Summary

The activation of molecular hydrogen is a key step in many important catalytic reactions, such as the hydrogenation and hydroformylation of alkenes, hydrogen metabolism and nitrogen fixation. This activation is usually achieved by transition metals, either homogeneously or heterogeneously. The crucial influence of the ancillary ligands on the stability, reactivity and selectivity of transition metal complexes is well established. In our group much research has been dedicated to the understanding of the influence of the steric and electronic properties of ancillary ligands on the catalytic performance of transition metal complexes. In particular, a series of wide bite angle diphosphines based on the Xanthene backbone (so called Xantphos type ligands) have been developed (Fig. 1). In this thesis the study of a series of hydride complexes of ruthenium, platinum and palladium, which contain wide bite angle diphosphines, is described.

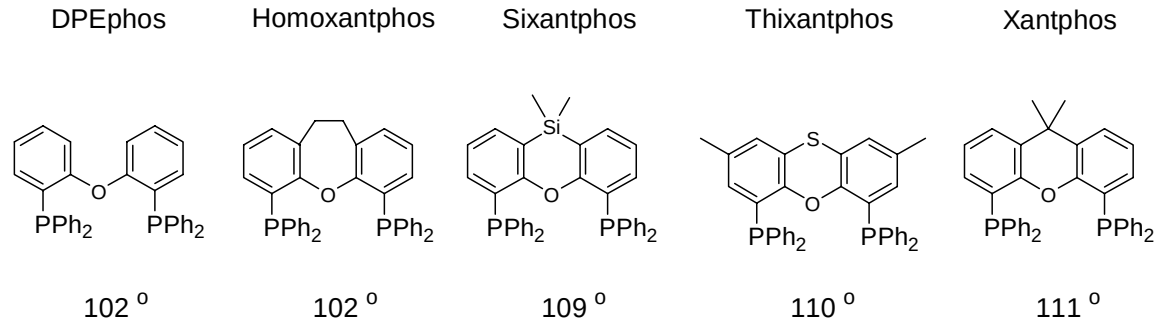
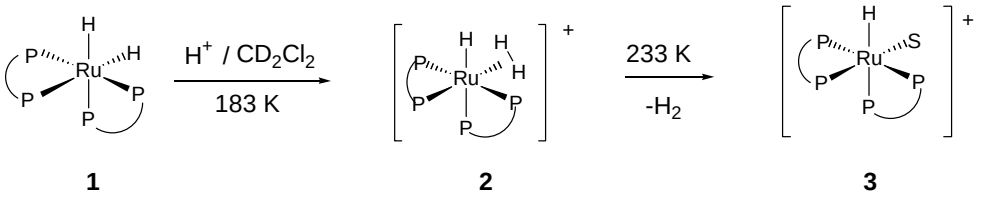


Figure 1. Xantphos-type ligands and natural bite angles.

C*hapter 1* is a bibliographic introduction on proton transfer reactions involving transition metal complexes. The transfer of acidic protons to metal hydrides to form dihydrogen complexes, and the reverse reaction, the heterolytic splitting of dihydrogen is presented. The influence of dihydrogen bonding, this is the electrostatic interaction between metal hydrides and weakly acidic protons, on proton transfer reactions is discussed.

Chapter 2 is dedicated to the study of ruthenium hydrido-dihydrogen complexes (**2**) containing Xantphos-type ligands. The bite angle and electronic properties of the diphosphines are systematically varied. Complexes **2** are prepared by low temperature protonation of the corresponding dihydrides (scheme 1). The presence of a dihydrogen

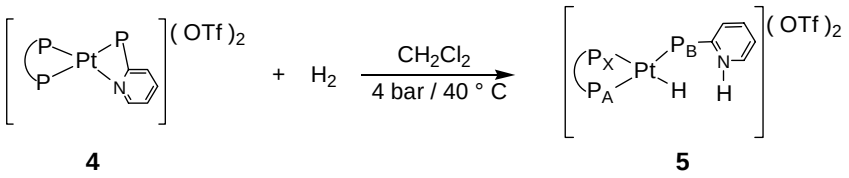
ligand was established by measuring the longitudinal relaxation time (T_1) in ^{1}H NMR. Complexes **2** are thermally unstable towards the loss of dihydrogen, yielding the cationic monohydrides **3**. No influence of the bite angle or the electronic properties of the diphosphines neither on the stability of the dihydrogen complexes nor on the H-H distance was observed. The wide bite angle of the Xantphos-type ligands causes poor orbital overlap between the metal fragment and the η^2-H_2 ligand, leading to reduced π back bonding into the latter ligand. This explains the negligible influence of the electronic properties of the ancillary ligands on the H-H distance.



1 **2** **3**

Scheme 1

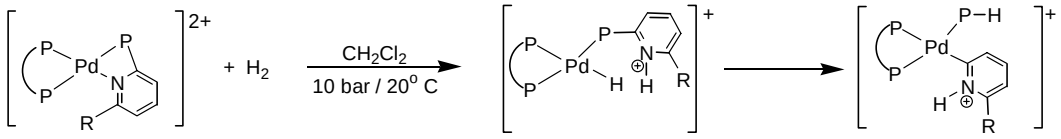
Chapter 3 deals with the coordination chemistry and reactivity towards dihydrogen of a series of platinum (II) complexes containing diphosphine with a wide bite angle and a diphenyl-2-pyridinephosphine (PPh_2Py) ligand (**4**). In complexes **4**, the diphosphine is *cis* –coordinated and the pyridylphosphine acts as a chelating ligand. Xantphos forms both *cis* and *trans* complexes. In the latter case Xantphos acts as a tridentate P, O, P ligand and the pyridylphosphine coordinates via the phosphorus atom only. Complexes **4** are able to activate dihydrogen under mild conditions (4 bar, 40 °C) to yield the hydride complexes **5** (scheme 2). In this reaction, the pyridyl moiety acts as internal base to assist the heterolytic splitting of dihydrogen. Complexes **5** contain both a hydride and an acidic proton (PyH^+) in the same molecule, but no dihydrogen bonds are formed. The relatively electron poor metal center in the dicationic compounds **5** probably decreases the net negative charge of the hydride ligand, which results in a too weak electrostatic interaction between the latter and the pyridinium proton. If the 2-pyridylphosphine ligand is replaced by a 2-aminopyridine ligand, the activation of dihydrogen requires more severe reaction conditions (10 bar, 50 °C). In this case, the heterolytic cleavage of dihydrogen leads to the hydride bridged dimers $[(diphosphine)_2Pt_2H_3]^+$.



4 **5**

Scheme 2

In *chapter 4* the dynamic behavior of palladium complexes analogous to those described in the previous chapter is presented. As for the platinum complexes, the pyridylphosphine acts as a chelating ligand to form the bis-chelate complexes $[(diphosphine)Pd(PPh_2Py)]^{2+}$ (**6**). Once again, with Xantphos both *cis* and *trans* isomers of **6** are formed, which are in fast exchange at room temperature. Complexes **6** react fast with dihydrogen, but the resulting hydride products undergo fast decomposition. In contrast, $[(dppf)Pd(PPh_2Py)]^{2+}$ reacts cleanly with H_2 to form the isolable hydride complex $[(dppf)PdH(PPh_2PyH)]^{2+}$ (**7**). This product slowly decomposes via P-C bond splitting on the pyridylphosphine ligand to yield $[(dppf)Pd(PHPh_2)(C_5H_4NH)]^{2+}$ (**8**, scheme 3). The latter reaction is much faster when a methyl substituent is introduced on the 6-position of the pyridyl ring.

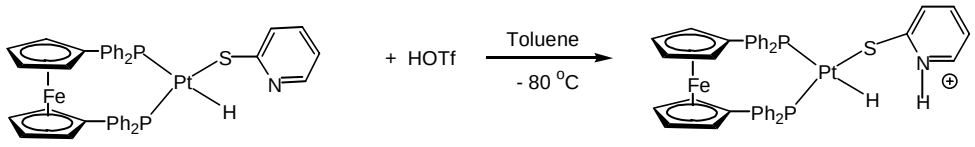


R= H **6** **7** **8**

R= Me **6-Me** **8-Me**

Scheme 3

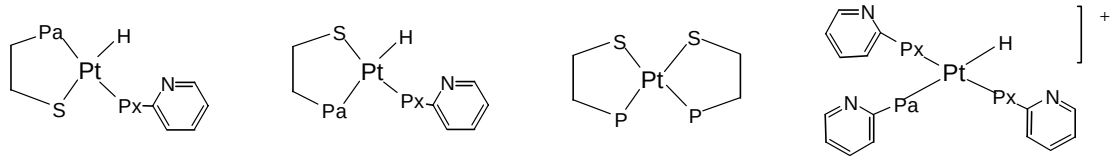
Chapter 5 deals with the study of platinum(II) complexes containing the sulfur-donor ligands pyridine-2-thiolate (Spy) or 2-(diphenylphosphino)ethanethiolate (dppet). These anionic ligands increase the electron density on the metal center compared to that of complexes containing neutral phosphines only (**5**, chapter 3). This would enhance the hydridic character of the hydride and therefore favor an electrostatic interaction with an acidic proton. Protonation of the neutral complex [(dppf)PtH(Spy)] (**9**) occurs at the nitrogen of the pyridyl moiety to yield complex **10** (scheme 4). An NMR study indicates a stronger σ-bond in **10** than in **5**, but no dihydrogen bond could be detected. Nevertheless, IR spectroscopy indicates the presence of a weak Pt-H---H-N interaction.



9 **10**

Scheme 4

The second part of chapter 5 deals with the reaction of $[Pt(PPh_2Py)_3]$ with $PPh_2(CH_2)_2SH$ (Hdppet), which was monitored by NMR. The kinetic product of this reaction is the hydride complex $[(dppet)PtH(PPh_2Py)]$ (**11**). In the presence of an excess of PPh_2Py, **11** undergoes ligand scrambling to form $[Pt(dppet)_2]$ (**12**) and $[PtH(PPh_2Py)_3]^+$(**13**). However, in the absence of free pyridylphosphine, the starting material $[Pt(PPh_2Py)_3]$ is re-formed, together with the bis-chelate complex **12**. The requirement of free PPh_2Py in solution for **13** to be formed indicates that it may act as a "proton transfer agent".



11 *trans* **11** *cis* **12** **13**

Scheme 5

In conclusion, throughout this thesis it was shown that the steric properties of the ancillary ligands play a crucial role on the reactivity of ruthenium, platinum and palladium complexes towards dihydrogen, as well as on the stability and chemical behavior of the resulting hydride or dihydrogen complexes.