catalyst of platinum with iridium or rhenium. Also the use of the platinum metal palladium in the oxidation of ethylene to vinyl acetate was introduced in industrial catalysis at this time. The use of platinum metals for car exhaust catalysts in the seventies gave a large boost to the use of platinum, rhodium and palladium for catalytic purposes. At that time, also improved hydro-isomerisation platinum based catalysts were introduced. In the eighties palladium catalysts were shown potential for the production of vinyl acetate from ethene and acetic acid and the production of vitamin K₄ (hydro-acetylation of 2-methyl 1,4-naphthoquinone). In the nineties precious and platinum metals were introduced as catalysts for the complete combustion of natural gas.⁸⁻¹¹

1.1.3 Platinum metals in industrial homogenous catalysis

Homogeneous platinum metal catalysts for industrial scale processes were introduced much later than heterogeneous platinum metal catalysts. Already in 1870, the first heterogeneous platinum metal catalysts were applied industrially. The first industrial process with a homogeneous platinum metal catalyst was introduced more than 80 years later. It involves the Wacker oxidation of ethylene to acetaldehyde using a palladium catalyst.⁸,¹² In the seventies a real boost in the application of homogenous catalysts was observed, resulting in three new industrial processes namely the palladium catalysed ethylene oxidation to acetaldehyde, the rhodium catalysed methanol carbonylation to acetic acid and a rhodium catalysed asymmetric hydrogenation to L-DOPA.⁸,⁹ The most important processes in the bulk chemical industry involving homogeneous platinum metal catalysts are given chronologically in Table 1.3.
Table 1.3 Platinum metals for homogeneous catalysis in bulk chemical processes.\textsuperscript{8,9}

<table>
<thead>
<tr>
<th>year</th>
<th>process</th>
<th>Catalyst (main component)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1950</td>
<td>Ethylene oxidation to acetaldehyde</td>
<td>Pd</td>
</tr>
<tr>
<td>1970</td>
<td>Acetic acid from MeOH (carbonylation)</td>
<td>Rh</td>
</tr>
<tr>
<td>1970</td>
<td>Improved hydroformylation</td>
<td>Rh</td>
</tr>
<tr>
<td>1970</td>
<td>L-DOPA process (fine chemicals)</td>
<td>Rh</td>
</tr>
<tr>
<td>1980</td>
<td>Methyl acetate (carbonylation)</td>
<td>Rh</td>
</tr>
<tr>
<td>1990</td>
<td>Polyketone (CO and ethene)</td>
<td>Pd</td>
</tr>
</tbody>
</table>

### 1.2 Homogeneous hydrogenation reactions with platinum metals

The first hydrogenation reaction involving a homogeneous catalyst is likely the reduction of quinone to hydroquinone by a homogeneous copper system (cuprous acetate-quinoline) in 1938 by Calvin.\textsuperscript{13} The real breakthrough in hydrogenation reactions catalysed by homogeneous catalysts was the discovery of the Wilkinson catalyst (RhCl(PPh\textsubscript{3})\textsubscript{3}) in the 1960’s for the reduction of olefins with hydrogen.\textsuperscript{12,14}

#### 1.2.1 Homogenous asymmetric hydrogenation reactions

Asymmetric catalysis is a powerful methodology for the synthesis of chiral components. An important transformation is the asymmetric hydrogenation of prochiral substrates using chiral homogeneous metal catalysts. Asymmetric hydrogenations are mostly performed with the platinum metals Rh, Ir and Ru.\textsuperscript{15} After the discovery of the Wilkinson catalyst for the hydrogenation of olefins, chemist also started working on catalysts for asymmetric hydrogenations, with an emphasis on chiral Rh/phosphine catalysts.\textsuperscript{14,16,17} A well known chiral phosphine ligand is CAMP 1, developed by Knowles in the 1970’s.\textsuperscript{18} This ligand was applied in the synthesis of L-DOPA 2, an anti Parkinson drug. The synthesis involves the hydrogenation of a prochiral cinnamic acid derivative (3) and yielded the hydrogenated product with an ee of 88\% (Scheme 1.1). This process is the first example of the use of asymmetric hydrogenation on an industrial scale.\textsuperscript{16,17}
Scheme 1.1 L-DOPA process with the rhodium CAMP catalyst.

Further improvements involved the use of the DIOP ligand 4 by Kagan (1971) and DIPAMP 5 (1974), leading to product ee’s of up to 95%.16,17,19,20
A major breakthrough in the field came by the introduction of the chiral BINAP ligand 6 in 1980 by Noyori\textsuperscript{17} Rh-BINAP catalysts also showed to be excellent catalysts for the asymmetric isomerisation of allylic amines. This invention was successfully applied in one of the steps of the \((-\text{-})\)-menthol process.\textsuperscript{17} Other versatile diphosphine ligands introduced at that time are the CHIRAPHOS (7) and SkewPhos (8) ligands, developed by Bosnisch (1980).\textsuperscript{18,21,22} Subsequent studies showed that Ru-BINAP catalysts are also very versatile for, among others, the asymmetric hydrogenation of various functionalized olefins (activated ketones, $\alpha,\beta$-unsaturated acids, allylic alcohols an enamides).\textsuperscript{17,19,20,23} A recent example of an industrial process involving a Ru-BINAP catalyst is the production of intermediate 10 from a $\alpha$-substituted-$\beta$-ketoester 9 (Scheme 1.2). This conversion is a key step on the synthesis of a carbapenem. This carbapenem is currently produced using this synthetic methodology at a scale of 100 tons per annum (Takasago process).\textsuperscript{15,24}

\begin{center}
\textbf{Scheme 1.2 Asymmetric hydrogenation by a ruthenium BINAP catalyst in a carbapenem process.}
\end{center}

In the early 90’s, Burk at Dupont developed the chiral phospholane ligands Duphos (11) and BPE (12). The ligands were especially used for Rh-catalyzed hydrogenations, examples are the synthesis of $\alpha$- or $\beta$-amino acids and the hydrogenation of arylenamides, itaconic acid derivatives, enol acetates.\textsuperscript{24} An example of the use of Rh-Duphos catalysts in industrial asymmetric
hydrogenation is given in Scheme 1.3. It involves the hydrogenation of dimethyl itaconate (14) to produce (s)-dimethyl methylsuccinate (15), which is a building block for the synthesis of several kinds of drugs (Dowpharma process).\textsuperscript{19,24,25}

Scheme 1.3 Very active and selective asymmetric hydrogenation of dimethyl itaconate, with a rhodium Duphos catalyst.

In 1993 Togni reported the synthesis of various Josiphos ligands (13), which were shown to be very efficient for asymmetric hydrogenations (C=N and C=C bonds, itaconic acid derivatives and enamides).\textsuperscript{12,23,26-28} The Josiphos ligands are particularly useful for library synthesis as the two chelating donors can be easily modified to provide ligands with a broad range in steric and electronic properties. An example of an industrial asymmetric hydrogenation reaction involving an iridium- Josiphos system (Xyliphos, 16) is the asymmetric hydrogenation of MEA imine (17) to an intermediate (18) in the (s)-metolachlor (19) process (GibaGeigy/Syngenta process). At a reaction temperature of 50 °C and a H\textsubscript{2} pressure of 80 bar, a TOF of 400,000 1/h and a product ee of 80% was obtained (Scheme 1.4).\textsuperscript{24,26}
Scheme 1.4 Very active hydrogenation of MEA imine with an iridium Xyliphos catalyst.

Examples of more recently developed chiral diphosphine ligands are BICP (20) developed by Zhang in 1997, MiniPHOS (21) reported by Imamoto in 1999 and SDP (22) developed by Zhou in 2003.\textsuperscript{18,29-31}

Research activities aiming at the discovery and use of monodentate phosphine ligands in asymmetric catalysis were very limited after the discovery of chiral diphosphine ligands.\textsuperscript{32} This was mainly due to the general belief that high stereo-discrimination in asymmetric catalysis was only possible by using diphosphine ligands. Almost 30 years after the discovery of CAMP,
pioneering studies by the groups of Feringa, de Vries and Minnaard (monodentate phosphoramidite 23), Pringle (monodentate phosphonites 24), Reetz (monodentate phosphites 25) and Zhou (monodentate spiro phosphoramidites 26) showed that comparable or even better performance for the rhodium catalysed asymmetric hydrogenation of e.g. α-dehydroamino acids and itaconic acid derivatives could be obtained with these types of ligands.

In general the synthesis of monodentate ligands is less complex compared to the synthesis of bidentate ligands and tuning the monodentate ligands is also relatively easy. An example of an industrial application of monodentate phosphorus ligands is the recently implemented asymmetric hydrogenation of the substituted acyclic acid 27 to 28 (Scheme 1.5), by using the phosphoramidate ligand 29 (mixed rhodium-29-PPh₃ catalyst), on a production scale by DSM.

Scheme 1.5 Asymmetric hydrogenation of the substituted acyclic acid 27, by a rhodium-29-PPh₃ catalyst, in the DSM process.
1.3 Homogeneous carbonylation reactions with platinum metals

Carbonylation reactions involve reactions of carbon monoxide with substrates, whereas hydrocarbonylation reactions are typically carried out with a mixture of CO and hydrogen instead of CO only. The first homogenous catalyst for carbonylation/hydrocarbonylation reactions was a cobalt catalyst (Roelen 1938), used for the production of aldehydes (commercialized in 1948). The first homogeneous platinum metal for a carbonylation reaction on industrial scale was a rhodium (iodide promoted) complex. It was applied for the synthesis of acetic acid from methanol (Scheme 1.6). This process has been commercialised by Monsanto (1968). Recently, the use of iridium for this reaction was successfully demonstrated on commercial scale by BP. Some other examples of carbonylation reaction are methoxycarbonylation, olefin-CO copolymerisation and hydrocarbonylation reactions, the latter will be discussed in more detail in following sections.

\[
\text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{Rh, I}_2} \text{CH}_3\text{COOH}
\]

Scheme 1.6 Monsanto acetic acid process.

1.3.1 Hydroformylation/hydrocarbonylation reactions

Catalytic hydroformylation and hydrocarbonylation reactions, also known as the oxo-synthesis, were by accident discovered by Roelen in the late thirties of the previous century. It was demonstrated that the reaction of ethene with CO and H\textsubscript{2} catalysed by cobalt resulted in the
production of mainly 1-propanal, some alcohols and minor amounts of ketones. Scheme 1.7 illustrates the hydroformylation of a 1-alkene (32). Two aldehydes may be formed, a linear (33) and a branched (34) product. For most applications, the linear aldehyde is the preferred product and the formation of branched products should be suppressed as much as possible. Initially the catalyst was a heterogeneous supported cobalt catalyst, later it became clear that the active species is actually a soluble homogeneous HCo(CO)₄ species.

The first cobalt-catalysed hydroformylations were performed at high syngas pressures (200-300 bar) to maintain catalyst stability. In the sixties, tertiary alkyl-phosphine ligands were introduced. These were shown to have a positive effect on catalyst stability and allowed the development of a lower pressure, higher temperature process (Shell process). The reaction is slower than the original process but it is more selective to the desired linear product. In the seventies the platinum metal rhodium was introduced as a hydroformylation catalyst. It showed to be more active and selective (towards linear product) than the cobalt-based catalyst under milder conditions. Since these discoveries, Rh-based catalysts have been further improved and tuned to give better selectivities and activities.

\[
\text{Cat} \rightarrow \begin{array}{c}
\text{R} \text{H} \text{2} \text{CO} \\
\text{32} \\
\text{R} \text{H} \text{2} \text{CO} \\
\text{33} \\
\text{R} \text{H} \text{2} \text{CO} \\
\text{34}
\end{array}
\]

Scheme 1.7 General representation of the hydroformylation of a 1-alkene

A major disadvantage of the use of rhodium catalysts is isomerisation of the α-olefin to internal olefins. Therefore the hydroformylation of higher alkenes is nowadays mainly still performed with cobalt catalysts.

1.3.2 Chemoselectivity in the oxo-synthesis

As already demonstrated in the 30’s by Roelen, the hydrocarbonylation of 1- alkenes allows the synthesis of aldehydes, alcohols and ketones. However, Roelen never succeeded in achieving reasonable chemoselectivity. Drent and Budzelaar were the first to show the selective formation
of ketones by hydrocarbonylation of higher olefins with a homogeneous palladium diphosphine catalyst (Scheme 1.8).  

\[
2 \text{R} + \text{H}_2 + \text{CO} \xrightarrow{\text{L}_2\text{PdX}_2} \text{monoketone}
\]

Scheme 1.8 Hydrocarbonylation of higher olefins to ketones with a homogeneous palladium diphosphine catalyst.

This catalyst was originally developed by Drent for the production of alternating copolymers from olefins and CO (Scheme 1.9).  

\[
\text{n CO} + \text{n CH}_2\text{=CH}_2 \xrightarrow{} \text{H}_3\text{C} \begin{array}{c}
\text{O} \\
\text{CH}_3 \\
\text{n}
\end{array}
\]

Scheme 1.9 Alternating copolymerisation of ethene and CO.

1.3.2.1 Palladium catalysed hydro-acylation and hydroformylation

In 2000 Drent and Budzelaar showed that it was possible to produce monoketones 37, aldehydes/alcohols 38 and oligoketones 39 from higher alkenes using homogeneous Pd catalysts of the type \(\text{L}_2\text{PdX}_2\) (\(\text{L}_2\) represents a diphosphine ligand and \(\text{X}\) stands for a weakly or non-coordinating counter ion (Scheme 1.10). The chemo-selectivity may be steered to the desired product by the choice of the diphosphine ligand, process conditions and solvent.  

Ligands with a relatively low basicity in combination with a strong acid favoured the selectivity towards oligoketones. An increase in ligand basicity shifts the selectivity towards monoketones. Suitable ligands for this purpose are alkyl substituted diphosphines, like 1,3-bis(di-sec-butylphosphino)propane (35). More basic ligand in combination with a relative weak acid favour aldehyde and alcohol formation.
Recently Drent et al. also demonstrated the hydroformylation of internal alkenes by a homogeneous palladium catalyst ((BCOPE)Pd(OTf)$_2$ 40). Here the catalyst was capable of isomerising the double bond to the terminal position resulting in the production of high quantities of linear alcohols.\textsuperscript{54}
1.3.3 Asymmetric homogeneous hydroformylation

In the early days, the asymmetric hydroformylation of alkenes to chiral products (Scheme 1.11) was mainly performed with cobalt, rhodium and platinum catalysts. Initially the branched aldehydes were only obtained with low ee’s.

![Scheme 1.11 Asymmetric hydroformylation of alkenes.](image)

The application of modified Pt/Sn catalyst with diphosphate ligands (e.g. (R,R)-DIOP 4), as developed by Consiglio et al for the asymmetric hydroformylation of styrene (and derivatives), led to branched aldehydes with considerably higher ee’s. Nowadays rhodium is mostly used for the asymmetric hydroformylation of alkenes. This was promoted by the development of (R,S)-BINAPHOS (41) by Takaya (1993) and biphosphite ligands (R,R)-Chiraphite (42) developed by Babin and Whiteker (1992). With BINAPHOS, > 95% ee was obtained for the asymmetric hydroformylation of substituted styrene, whereas ee values up to 90% were obtained for the hydroformylation of styrene using Chiraphite.

![images of ligands 41, 42, and 43.](image)

More recently Zhang et al developed (R,S)-Yanphos (43) a hybrid phosphine-phosphoramidite ligand. It showed high reactivity and enantioselectivity for the rhodium catalyzed hydroformylation of styrene derivatives and vinyl acetate. Scheme 1.12 illustrates the rhodium catalyzed asymmetric hydroformylation of styrene 44 using ligands 41 and 43.
Scheme 1.12 Rhodium catalyzed asymmetric hydroformylation of styrene with BINAPhOS and Yanphos.

Other recently developed and effective ligands for the asymmetric hydroformylation are (S,S)-Kelliphite (46) and (S,S)-ESPHOS (47, for vinylacetate and allyl cyanide)\(^{63-65}\), the bisphosphite ligand 48 (for styrene)\(^{66}\), (S,S,S)-bisdiazaphos 49 (allyl cyanide, styrene, vinyl acetate)\(^{65,67}\) and (R,R)-Binaphine 50 and (R,R)-Ph-BPE 51 (for styrene).\(^{68,69}\)
1.3.4 Asymmetric homogeneous hydro-acylation reactions

Asymmetric hydro-acylations of 1-alkenes and syngas may provide an interesting route for chiral $\alpha$-methyl substituted ketones (Scheme 1.13).

\[
\begin{align*}
2 \text{ R} & \text{CH} = \text{CH}_2 + \text{H}_2 + \text{CO} \xrightarrow{\text{L}_2\text{Pd}^\#X_2} \alpha\text{-methylketone} \\
\text{1-alkene} & \\
\end{align*}
\]

Scheme 1.13 Asymmetric hydro-acylations of 1-alkenes.

Such chiral ketones may be interesting building blocks for further chemistry to obtain novel products. To the best of our knowledge the asymmetric synthesis of $\alpha$-methyl substituted ketones has only been accomplished by reducing $\alpha$-methyleneketones by means of baker’s yeast (Emulzint®) (Scheme 1.14).\(^{70-72}\) Good results were obtained in for example the reduction of $\alpha$-methyleneketone with $R_1 = \text{Me}$ and $R_2 = n$-hexyl in water at 30 ºC. Here a conversion of 70% was obtained after 2 h with a product ee of $> 99\%$.\(^{72}\)

\[
\begin{align*}
\text{R}_1\text{C} & \text{O} \xrightarrow{\text{Baker’s yeast}} \text{R}_1\text{C} \text{O} \\
\text{R}_1 & = \text{Me} \\
\text{R}_2 & = n\text{-hexyl} \\
\end{align*}
\]

Scheme 1.14 Reduction of methyleneketones by baker’s yeast.

To the best of our knowledge, the asymmetric hydro-acylation of olefins with synthesis gas by using homogeneous platinum metal catalysts has not been performed to date.
1.4 Aims and outline of this thesis

This thesis deals with the use of platinum metal group catalysts in homogeneous catalysis. The emphasis is on the use of homogeneous palladium complexes for the asymmetric synthesis of chiral ketones from syngas and olefins. This is an unexplored research area with the potential to synthesise (chiral) ketones for the bulk and fine-chemical industry. The objective was the identification of suitable catalysts and process conditions to achieve a high chemo-, regio- and enantioselectivity for the reaction. In addition, the use of chiral Rh complexes for the asymmetric synthesis of a propionic acid derivative and the use of Ru complexes for the synthesis of $\gamma$-valerolactone from simple carbohydrates like D-glucose and D-fructose was explored.

Chapter 1 gives an overview of the use of platinum group metals in catalysis with an emphasis on homogeneous catalysis.

In Chapter 2 the results for the achiral hydro-acylation of 1-alkenes with syngas to mono-ketones using a homogeneous palladium catalyst of the type $L_2\text{PdX}_2$ are reported. In this study $L$ was an alkyl-substituted diphospine ($1,3$-bis(di-sec-butylphosphino)propane) and $X$ a non-coordinating anion (obtained from trifluoromethanesulfonic acid). The aim was to study the effect of process conditions on the chemo- and regioselectivity and to determine the optimum reaction conditions for the synthesis of monoketones. This contribution serves as a preliminary investigation for the development of an asymmetric version of the hydro-acylation reaction.

Chapter 3 describes an exploratory screening study on the asymmetric hydro-acylation reaction to chiral ketones using Pd-complexes of the type $L_2\text{PdX}_2$. The major objective was the identification of suitable chiral diphosphine ligands for the transformation. A broad variety of chiral diphosphine ligands was tested (Josiphos, Duphos, FerroTANE and Walphos ligands) and the best was selected for further studies.

Chapter 4 describes experimental studies on the asymmetric hydro-acylation reaction using a homogeneous Pd catalyst with a chiral Josiphos ligand. The effect of process conditions like reaction temperature, partial hydrogen and carbon monoxide pressure on the product ee and yield
was investigated in detail. The results were quantified using statistical modelling techniques, allowing selection of the optimum reaction conditions.

**Chapter 5** deals with the enantioselective hydrogenation of methyl 2-acetamido acrylate to (R)-2-Acetylamino-propionic acid methyl ester with hydrogen using a Rhodium/MonoPhos™-complex in iso-propanol. The primary aim was the development of a kinetic model applicable for a broad range of reaction conditions. The information may be used for batch up scaling purposes and also to gain insights on mechanism of the catalytic reaction.

**Chapter 6** describes experimental studies on the one pot synthesis of γ-valerolactone from simple carbohydrates (D-glucose, D-fructose, cellulose). γ-Valerolactone is considered an interesting bio-based chemical with high application potential in the biofuel and chemical industry. The initial objective was the identification of efficient homogeneous catalyst for the hydrogenation reaction using either hydrogen or formic acid. However, the homogeneous Ru-catalyst that was tested was not very efficient and the focus shifted to heterogeneous Ru catalysts. The study was exploratory in nature and aimed to identify the most suitable catalysts for this conversion and optimisation of process conditions.
1.5 References


5. http://www.taxfreegold.co.uk/preciousmetalpricesusdollars.html


