Transition metal catalysts for the conversion of biomass inspired substrates
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Citation for published version (APA):

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Chapter 2
Hydrogenolysis of Esters

\[
\begin{align*}
\text{ESTER HYDROGENOLYSIS} & \quad \xrightarrow{R_1-O-\overset{\text{cat}}{\text{H}_2}} \quad R_1-OH + R_2\text{-OH} \\
\text{Ru} & \quad \text{solvents} \\
\text{Additives} & \\
\text{CPC} & \quad \text{Conditions}
\end{align*}
\]
Abstract

The performance of a previously reported Ru(acac)$_3$/triphos system for the hydrogenolysis of esters such as dimethyl oxalate, dimethylphthalate and benzyl benzoate was re-evaluated, prompted by the fact that the reported results could not be reproduced. It was found that the Ru(acac)$_3$/triphos system without additives performed well in 1,1,1,3,3,3-hexafluoro-2-propanol (FIPA), but less well in other alcohols. To improve on the environmentally harmful FIPA, we found that a dioxane system, applying low pressures and high temperatures (40 bar H$_2$ and 210 °C), was also capable of converting some esters, showing the feasibility of using halogen-free solvents. Furthermore, the application of another, tridentate diphosphino-NHC (PC$_{NHC}$P) ligand in several hydrogenolysis reactions was tested. It was found that, although in PC$_{NHC}$P a stronger donating NHC moiety replaces one of the phosphine moieties in triphos, the Ru-PC$_{NHC}$P system was less active than the Ru-triphos system. Investigation into the formation of a Ru-PC$_{NHC}$P complex did not lead to well-defined species. Instead, a polymeric species was obtained which could be transformed into an active species under elevated hydrogen pressures. A second, dicarbene-phosphine ligand, (CNHC$_2$PC$_{NHC}$) was also synthesized to test the influence of a second NHC moiety, but preliminary in-situ results showed no activity at all.

2.1 Introduction

Hydrogenolysis of esters involves the reduction of the ester to the corresponding alcohols by molecular hydrogen. It is an industrially important reaction that is not easily achieved catalytically with molecular hydrogen because of its approximate thermo-neutrality, as indicated in Chapter 1. Our research group has previously contributed to important discoveries in this area, in particular through studies by Teunissen and Elsevier which involved the development of a working system consisting of Ru(acac)$_3$ and a triphosphine system in various solvents, among which several alcohols including the polar alcohol 1,1,1,3,3,3-hexafluoro-2-propanol (FIPA).

Apart from activated esters such as dimethyl oxalate (DMO), more challenging substrates such as benzyl benzoate could also be successfully converted into the respective alcohols within (industrially) reasonable space-time yields (Scheme 1). Later studies by van Engelen indicated that the Ru(acac)$_3$/triphos system could also successfully be applied in systems with i-propanol as the protic solvent (instead of FIPA), omitting additives (such as Zn or NEt$_3$).

We intended to continue research in this field by investigating other ligands, in particular systems based on ligand structures elaborated below. The starting point consisted of the reports by van Engelen mentioned above. Unfortunately, after many trials involving numer-
ous variations of qualities, suppliers and reaction variables such as solvent, temperature and so on, we could not reproduce the reported results. Close inspection of the material in the thesis by van Engelen indicated that several errors may have been introduced when comparing to the papers by Theunissen.\cite{1,2} Consequently, the course of the investigation diverged into a different direction: we decided to re-evaluate the activity of the Ru-triphos system. Also, we decided to initiate an investigation into the solvent system in order to find a more benign ('greener') solvent system, in which esters could still be converted into alcohols.

One of the aims of this study is to increase the rate of the hydrogenolysis reactions. In order to achieve this goal, strong donor ligands are required to aid the formation of metal-hydride species and to increase electron density at the metal center. Traditionally, phosphines have been used as donating ligands, but over the last decade, N-heterocyclic carbenes (NHCs) have become prominent donor ligands complementary to or as suitable replacements for phosphine ligands.\cite{5} Incorporating an NHC into ligand-systems containing other, more classical, donating functionalities such as phosphines creates options for design of new ligands that are candidates for enhancing catalytic activity in combination with appropriate (transition) metals.

The effectiveness of combining an NHC moiety with a phosphine in one ligand system has already been demonstrated for C-C coupling reactions,\cite{6,7} for instance by the group of Lee, who developed a tridentate diphosphino-NHC ligand (PC\textsuperscript{NHC}P, Figure 1). In this ligand, an imidazole is linked with two phosphines via an ethylene linker forming a (rather flexible) pincer framework.\cite{8} Alternatively, one may invert this system and hence we developed a novel dicarbene-phosphine ligand (C\textsuperscript{NHC}PC\textsuperscript{NHC}, Figure 1). This C\textsuperscript{NHC}PC\textsuperscript{NHC} ligand was developed in collaboration with the group of Hahn,\cite{9} where a phosphine moiety is linked to two imidazolium units via an ethylene linker. After deprotonation at C2 of both imidazolium

\textbf{Scheme 1.} Conversion of dimethyl oxalate and benzyl benzoate using the Ru-triphos system by Teunissen and van Engelen.\cite{1-4}
Chapter 2

fragments, a dicarbene-phosphine ligand would emerge. This second NHC should add even more electron donating power compared to the PC\textsuperscript{NHC}P ligand and may also induce interesting reactivity.

\[ \text{triphos} \quad \text{PC}^{\text{NHC}} \quad \text{C}^{\text{NHC}} \text{PC}^{\text{NHC}} \]

**Figure 1.** The tridentate ligands used in this investigation: triphos and imidazolium salts PC\textsuperscript{NHC}P and C\textsuperscript{NHC}PC\textsuperscript{NHC} which, upon deprotonation, coordinate via both the phosphines and the carbenes.

The ester substrates that have been evaluated in this research are depicted in Scheme 2. We chose to use these substrates specifically in order to compare initial results with the results previously obtained for the Ru(acac)\textsubscript{3} / triphos system. Additionally, we envisaged the use of esters that originate from or are relevant to biomass conversion. Highly functionalized, linear and aromatic esters as well as lactones all occur in processed biomass. Hydrogenolysis of such substrates is an important step in the further breakdown and functionalization of so-called platform molecules.\textsuperscript{[10-13]}

**Scheme 2.** Overview of substrates used for ester hydrogenolysis and the corresponding products.

\[ \text{DMO} \xrightarrow{\text{[cat]} \ H_2} \text{MG} \xrightarrow{\text{[cat]} \ H_2} \text{EG} \]
\[ \text{DMPhth} \xrightarrow{\text{[cat]} \ H_2} \text{Phth} \xrightarrow{\text{[cat]} \ H_2} \text{BDM} \]
\[ \text{BB} \xrightarrow{\text{[cat]} \ H_2} \text{BA} \]
\[ \text{MP} \xrightarrow{\text{[cat]} \ H_2} \text{rPrOH} \]
Dimethyl oxalate (DMO) has two conjugated ester functions. One of the ester functions activates the other one towards hydrogenolysis, making the first hydrogenolysis step, where methyl glycolate (MG) is formed, easier than the second step that is needed to form ethylene glycol (EG). Therefore, this reaction is a good indicator of the potential of a catalyst. However, the substrate is very prone to transesterification reactions (see below) and therefore alcoholic solvents (in this case other than MeOH) can give rise to several side products. Both products of DMO (and derivatives thereof) are of interest in terms of industrial applications: the first hydrogenated glycolate products are used as solvents for coatings and the second hydrogenated product ethylene glycol is used as frost-protection agent in cars and in the production of polyesters.\cite{14} Dimethyl phthalate (DMPhth) is less susceptible to transesterification and therefore most of the complications and exceptions that one finds for DMO are not encountered for DMPhth. This substrate is, however, more difficult to convert into alcohols, because the ester moieties are less reactive. After the first ester moiety has been hydrogenolyzed, the molecule undergoes an intramolecular transesterification to form the lactone phthalide (Phth), which needs a second hydrogenolysis step to form 1,2-bishydroxymethyl benzene (BDM). Finally, benzyl benzoate (BB) is the hardest to convert to its product, benzyl alcohol (BA), since the ester function is very unreactive. Methyl propionate (MP) is an unactivated linear ester that can be hydrogenolyzed into \(n\)-propanol (\(n\)PrOH) and methanol (MeOH).

Transesterification is a process where the ester of one alcohol is converted into the ester of another alcohol.\cite{15} Primary alcohols are prone to transesterification, and more bulky alcohols such as secondary and tertiary alcohols are less reactive. Conducting the reaction in an alcoholic solvent will therefore always encompass the possibility of transesterification side products. Especially DMO is very susceptible to transesterification, see Scheme 3.

\[
\begin{align*}
\text{OO} & \quad \text{OH} \\
\text{O} & \quad \text{OH} \\
\text{H}_2 & \quad \text{H}_2 \\
\text{+ MeOH} & \quad \text{+ MeOH} \\
\text{transesterification with } \text{i-propanol} & \quad 
\end{align*}
\]

Scheme 3. Possible transesterification products of DMO

Frediani,\cite{16} Leitner,\cite{17} Crabtree,\cite{18,19} and Cole-Hamilton\cite{13} all reported successful systems for the hydrogenation of methyl esters, lactones (the C=O function), and free carboxylic ac-
ids. The system by Frediani requires zinc as additive in MeOH for the conversion of dimethylfumarate (through several intermediates) to butanediol. Leitner found that the Ru(acac)$_3$/triphos system is able to both hydrogenate and dehydrate, and manages to convert itaconic acid to 3-methyl-tetrahydrofuran (3-MTHF) and levulinic acid to 2-MTHF in dioxane, at 100 bar H$_2$ and 195 °C. For the last dehydration step to create the MTHF addition of acid is needed. Crabtree, in cooperation with Davy Process Technology, found a route in which methyl propionate and dimethyl maleate could be converted for >99% when performing the reactions at high temperatures (220°C) and 50 bar H$_2$ and adding 10 % v/v water to the reaction mixture (or working in water as solvent). It was believed that the added water allows, primarily, for a water-gas-shift reaction to take place, regenerating poisoned catalyst rendered inactive by decarbonylation of an aldehyde intermediate and formation of the ruthenium carbonyl complex [RuH$_2$(CO)(triphos)]. Cole-Hamilton and co-workers have reported the Ru(acac)$_3$/triphos system for the hydrogenation of α,ω-diester 1,19-nonadecanedioate to the respective diol, using dioxane mixed with H$_2$O (either 10% or 50%) applying 40 bar H$_2$ and 220°C. They propose another role of the added water: it might also hydrolyze the starting diester to the carboxylic acid and subsequently assist in hydrolyzing the formed intermediate oligoesters.$^{[13]}$

The re-evaluation of the Ru(acac)$_3$/triphos system, the search for ‘new’ reaction conditions and an exploration of the PC$^{NHC}$P and C$^{NHC}$PC$^{NHC}$ ligand are described below. Additionally, complexation of the PC$^{NHC}$P ligand to ruthenium and its behavior were studied.

### 2.2 Synthesis, Results and Discussion

**PC$^{NHC}$P ligand and attempts to obtain its Ru complexes**

The synthesis of the PC$^{NHC}$P imidazolium salt 3 and the formation of its silver, palladium and ruthenium complexes were previously reported by the group of Lee.$^{[20,21]}$ The synthetic route towards the ligand, shown in Scheme 4, encompasses a phase transfer catalytic alkylation of the imidazole with dichloroethane to form 1, and a second alkylation with dichloroethane to obtain the intermediate imidazolium chloride 2.

Intermediate 2 can then be doubly functionalized with phosphine groups using KPPh$_2$ to obtain PC$^{NHC}$P ligand 3 in an overall yield of around 15% in three steps. The reported complexation of 3 can proceed via either transmetallation or a direct C-H activation without the need for a base. A dinuclear complex is formed with ruthenium, where the ligand adopts a facial geometry, with three chlorides bridging between the ruthenium centers to form complex 4. A facial geometry was envisaged to be beneficial for an optimal hydride transfer to an
ester moiety. It has been reported that mononuclear compounds could be obtained from the \([\text{Ru}_2(\mu-\text{Cl})_2(\text{PC}^\text{NHC})_2]\) complex 4 by bubbling CO through the mixture.\(^{[21]}\) The mononuclear complex, however, shows a meridional coordination geometry and one additional CO has been incorporated. Our attempts to directly synthesize mononuclear Ru-complexes proved to be difficult.

\[
\begin{align*}
\text{HN-} & \text{N} + \text{Cl-} \rightarrow \text{KOH/HCO}_2 \rightarrow \text{HOCl}_2 \rightarrow \text{Cl-} \rightarrow \text{Cl-} \\
\text{Cl-} & \rightarrow \text{N-} \rightarrow \text{Cl-} \\
\text{Cl-} & \rightarrow \text{N-} \rightarrow \text{Cl-} \\
\text{Cl-} & \rightarrow \text{N-} \rightarrow \text{Cl-} \\
\text{Cl-} & \rightarrow \text{N-} \rightarrow \text{Cl-} \\
\text{Cl-} & \rightarrow \text{N-} \rightarrow \text{Cl-} \\
\text{Cl-} & \rightarrow \text{N-} \rightarrow \text{Cl-} \\
\text{Cl-} & \rightarrow \text{N-} \rightarrow \text{Cl-} \\
\text{Cl-} & \rightarrow \text{N-} \rightarrow \text{Cl-} \\
\end{align*}
\]

\[\text{Scheme 4. Synthesis of } \text{PC}^\text{NHC} \text{ ligand 3 (above) and the } [\text{Ru}_2(\mu-\text{Cl})_2(\text{PC}^\text{NHC})_2]\text{Cl complex 4 (below) which is obtained via direct C-H activation, as described in ref [21].}\]

Attempts to obtain such monomeric species from reaction of 3 with Ru(acac)\(_3\), cis-RuCl\(_2\)(dms)\(_3\), or trans-RuCl\(_2\)(MeCN)\(_4\) in the presence as well as absence of various bases, did not succeed. Varying reaction conditions and employing various precursors (RuCl\(_2\)(PPh\(_3\))\(_3\), RuCl\(_3\), RuHCl(CO)(PPh\(_3\))\(_3\), or trans-RuCl\(_2\)(pyridine)\(_4\)) did not yield satisfactory results either. Additionally, even though the silver complex of the PC\(^{NHC}\) ligand (Ag(PC\(^{NHC}\))) could be synthesized in high yields following the procedure of H.M. Lee,\(^{[21]}\) transmetallation of [RuHCl(CO)(PPh\(_3\))\(_3\)] and cis-RuCl\(_2\)(dms)\(_3\), with Ag(PC\(^{NHC}\)) also did not result in a well-defined mononuclear ruthenium complex. Instead, the species obtained appeared to be coordination polymers, which will be discussed later under Polymeric Ru(PC\(^{NHC}\)) coordination compounds.

**C\(^{NHC}\)PC\(^{NHC}\) ligand**

Synthesis of the C\(^{NHC}\)PC\(^{NHC}\)-imidazolium salt 8, shown in Scheme 5, was performed following an unpublished procedure by O. Kaufhold, developed in cooperation between our group and the group of Hahn. The tertiary phosphine 5 was successfully formed via a base catalyzed hydrophosphination of 1-vinylimidazole with phenylphosphine, which was confirmed by the appearance of only one signal in the \(^{31}\)P-NMR spectrum at \(\delta = -34.9\) ppm. Additionally, the ethylene linker was clearly observed as multiplets, indicative of the second order
AA’BB’XX’spin system expected. Addition of alkylating agents to 5 would inevitably lead to product mixtures with different N- and P-alkylated species. It was therefore decided to protect the tertiary phosphine via sulfurization. This was easily achieved by adding elemental sulfur to 5 in boiling toluene to give the phosphine sulfide 6. This reaction was quantitative and formation of the product was confirmed by a large downfield shift in the $^{31}$P-NMR spectrum to $\delta = 39.1$ ppm. 6 was then alkylated at the N-position using methyl iodide, forming 7. For deprotection of the phosphorus, a reported method using Raney-Nickel was followed. [22] This method proved cumbersome and even though precautions were taken to minimize the presence of air and water, sideproducts remained present. Correct timing when to stop the reaction appears to be essential. Compound 8 showed a resonance at $\delta = -34.3$ ppm in the $^{31}$P-NMR spectrum, which is shifted upfield compared to 7, confirming the successful removal of the protecting sulfur atom. The imidazolium proton was observed at $\delta = 9.26$ ppm in the $^1$H-NMR spectrum of 8.

Scheme 5. Synthesis of the C$_{\text{NHC}}$PC$_{\text{NHC}}$ ligand, via a base catalyzed hydrophosphination to form 5, protection of the phosphorus with sulfur to form 6, alkylation of the of the imidazole yielding 7 and subsequent deprotection to obtain the final product 8. [9]

Polymeric Ru(PC$_{\text{NHC}}$P) Coordination Compounds

A suitable ruthenium precursor for the formation of mononuclear Ru complexes was expected to be found in the well-known (but poorly understood) ruthenium-blue solution. This convenient starting material was discovered in the 1920’s and since then several routes to obtain this blue solution have been explored. In essence, it encompasses the reduction of hydrated ruthenium(III) chloride in a H$_2$O / EtOH mixture. A dark-blue solution is obtained of which the precise constitution is unknown, but coulometric measurements have shown that Ru(II)-species are present, among which the Ru$_5$Cl$_{12}$~2~ cluster anion,[23] as well as several other mixed valence chloro-complexes.
The Ru-blue solution was reported to be a suitable precursor for the formation of well-defined complexes, rigid bi- and tridentate ligands like phenanthroline and terpyridine directly formed monomeric Ru-complexes.\textsuperscript{[24]} However, when we attempted to extend this procedure to the PC\textsuperscript{NHC}P pre-ligand 3, by adding the ligand to Ru-blue in a 1:1 molar ratio, with or without KO\textsubscript{t}Bu, (see Scheme 6), this resulted in formation of a light brown solid that appeared to be insoluble in almost all solvents, including DMSO. Presumably, the combination of ‘naked’ ruthenium and a flexible imidazolium salt as ligand resulted in the formation of coordination polymers or oligomers. For the remaining text this material will be indicated as 9.

Scheme 6. Schematic representation of the formation of oligomeric / polymeric species 9 obtained by addition of PC\textsuperscript{NHC}P ligand to a ruthenium-blue solution. The scheme serves to illustrate a possible structure of this coordination polymer. A conceivable structure of the repeating unit is shown in the frame.

Elemental analysis of the CNH content of 9 indicates a molecular formula of C\textsubscript{30}H\textsubscript{33}N\textsubscript{2}P\textsubscript{2}Ru. Coordination polymers are notoriously difficult to analyze using elemental analysis due to end-group deviations and other irregularities that might arise during their formation. However, the result of elemental analysis is close to C\textsubscript{31}H\textsubscript{31}Cl\textsubscript{3}N\textsubscript{2}P\textsubscript{2}Ru which could correspond to a mononuclear RuCl\textsubscript{3}(PC\textsuperscript{NHC}P) species. In case of a 1:1 ratio Ru:L (as found in this case), one- or two-dimensional polymers are generally formed.\textsuperscript{[25]}

Solid-state \textsuperscript{13}C and \textsuperscript{31}P-NMR spectra of 9 are shown in Figures 3 and 4. The \textsuperscript{13}C-NMR peak at δ = 175 ppm correlates to the imidazol-2-ylidene carbene signal, the one around 128 ppm is ascribed to imidazole backbone and phenyl signals and peaks at 46 and 30 ppm to the ethylene linker CH\textsubscript{2} signals. The \textsuperscript{31}P-NMR shows three signals, at δ = 46, 35 and 11 ppm. The peak resonating at δ = 11 ppm can be ascribed to a pendant phosphine arm, not coordinated to ruthenium. The two peaks at δ = 35 and 46 ppm are reminiscent of coordinated phosphine
moieties. The peaks in the solid state NMR are rather broad, due to (residual) anisotropic interactions that are not averaged out. The polymer was not crystalline, which also adds to the line widths observed. In a later stage, the insoluble polymer 9 was applied in catalysis and the catalytic species created by breaking open the polymer using $H_2$ showed hydrogenolysis activity (see Ester Hydrogenolysis Experiments).

The polymeric species 9 was subjected to elevated $H_2$-pressures to see if a defined ruthenium complex was formed. After applying elevated temperature and pressure (100°C, 80 bar $H_2$) overnight to a suspension of 9 in $i$-propanol, a clear yellow solution was obtained. After work-up, $^1H$ and $^{31}P$-NMR showed evidence that the coordination polymer was broken up and rearranged into a dinuclear species. $^{31}P$-NMR showed only a two doublets at $\delta = 47.8 (J = 31.5 \text{ Hz})$ and 43.2 ($J = 31.5 \text{ Hz}$) ppm, and $^1H$-NMR showed a well-defined Ru-species.

Figure 3. Solid state $^{13}C$-NMR of PCNCP-coordination polymer 9, spinning side bands indicated as SS.

Figure 4. Solid state $^{31}P$-NMR of PCNCP-coordination polymer 9. Spinning side bands are indicated as SS, and both to the left and right is another small set of spinning side bands visible.
After careful comparison, the species could be identified as the dinuclear Ru-PC\textsubscript{NHC} complex 4 (see Scheme 3) reported by Lee, who observed two doublets at $\delta = 48.5$ and 43.4 ppm ($J = 31.3$ Hz).\textsuperscript{[21]} In the $^1\text{H}$-NMR, every proton signal matched in both shift and multiplicity. High-pressure NMR (HP-NMR) experiments for $^{31}\text{P}$ showed that 9 already transformed into a different species within 10 minutes of measuring at 80 bar $\text{H}_2$ and 100°C in $i$-prop-$d_8$. However, since the final species bears almost full similarity with 4, we hypothesize that after cooling and depressurizing, the thermodynamically most stable species is formed as the chloro-bridged dinuclear Ru(\text{PC\textsubscript{NHC}}) complex 4. This is supported by the fact that no hydride species were found in the measured region, for both the isolated species and the HP-NMR experiment.

**Ester Hydrogenolysis Experiments**

**Ru-triphos system**

Relevant results obtained with the Ru(acac)\textsubscript{3}/ triphos system as reported by Teunissen are shown in Table 1.\textsuperscript{[1,2]}

<table>
<thead>
<tr>
<th>Substr.</th>
<th>Ru:S:Add</th>
<th>Conditions\textsuperscript{[a]}</th>
<th>Solv.</th>
<th>Add.</th>
<th>Conv. \textsuperscript{[b]}</th>
<th>TON\textsuperscript{[c]}</th>
<th>TOF\textsuperscript{[d]}</th>
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<tbody>
<tr>
<td>1 DMO</td>
<td>1:100:26</td>
<td>T 100 p(H\textsubscript{2}) 70 t 16</td>
<td>MeOH</td>
<td>Zn</td>
<td>95(E)</td>
<td>160</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>1:500:0.35</td>
<td>T 100 p(H\textsubscript{2}) 70 t 16</td>
<td>MeOH</td>
<td>Zn</td>
<td>84(E)</td>
<td>857</td>
<td>54</td>
</tr>
<tr>
<td>3 DMPht</td>
<td>1:65:0</td>
<td>T 100 p(H\textsubscript{2}) 85 t 16</td>
<td>MeOH</td>
<td>-</td>
<td>30(P)</td>
<td>19</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>1:65:45</td>
<td>T 100 p(H\textsubscript{2}) 85 t 16</td>
<td>MeOH</td>
<td>HBF\textsubscript{4}</td>
<td>79(P)</td>
<td>53</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>1:65:15</td>
<td>T 100 p(H\textsubscript{2}) 85 t 16</td>
<td>IPA</td>
<td>HBF\textsubscript{4}</td>
<td>18(P)</td>
<td>103</td>
<td>6</td>
</tr>
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General conditions: Approximately 15 ml solvent and 15-20 μmol Ru(acac)\textsubscript{3} were used, catalyst was formed in situ with 1 to 1.5 eq of triphos. [a] T in °C, p(H\textsubscript{2}) in bar, t in hr. [b] Conversion is specified to which product is formed. [c] TON is reported in mol\textsubscript{sub}_\text{cat}·mol\textsuperscript{-1}. [d] TOF in mol\textsubscript{sub}_\text{cat}·mol\textsuperscript{-1}·hr\textsuperscript{-1}. Ru:S:Add ratios are rounded off in order to compare numbers more easily. All results taken from ref [1] and [2].
For catalytic hydrogenolysis of DMO, MeOH was successfully applied as solvent in the presence of Zn as additive (entry 1 and 2). Since DMO and its transesterification product with MeOH are degenerate species, transesterification does not lead to unwanted side products and the productive reaction slowly proceeds to form EG. For the other substrates, MeOH was reported to be less suitable. DMPhth was converted for less than 80% to the first hydrogenated product Phth in MeOH when HBF₄ was added (entry 4), but changing the solvent from MeOH to i-propanol increased conversion to almost 80% of second hydrogenated product BDM (entry 5). Teunissen makes no report of attempting conversion of BB in MeOH but used i-propanol (IPA) as the solvent straight away, showing that these substrates are readily converted in the presence of either HBF₄ or NEt₃ (entry 6 and 7). When switching the solvent to hexafluoro i-propanol (FIPA), successful conversion of BB was reported, but with the need of additives (entry 8). In Table 2 our re-evaluation of the activity of the triphos ligand using the in situ generated Ru(acac)₃/triphos system is shown.

Table 2. Re-evaluated results using the Ru(acac)₃/triphos system.

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</tbody>
</table>

General conditions: Approximately 15 ml solvent and 14 μmol Ru(acac)₃ was used. Catalyst was formed in situ with 2 eq of triphos. [a] T in °C, p(H₂) in bar, t in hr. [b] Conversion is specified to which product is formed. [c] TE = Transesterification products visible, <10% of total product yield.
In IPA (with and without additives, entry 1 and 3) conversion takes place, but transesterification products are obtained. The second ester moiety is hydrogenolyzed only at increased pressure (entry 4). DMPhth was difficult to convert in IPA (entry 5) when compared to its fluorinated counterpart FIPA (entry 6). We did not manage to convert BB at all, except when FIPA was used as solvent (entry 9). It became clear from these results, that conversion of esters without using additives is possible. However, the activities we found were substantially lower than the ones in Table 1, reported by Teunissen, and in several cases FIPA was still needed as the solvent to achieve substantial conversion.

**Evaluation of the Solvent**

We continued our investigation by applying the conditions reported by Crabtree\[19\] and Cole-Hamilton.\[13\] Additionally, we evaluated the influence of a Hastelloy autoclave instead of one made of stainless steel with a glass liner on the reproducibility of the results. In this case there appears to be no influence. The results obtained with this system are shown in Table 3.

A replacement for the halogenated solvent was sought in dioxane, which has the additional advantage, as a non-protic solvent, that transesterification reactions do not occur. However, attempts to convert DMO using this system (dioxane, 210 °C, 40 bar H\(_2\)) posed several problems.

Using solely dioxane as solvent did not lead to any conversion, not even over an extended period of time (Table 3, entry 1). Conducting the catalysis in water or in an IPA/water mixture (50/50; entries 2 and 3) resulted in a fast increase in pressure within the autoclave, rapidly increasing from 70 bar to 170 bar, already during heating. The amount of pressure that was built up and the soda-like behavior of the reaction mixture afterwards indicated decomposition. Probably decarbonylation of the substrate with release of CO\(_2\) occurred, due to addition of water which caused the ester to hydrolyze to the acid, after which decarboxylation could take place under these conditions. Moderate conversions could be obtained for DMPhth in a dioxane/water mixture, even when using the standard 120 °C and 80 bar H\(_2\) (entry 4) and the result was further improved when the temperature was raised from 120 to 190 °C (entry 5).

Using water as the only solvent did not result in conversion of the ester. Instead full hydrogenation of the aromatic ring was observed (entry 6). \(^1\)H-NMR analysis of the reaction mixture indicated almost full conversion (>95%) to the product shown in Figure 5. One reason for this might be that these conditions lead to decomposition of the catalyst (a black film on
Chapter 2

The autoclave liner was observed), and heterogeneous Ru-particles perform the hydrogenation of the aromatic ring.

Table 3. Conversion of ester substrates, checking the influence of water on the system.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 DMO</td>
<td>1:100:0</td>
<td>210 40 65</td>
<td>dioxane</td>
<td>-</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1:500:0</td>
<td>190 50 -</td>
<td>H₂O</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1:500:0</td>
<td>210 70 -</td>
<td>IPA</td>
<td>H₂O 50%</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4 DMPth</td>
<td>1:100:0</td>
<td>120 80 16</td>
<td>dioxane</td>
<td>H₂O 5%</td>
<td>20(Phth)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1:200:0</td>
<td>190 70 16</td>
<td>dioxane</td>
<td>H₂O 5%</td>
<td>66(Phth)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10(BDM)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1:100:0</td>
<td>120 80 16</td>
<td>H₂O</td>
<td>-</td>
<td>- [c]</td>
<td></td>
</tr>
<tr>
<td>7[4] MP</td>
<td>1:100:0</td>
<td>210 40 16</td>
<td>dioxane</td>
<td>-</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1:100:0</td>
<td>210 40 16</td>
<td>dioxane</td>
<td>H₂O 10%</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1:100:0</td>
<td>210 40 16</td>
<td>MeOH</td>
<td>-</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1:100:20</td>
<td>210 40 16</td>
<td>dioxane</td>
<td>Zn</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1:500:0</td>
<td>190 70 15</td>
<td>H₂O</td>
<td>-</td>
<td>73</td>
<td></td>
</tr>
</tbody>
</table>

General conditions: 15 ml of solvent and 14 μmol Ru(acac)₃ was used. Ru(acac)₃: triphos = 1:2. [a] T in °C, p(H₂) in bar, t in hr. [b] Conversion is specified to which product is formed. [c] converts to a product where the aromatic ring was hydrogenated. [d] Conditions from entry 7 taken from a patent.[18]

Figure 5. Hydrogenation of the aromatic ring of DMPth, probably facilitated by decomposed Ru-complex forming a heterogeneous Ru-catalyst.

In this system, the linear ester methyl propionate (MP) was also used as test substrate. Using dioxane as solvent appeared to be successful and the Ru(acac)₃: triphos = 1:2 sys-
tem led to 21% conversion of MP into n-prOH and MeOH (entry 7). Adding Zn or H₂O did not improve the conversion (entries 8 and 10). This was remarkable, since Zn was shown above (Table 1 and 2) to generally improve conversion. The application of Crabtree conditions, employing H₂O as solvent, gave 73% conversion (entry 11). It should be noted however; that in this last case a pressure of 70 bar H₂ was used, as reported in the patent where a conversion up to 95% was reported. When MeOH was applied as solvent (entry 9), no conversion was achieved under the same conditions and one can speculate that higher pressures, comparable to those reported in Table 1 and 2, might be necessary.

**Ru-PCNHC₃P system**

The activity of the Ru-PCNHC₃P system was compared to the Ru-triphos system discussed above. Several catalytic trials involving various approaches to introduce the catalytically active species have been performed and these are shown in Table 4. Generally, we aimed to form the catalytic species in situ from Ru(acac)₃ and the PCNHC₃P ligand 3. To allow the NHC to coordinate to the metal, the imidazolium salt had to be deprotonated. However, Lee also mentioned C-H activation of the imidazolium C₂. This was confirmed by preparing the dinuclear Ru(PCNHC₃P) complex 4 as shown in Scheme 4.

Hence, we tested two approaches: with and without adding KO-tBu as a base. Additionally, we also applied complex 4 in order to be sure to start from a pre-catalyst where the NHC is coordinated to the ruthenium center.

Interestingly enough, when the PCNHC₃P coordination polymer 9 was tested as catalyst for DMO in IPA, a higher conversion as compared to all previously mentioned results was observed and, more noticeably, transesterification products were not detected (entry 5). The fact that 9 gives a higher conversion than 4 indicates that during catalysis, polymer 9 forms a different active species than the one formed from dinuclear complex 4. Thermodynamically, the most stable species in the absence of H₂ pressure is the [[Ru₂(μ-Cl)₃(PCNHC₃P)₂]Cl] complex 4.

In the case of DMPth, no conversion was found when using IPA or dioxane with 5% water as solvent (entries 7 and 8). FIPA is still needed to achieve conversion, this time 67% to the first hydrogenated product (entry 9). Without adding KO-tBu the conversion amounted to 16% (entry 10), which is a trend opposite to that found for DMO. Also in this case, the PCNHC₃P ligand gives the catalyst with inferior activity compared to the system derived from triphos.
Table 4. Results obtained with Ru(acac)$_3$/PCNHC$_P$ catalyst

<table>
<thead>
<tr>
<th>Substr.</th>
<th>Catalyst</th>
<th>Ru:S:Add</th>
<th>Conditions$^{[a]}$</th>
<th>Solv.</th>
<th>Add.</th>
<th>Conv. $^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T$(°C) $p$(H$_2$) t(hr)</td>
<td></td>
<td></td>
<td>(%)</td>
</tr>
<tr>
<td>1</td>
<td>DMO</td>
<td>Ru/PCNHC$_P$ 1:1000:0</td>
<td>120 80 16 IPA -</td>
<td>70(MG)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ru/PCNHC$_P$ 1:1000:0</td>
<td>120 80 16 MeOH -</td>
<td>51(MG)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ru/PCNHC$_P$ 1:1000:275</td>
<td>120 80 16 IPA H$_2$O</td>
<td>31(MG)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ru/PCNHC$_P$ 1:1000:0</td>
<td>120 80 16 IPA -</td>
<td>96(MG)$^{[c]}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ru/PCNHC$_P$ 1:100:2</td>
<td>120 80 16 IPA KO$\tau$Bu</td>
<td>49(MG)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>DMPhth</td>
<td>Ru/PCNHC$_P$ 1:1000:0</td>
<td>140 80 16 IPA -</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Ru/PCNHC$_P$ 1:100:2</td>
<td>120 80 16 IPA KO$\tau$Bu</td>
<td>67(Phth)</td>
<td></td>
<td></td>
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<tr>
<td>8</td>
<td>Ru(acac)$_3$ 1:100</td>
<td>120 80 16 IPA FIPA KO$\tau$Bu</td>
<td>16(Phth)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Ru/PCNHC$_P$ 1:1000:100</td>
<td>120 80 16 IPA NEt$_3$</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Ru/PCNHC$_P$ 1:500:275</td>
<td>120 80 16 IPA H$_2$O</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Ru/PCNHC$_P$ 1:100:0</td>
<td>210 40 16 IPA KO$\tau$Bu</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>BB</td>
<td>Ru/PCNHC$_P$ 1:3000:0</td>
<td>120 80 16 IPA -</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Ru/PCNHC$_P$ 1:1000:100</td>
<td>120 80 16 IPA NEt$_3$</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Ru/PCNHC$_P$ 1:500:275</td>
<td>120 80 16 IPA H$_2$O</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Ru/PCNHC$_P$ 1:100:0</td>
<td>210 40 16 IPA KO$\tau$Bu</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>MP</td>
<td>Ru/PCNHC$_P$ 1:100:0</td>
<td>210 40 16 IPA FIPA KO$\tau$Bu</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Ru/PCNHC$_P$ 1:1000:0</td>
<td>120 80 16 IPA KO$\tau$Bu</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

General conditions: 15 ml of solvent and 14 μmol Ru(acac)$_3$ was used. Ru(acac)$_3$: PCNHC$_P$ ligand 3 = 1:2, the catalyst is prepared in situ, except for entries 3, 5 and 8. 4 = [Ru$_2$(μ-Cl)$_3$(PCNHC$_P$)$_2$]Cl and 9 = PCNHC$_P$ polymer. $^a$ T in °C, $p$(H$_2$) in bar, t in hr. $^{[b]}$ Conversion is specified to which product is formed. $^{[c]}$ no transesterification products detected. In all other cases, 5-15% of total conversion consists of transesterification products. $^{[d]}$ a dioxane / 5% H$_2$O mixture was used. $^{[e]}$ no ligand added, catalyst decomposed.

A blanc reaction (entry 11) resulted in the formation of a black film on the autoclave liner and no conversion whatsoever was observed, indicating decomposition of Ru(acac)$_3$ under these conditions. This experiment confirmed the need of a stabilizing ligand in order to form catalytically active species. Unfortunately, for BB (entries 12-15), no conversion could be achieved when using the Ru-PCNHC$_P$ system, even when FIPA was applied as the solvent. When we applied the dioxane solvent system for MP (40 bar H$_2$ and 210 °C), no conversion was observed using the Ru-PCNHC$_P$ system (entry 16). Changing the solvent to MeOH did not improve on this (entry 17).
Chapter 2

Ru-C\textsuperscript{NHC}PC\textsuperscript{NHC} system

A few tests to probe the activity of the Ru-C\textsuperscript{NHC}PC\textsuperscript{NHC} system were performed using DMO as the substrate. A system derived from Ru(acac)\textsubscript{3} / C\textsuperscript{NHC}PC\textsuperscript{NHC} ligand / KO\textsubscript{t}Bu (1 : 2 : 4) in HFIP at 120 °C, at 80 bar H\textsubscript{2} pressure during 16 hr showed no conversion. Due to difficulties encountered in the preparation of larger amounts of the ligand it was decided to halt further studies.

2.3 Summary and Conclusions

The results involving a triphos system without additives in non-fluorinated alcohols\cite{4} were not reproducible employing the starting materials and substrates that we used in this study. Hence, full conversion of substrates such as benzyl benzoate could not be obtained. Careful re-evaluation of this system, starting from the results of Teunissen,\cite{1,2} indeed did reveal activity without additives in the conversion of DMPhth into DMO. Full conversions could only be obtained for the activated ester DMO. Replacement of halogenated solvents like FIPA by solvents such as dioxane and/or H\textsubscript{2}O, in order to find more benign conditions, appeared to be less productive; using these solvents did not amount to the same level of conversion as when compared to using FIPA. On the positive side, we could illustrate the feasibility of a halogen-free solvent system in the sense that the desired reactions do proceed albeit at lower rates and producing lower overall conversion.

The PC\textsuperscript{NHC}P pre-ligand 3 shows some activity in the hydrogenolysis of esters, but does not meet the standards of triphos. Additionally, it is unsure what the most active species is: adding KO\textsubscript{t}Bu gave better results for one substrate and worse for another. Activities for in situ generated catalyst closely resemble the preformed dinuclear [Ru\textsubscript{2}(μ-Cl)\textsubscript{3}(PC\textsuperscript{NHC}P)\textsubscript{2}]\textsubscript{Cl} complex 4, and polymeric species 9 formed an active species where no transesterification activity was found for DMO. These polymeric species were obtained by addition of 3 to a ‘Ru-blue’ solution and studies of the species under elevated pressures show that an unknown species is formed, but after removal of hydrogen pressure the species appears to reorganize to the thermodynamically more stable 4.

The synthesis of C\textsuperscript{NHC}PC\textsuperscript{NHC} ligand 8, which was developed in collaboration with the group of Hahn, was also described. The ligand is difficult to handle and hard to obtain pure in significant amounts. Preliminary results of an in situ prepared Ru(acac)\textsubscript{3}C\textsuperscript{NHC}PC\textsuperscript{NHC} catalyst show no activity in the conversion of DMO. No further investigation using this ligand was performed. If one were to continue with this ligand, a template-controlled synthesis route is advised.\cite{26}


2.4 Experimental Section

General Remarks

All experiments were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were freshly distilled under an argon atmosphere from sodium benzophenone ketyl (Toluene, THF, pentane and diethyl ether) and from CaH₂(CH₂Cl₂ and MeCN). Dioxane, MeOH and i-ProH were distilled from CaH₂ under a nitrogen atmosphere and were stored over 4Å molecular sieves. Substrate purification: DMO was purified by repeated crystallization from EtOH. Dimethylphthalate, methyl propionate and benzyl benzoate were purified as follows: 10 ml of ester was washed overnight with a 2 M NaHCO₃ solution (200 mL). The mixture was extracted with DCM after which the collected fractions were dried using MgSO₄. After filtration, the mixture was concentrated in vacuo and the ester was dried overnight on sikkon Blue (CaSO₄ with indicator). After removal of the CaSO₄, the ester was fractionally distilled under reduced pressures, and stored under a nitrogen atmosphere over 4Å molecular sieves. Deuterated solvents (CDCl₃ and CD₂Cl₂) were distilled from CaH₂ under a nitrogen atmosphere and stored over 4Å molecular sieves. DMSO was purchased as dry solvent. Ru(acac)₃ was recrystallized from toluene and triphos (1,1,1-tris(diphenylphosphinomethyl)ethane) was recrystallized from a boiling hexanes solution. PC₃NHC₃P ligand [8] and dinuclear Ru-PC₃NHC₃P complex [21] were prepared according to literature procedures. Other reagents were obtained commercially and used as received. NMR spectra in solution were recorded on either a Bruker AMX400 MHz, Bruker DRX 300 MHz, Varian Mercury 300 MHz or Varian INOVA 500 MHz. Solid-state NMR was performed on a DMX 400 MHz at 100.44 MHz for 13C and 161.70 MHz for 31P in a solid state experiment with magic angle spinning (CP-MAS NMR) at a spin frequency of 12 kHz for 13C and 11 kHz for 31P, contact time = 2 ms, pulse delay = 2 s. High-Pressure NMR was conducted on a Bruker DRX 300 MHz using a 10 mm sapphire tube. 1H and 13C{1H} chemical shifts (δ) are reported in ppm downfield from TMS, and 31P{1H} chemical shifts are reported in ppm downfield from 85% H₃PO₄. Abbreviations used in the reporting of NMR spectra are b = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four-sector mass spectrometer coupled to a JEOL MSMP7000 data system.

Preparation of bis(di-1H-imidazolylethyl)phenylphosphine 5

Potassium t-butoxide (1.0 g, 8.9 mmol) was dissolved in 160 mL THF and phenylphosphine (5.2 ml, 47 mmol) was carefully added and stirred for 15 min. Vinylimidazole (8.7 ml, 96 mmol) was added dropwise and the yellow solution was stirred for 20 hr. All volatiles were removed in vacuo, the residue was washed with 20 mL water and extracted with 100 ml
DCM. The organic phase was dried over MgSO₄, filtered and concentrated in vacuo to yield the product as a pale yellow oil (88%). °H-NMR (300MHz, C₆D₆): δ = 7.19 (s, 2H, CH), 7.17 (m, 3H, o-H₈Ar + im-H), 7.13 (m, 3H, m-H₈Ar + p-H₈Ar), 6.39 (s, 2H, CH), 3.18 (m, 2H, PCH₂a), 1.33 (m, 2H, PCH₂b) ppm. °P-NMR (121 MHz, C₆D₆): δ = -34.9 (s) ppm.

Preparation of bis(di-1H-imidazolylethyl)phenylphosphine sulfide 6
A mixture of 5 (12.3 g, 41.2 mmol) and elemental sulfur (1.52 g, 47.4 mmol) in 80 ml toluene was heated under reflux for 30 min. After cooling to RT the suspension was filtered and the solid extracted with DCM. Removal of the solvent in vacuo gave a colorless solid (59%). °H-NMR (300MHz, CDCl₃): δ = 7.73 (m, 2H, o-H₈Ar), 7.48 (m, 3H, m-H₈Ar + p-H₈Ar), 7.40 (br s, 2H, im-H), 6.88 (s, 1H, CH), 6.77 (s, 1H, CH), 4.35 (tdd, J = 14.2, 8.1, 6.3 Hz, 1H, NC₃H₂a), 4.08 (tdd, J = 14.2, 8.1, 6.3 Hz, 1H, NC₃H₂b), 2.50 (dddd, J = 14.4, 10.3, 8.2, 6.3 Hz, 1H, PCH₂a), 2.30 (dddd, J = 14.4, 10.3, 8.2, 6.3 Hz, 1H, PCH₂b) ppm. °P-NMR (121 MHz, CDCl₃): δ = 39.1 (s) ppm.

Preparation of [bis(3-methyl-1H-imidazolylethyl)phenylphosphine sulfide] iodide 7
Methyliodide (3.1 ml, 50 mmol) was added to a solution of 6 (3.3 g, 10 mmol) in 50 ml DCM and stirred for 20 hr. Two layers formed and the lower, oily white layer was washed with 4 x 20 ml Et₂O resulting in a white powder as product (96%). °H-NMR (400.1 MHz, CD₃OD): δ = 8.85 (s, 2H, im-H), 7.90 (m, 2H, o-H₈Ar), 7.61 (m, 1H, p-H₈Ar), 7.53 (t, J = 1.7 Hz, 2H, CH), 7.50 (m, 2H, m-H₈Ar), 7.28 (t, J = 1.7 Hz, 2H, CH), 4.61 (m, 4H, NCH₂), 3.75 (s, 6H, CH₃), 3.25 (dt, J = 23.4, 8.3 Hz, 1H, PCH₂a), 2.93 (tt, J = 14.7, 5.7 Hz, 1H, PCH₂b). °P-NMR (162.0 MHz, CD₃OD): δ = 39.0 (s) ppm.

Preparation of bis(3-methyl-1H-imidazolylethyl)phenylphosphine iodide 8
Humid Raney-Nickel (5 g, 58 mmol) was washed 5 times with 15 ml MeCN: each time MeCN was added under vacuum and stirred for 10 min before the solvent was removed and the next washing was commenced. Subsequently, 7 (0.5 g, 0.81 mmol) was added, suspended in 20 ml acetonitrile and the mixture was degassed using freeze-pump-thaw. After this sequence, the mixture was stirred for 3 hr at RT and progress of the reaction was monitored using °P-NMR. Upon completion, the metal was filtered off over a pad of celite and the solvent removed in vacuo affording a pale yellow gel (yield nd). °H NMR (400.1 MHz, CD₃CN): δ = 9.26 (s, 2H; im-H), 7.72 (m, 2H; CH), 7.68 (m, 2H; o-H₈Ar), 7.47 (m, 5H; CH + m-H₈Ar + p-H₈Ar), 4.44 (m, 4H; NCH₂), 3.90 (s, 6H; CH₃), 2.62 (m, 4H; PCH₂) ppm. °P-NMR (162.0 MHz, CD₃CN): δ = -34.3 (s) ppm.

Preparation of Ru-coordination polymer 9
RuCl₃ • 3 H₂O (0.25 g, 0.95 mmol) was dissolved in a H₂O / EtOH mixture (10 / 15 ml) and refluxed for approximately 4 hr until the color of the solution was deep blue. PC₅NHCP ligand
3 (0.66 g, 1.25 mmol) and KOrBu (0.15 g, 1.33 mmol) were dissolved in 5 ml EtOH and in a quick movement added to the ruthenium-blue solution. This was refluxed for another hour, during which a color change was observed from blue to dark green to brown, and a light brown precipitate was formed. After cooling, the precipitate was filtered off, washed with 2 x 10 ml Et₂O and dried in vacuo. CP-MAS ¹³C-NMR: δ = 175 (NCN), 128.3 (im C= = C and CAr), 46.7 (CH₃), 29.4 (CH₂) ppm. CP-MAS ³¹P-NMR: δ = 46.6, 35.3, 11.1 ppm. Anal. Calcd. for C₃₁H₳₃Cl₃N₂P₂Ru: C, 53.10; H, 4.46; N, 4.00. Found: C, 51.33; H, 4.72; N, 4.10 which relates to approximately C₃₀H₳₃N₂.

Pressurizing Ru-coordination polymer 9 with H₂
Ru-PCₙHₙP coordination polymer 9 (0.5 gr) was weighed in an autoclave beaker and the autoclave was flushed 3 times with nitrogen/vacuum cycles. Under an outflow of nitrogen gas, 20 ml of i-propanol was added. The autoclave was then pressurized to 80 bar H₂ and heated to 100 °C for 16 hr. The solution was transferred from the autoclave into a Schlenk tube and the solvent was removed under reduced pressures. ¹H-NMR (300 MHz, CD₂Cl₂) δ = 1.00 (br, 1H, CH), 2.49 (br, 1H, CH), 2.62 (m, 1H, CH), 2.83 (m, 1H, CH), 4.27 (m, 2H, CH), 4.51 (m, 1H, CH). 5.51 (m, 2H, H Ar), 5.78 (br, 1H, CH), 6.76-7.53 (m, 18H, H Ar and imi-H), 7.81 (m, 2H, H Ar), 8.20 (m, 2H, H Ar) ppm. ³¹P-NMR (162 MHz, CD₂Cl₂) δ = 47.81 (d, J = 31.6 Hz), 43.23 (d, J = 31.5 Hz) ppm. Identified as [Ru₂(μ-Cl)₃(PCₙHₙP)₂]Cl₄, as reported by H.M. Lee[21].

High-Pressure NMR experiment of 9
Polymeric Ru-PC₉H₉P species 9 (20 mg) was weighed in a Schlenk tube and stirred in 2 ml i-prop d₆. The solution was transferred to a 10mm sapphire high-pressure NMR tube inside a glovebox. The tube was then pressurized to 80 bar H₂ and ³¹P-NMR was taken every 10 minutes, starting t = 0.

General Remarks for catalysis experiments
Hydrogenolysis experiments were conducted in a homebuilt stainless steel autoclave, using magnetic stirring and external heating by an electrical heating device, controlled by measurement of the temperature within the reaction mixture. A Viton O-ring was used as seal to ensure leak-proof working. The autoclave was also equipped with an inlet which allowed us to fill the autoclave under an outflow of nitrogen-gas, ensuring handling of the catalysis mixture under inert conditions.

Unless specifically stated otherwise, the amounts and conditions described here were used in the hydrogenation reactions. Standard Schlenk techniques were used. The catalytic mixture was prepared by weighing Ru(acac)₃ (5.6 mg, 14 μmol) and the appropriate ligand (28 μmol) in a schlenk and dissolving them in 15 mL solvent. The mixture was stirred until
a homogeneous solution was obtained, and subsequently, the appropriate amount of substrate was added. The autoclave was flushed three times using vacuum/nitrogen, and under an outflow of nitrogen gas the catalysis mixture was transferred into the autoclave via a syringe with needle. The autoclave was then flushed with 3 x 10 bar H₂, and brought to a final pressure of 80 bar H₂. It was then heated to 120 °C and stirred for 16 hr. After cooling to RT the pressure was released and the contents were taken out of the autoclave for analysis.

Transesterification products were identified after work-up and analysis of the reaction mixtures post-catalysis. In ¹H-NMR either one or two overlapping signals at around 5 ppm for the i-propanolic CH were found, a shift indicative of the CH being located next to an electronegative oxygen group.

**Acknowledgements**
Claes de Graaff is thanked for his contributions to the work described in this thesis. Prof. Dr. David Cole-Hamilton and Peter Pogorzelec are gratefully acknowledged for the cooperation at the University of St. Andrews and for facilitating part of this research in their labs.

**2.5 References**

Chapter 2