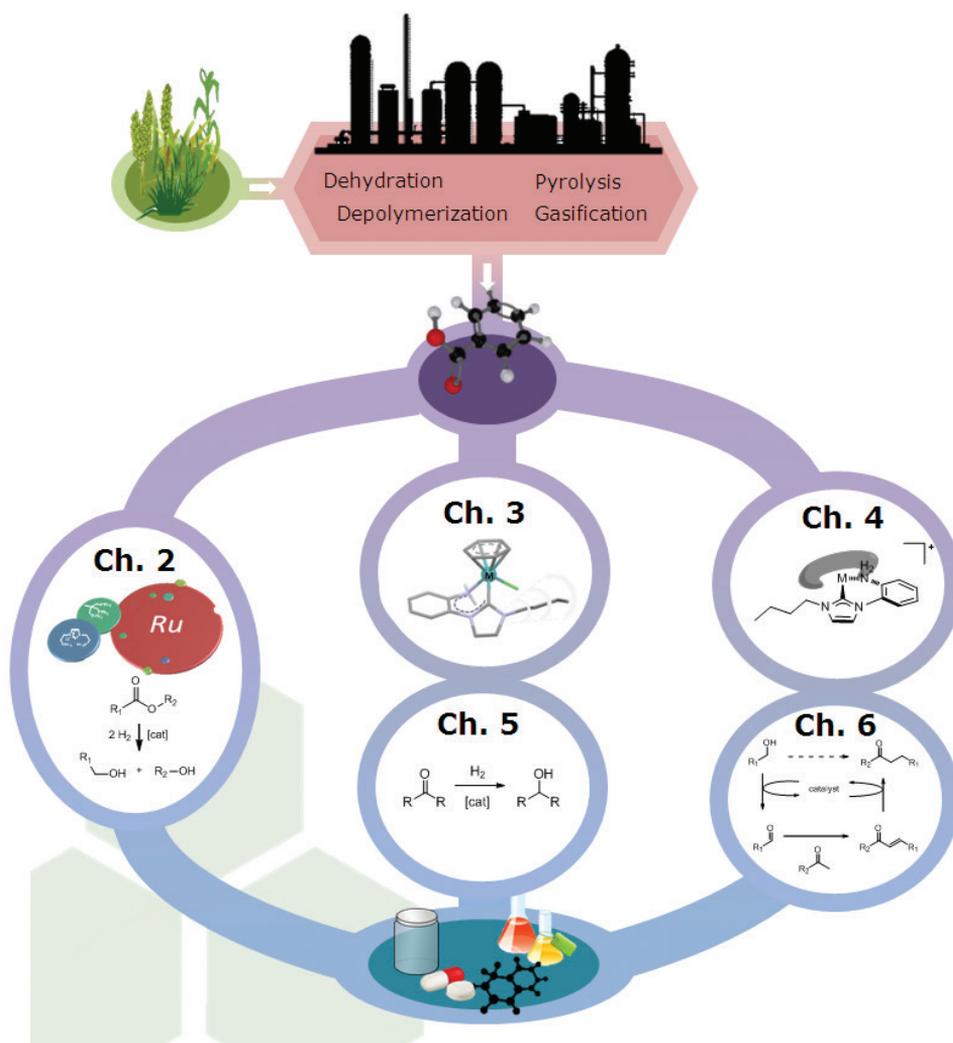




Transition Metal Catalysts for the Conversion of Biomass Inspired Substrates
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Summary



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Contemporary society relies heavily on fossil fuels to produce energy, fuels and chemicals. The growing scarcity of the fossil fuel supply together with environmental concerns stemming from pollution and increasing energy consumption initiated a demand for renewable resources. Governments and industries are now looking into ways for sustainable materials to replace a significant fraction of petroleum-derived fuels and chemicals with biomass-based alternatives. Biomass is the feedstock of choice when it comes to finding a renewable carbon source. Especially lignocellulosic biomass provides components that can be transformed into a considerable range of chemical building blocks with high application potential.

Catalytic transformations play a crucial role converting biomass into high-value products. For the fine-chemical and pharmaceutical industries, where highly functionalized special molecules are the target, it is important to have very active and selective catalysts in order to create the desired product in an economically and environmentally viable way. Molecularly defined homogeneous catalysts are top-candidates where selectivity is concerned and the design of the ancillary ligands involved in the formation of such catalytically active complexes plays a major role in steering reactivity and selectivity. The research underlying this thesis tries to contribute to the development of such systems by the design of suitable ligands and catalysts and evaluating these in catalytic transformations that are relevant for conversion and functionalization of biogenic substrates.

In Chapter 1 a general introduction to the specific topics in this thesis is provided. First, the properties and the role of *N*-Heterocyclic carbenes (NHCs) as ligands for homogeneous catalysts are discussed. Next, the development of hemi-labile or bifunctional ligands is described and several successful examples of the application of complexes containing cooperative ligands are reviewed. Then, the topic of biomass and the role it plays is briefly introduced. Driven by the functionalities that occur in biomass-inspired substrates, we anticipated three types of catalytic conversions to be relevant in this project, which are briefly discussed and reviewed: hydrogenation of polar substrates in general, hydrogenolysis of esters and direct α -alkylation of ketones with unsaturated alcohols.

At the start of this project, attention was directed towards the conversion of esters into alcohols. In Chapter 2 a re-evaluation is given of a system that was reported to successfully convert esters, a Ru(acac)₃ / triphos system (see Figure 1) previously reported in the Elsevier group. It was found that previous results obtained using a system without additives and without fluorinated alcohols, that was able to quantitatively convert esters, were not reproducible. We found that replacing the environmentally harmful fluorinated alcohols for dioxane gives a reasonably well-performing system. Applying low pressures and high tem-

peratures, some of the ruthenium hydrogenolysis catalysts are active catalysts for the hydrogenolysis of several esters into their constituting alcohols. None, however, improved on the results obtained with the reported fluorinated systems. A second part of this investigation concerned the synthesis and application of tridentate diphosphino-NHC ($PC^{NHC}P$) and diNHC-phosphine ($C^{NHC}PC^{NHC}$) ligands, in which stronger donor NHC moieties replace one or two of the phosphine moieties of triphos (Figure 1). The $Ru(C^{NHC}PC^{NHC})$ system showed no activity in ester hydrogenolysis at all, whereas the $Ru(PC^{NHC}P)$ system appeared to be less active than the Ru-triphos system.

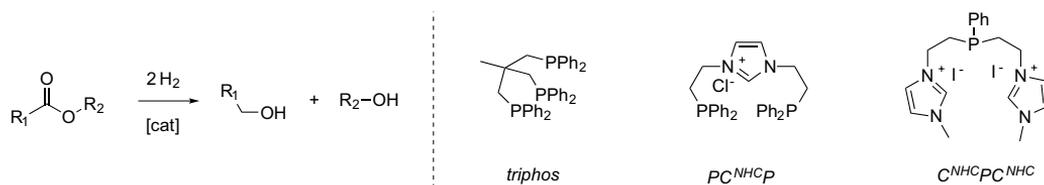


Figure 1. Schematic hydrogenolysis of esters and the ligands applied in this catalysis.

Chapters 3-6 concern the development of a bidentate NHC-amine ligand and application of several of its late transition metal complexes in catalytic hydrogenation and C-C coupling reactions, relevant for biomass conversion.

In Chapter 3 we discuss the synthesis of a novel NHC-amine ligand ($C^{NHC}-NH_2$) and of a series of M-half sandwich complexes ($M = Ru, Ir$ and Rh), shown in Figure 2. These complexes are spectroscopically and structurally compared with analogous complexes, using mainly NMR spectroscopy and X-ray diffraction studies. These investigations revealed that the combination of the small chelate ring size and resonance conjugation in the new $C^{NHC}-NH_2$ ligand increases the electron-donating capacities of the NHC compared to non-conjugated and/or seven-membered ring chelates. Therefore, the small chelate $C^{NHC}-NH_2$ ligand is a stronger donating ligand when coordinated to a metal than its larger ring analogues. Additionally, the non-optimal orbital overlap caused by the smaller and somewhat strained six-membered ring chelate in the developed complexes with $C^{NHC}-NH_2$ can promote dissociation of the amine.

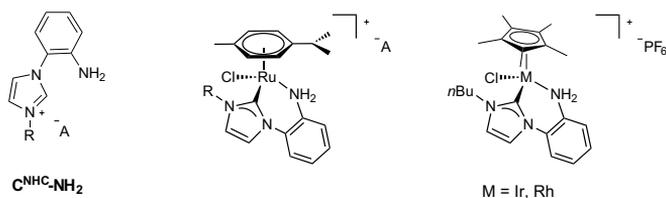


Figure 2. The $C^{NHC}-NH_2$ ligand and M-half sandwich complexes $[Ru(p\text{-cym})Cl(C^{NHC}-NH_2)]A$ (A^- = counter anion) and $[MCp^*Cl(C^{NHC}-NH_2)]PF_6$ ($M = Ir, Rh$).

Chapter 4 deals with the development of another set of complexes (Ru, Ir and Rh) containing the C^{NHC-NH_2} ligand, where in some cases cod is applied as ancillary ligand (see Figure 3). Using these complexes, three coordination modes of the C^{NHC-NH_2} ligand were studied: neutral monodentate, neutral bidentate and anionic bidentate. The structural parameters of these differently coordinated ligands were examined using NMR spectroscopy, X-ray diffraction studies and DFT calculations. It was shown that the conjugation within the aniline ring plays a major role in determining ligand properties. Bond distances that were found for the aromatic bonds within the aniline ring became inequivalent when a charge was created on the ligand, correlating to the influence of a delocalized structure. For $M(cod)$ complexes ($M = Ir, Rh$), the ligand coordination mode was found to be reversible between neutral monodentate and anionic bidentate upon deprotonation with base and protonation with acid. The neutral bidentate coordination mode was only achieved via a direct synthesis. An interesting mono-chlorobridged Ru-dimer was developed containing two forms of the C^{NHC-NH_2} ligand: the neutral bidentate and the anionic bidentate coordination mode. This results in a bis-ruthenium(III) species which was anticipated to be paramagnetic. However, strong antiferromagnetic coupling between the two $S = \frac{1}{2}$ ruthenium centers leads to an open-shell singlet state and effects diamagnetic behavior. The mono-chloro bridged dimer is further stabilized via two hydrogen bonds between an amine proton at one and a chloride at the other ruthenium center.

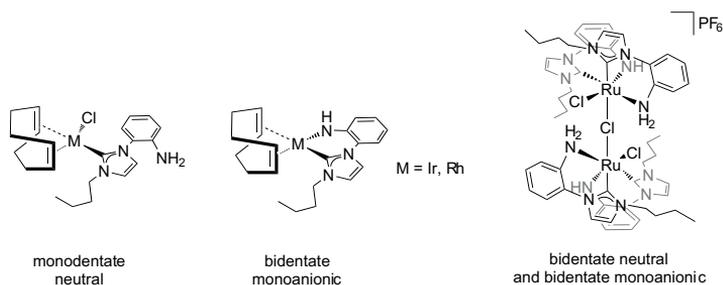


Figure 3. Synthesized complexes with the C^{NHC-NH_2} ligand in three different coordination modes. $M(cod)$ ($M = Ir, Rh$) complexes with a monodentate neutral and bidentate monoanionic ligand, and an unusual diamagnetic bis-ruthenium(III)-complex with bidentate neutral and bidentate monoanionic ligands.

Chapter 5 details the application of half-sandwich complexes in the hydrogenation of polar bonds (see Figure 4). The structural variations in the chelate ring size of the C^{NHC-NH_2} ligands that were investigated in Chapter 3 revealed that, when applied in catalysis, smaller chelate ring-sizes in combination with ring-conjugation in the ligand are beneficial for the activity of these types of catalysts: using small chelate size $[Ru(p-cym)Cl(C^{NHC-NH_2})]A$ ($A =$

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counter anion) complexes, higher TOFs were observed than for the larger ring analogues. A similar, but much smaller effect was found for analogous MCp^* ($\text{M} = \text{Ir}, \text{Rh}$) complexes with different chelate ring sizes. The smaller influence of the structural variation stems from mechanistic differences of $\text{C}^{\text{NHC}}\text{-NH}_2$ complexes bearing a *p*-cymene moiety and complexes bearing a Cp^* moiety. The *p*-cymene complexes are believed to follow an inner-sphere mechanism, whereas the Cp^* complexes are believed to follow an outer-sphere mechanism. Increasing the steric bulk of the alkyl substituent on the NHC aided the reaction, showing almost no induction period and formation of a more active catalyst for the *n*Bu complex compared to complexes with smaller Me and Et substituents. Additionally, the most successful complex $[\text{Ru}(\textit{p}\text{-cym})\text{Cl}(\text{C}^{\text{NHC}}\text{-NH}_2)]\text{PF}_6$ was applied in the hydrogenation of biomass-inspired substrates (Figure 4), showing the applicability of this motif in hydrogenation reactions for biomass conversion.

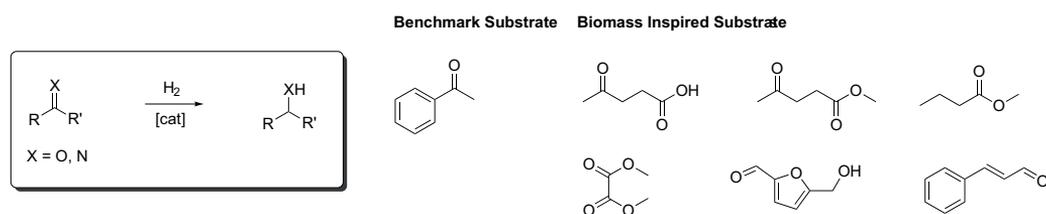


Figure 4. Schematic hydrogenation of polar bonds (left) and the substrates used in this chapter (right).

Chapter 6 contains the results obtained with a selection of complexes containing the $\text{C}^{\text{NHC}}\text{-NH}_2$ ligand, either with half-sandwich or cod as ancillary ligand, in the direct α -alkylation of ketones with alcohols, shown in Figure 5.

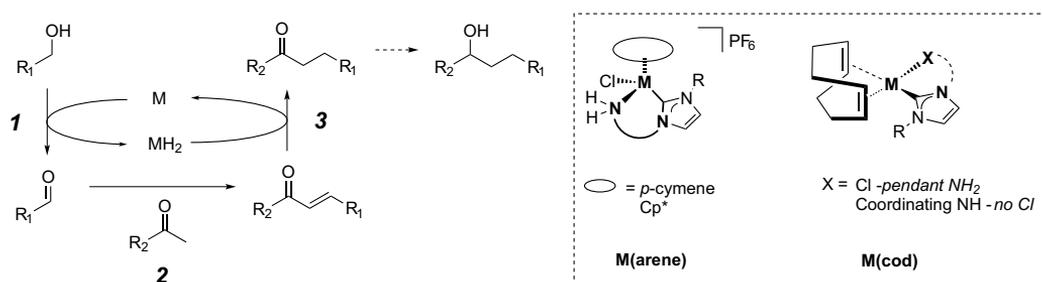


Figure 5. Direct α -alkylation of ketones with alcohols, and the general structure of the catalysts that were applied in this transformation. $\text{M}(\text{cod})$ complexes with a coordinating NH moiety were shown to function as internal base.

Although all catalysts were active in this alkylation reaction, it was found that the selec-

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tivity of the reaction strongly depended on the hydrogenation activity of the catalyst and the choice of substrate. Small substrates sterically allowed for a faster formation of higher alkylated products, while the more bulky substrates led to less side products. For $M(\text{cod})$ ($M = \text{Ir}, \text{Rh}$) complexes the ligands were found to function as internal base, when coordinating in a monoanionic bidentate fashion, replacing the external base needed for this reaction. Two biomass inspired / natural alcohols (ethylene glycol and geraniol) were tested to evaluate the applicability of this reaction in the functionalization of biomass. Although the larger alcohol substrate geraniol was successfully applied in this reaction, selectivity remains an issue that needs to be improved upon in future studies.

The research described in thesis provides an increased insight in the applicability of the NHC-amine ligand scaffold. The fact that the NHC is in conjugation with an amine was shown to make a clear difference in catalytic properties compared to similar non-conjugated systems. Conjugation even influences the intrinsic reactivity, determining whether a complex can be made or not. This understanding of the influence on donor strength of our conjugated NHC-amine contributes to future rational design of catalysts. Furthermore, the application of NHC-amine containing complexes in conversion of polar bonds and direct alkylation reactions functions as basis for further research concerning the application of homogeneous catalysts in the transformation of biomass derived compounds.