1 Introduction

1.1 Ligands - Coordination Chemistry - Catalysis

The term ligand [latin, ligare = bind] has its origin in coordination chemistry. It denotes a molecule that is able to bind to a metal center in most cases *via* one or several free electron pairs.[1] Ligands can be described by the number of electron-pair donor atoms as monodentate, bidentate, tridentate *etc.* ligands. The latter are also called chelating ligands [greek, chele = (crab's) claw]. A typical classification of ligands is according to their electronic properties. They serve either as a σ-donating, σ-donating/π-accepting, or σ,π-donating/π-accepting ligands.[2] A more practical, often encountered approach is the classification of ligands according to their donor atoms, especially when larger molecules and molecules containing heteroatoms are regarded (compare 1.2).

Coordination chemistry was already established in the 19th century. In 1893 Alfred Werner suggested an octahedral arrangement of ligands coordinated to a central metal ion for many compounds. This explained, for example, the appearance and reactivity of four different cobalt(III) complexes (Figure 1.1), when $CoCl_2$ is dissolved in aqueous ammonia and then oxidized by air to the +3 oxidation state. The formulas of these complexes can be written as depicted in Figure 1.1. Werner's work was rewarded with the Nobel prize in 1913.[3]

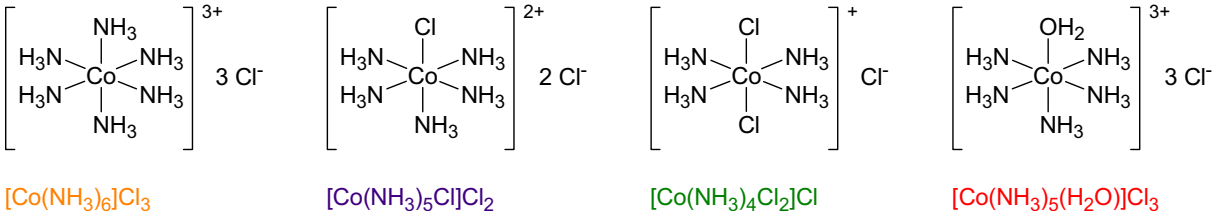


Figure 1.1: *"Werner-complexes"*

Coordination chemistry is mainly chemistry of transition metal compounds. Here, ns-, np- and nd-orbitals are valence orbitals, while the participation of nd-orbitals in main group metal chemistry is the exception. Figure 1.2 shows the different orbital interactions: σ-donating interaction takes place between s, p_z and d_z^2-orbitals of the transition metal and s and p_z orbital of the ligand. π-donating and π-accepting (retrodative) interaction occurs between p_x, p_y, d_{xz}, and d_{xy} atomic orbitals of the transition metal and p_x, p_y, d_{xz}, and d_{xy} of the ligand.

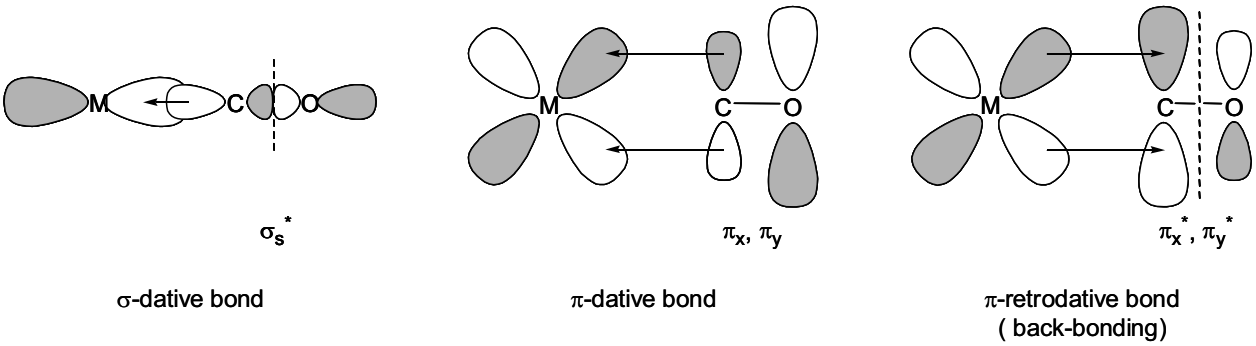


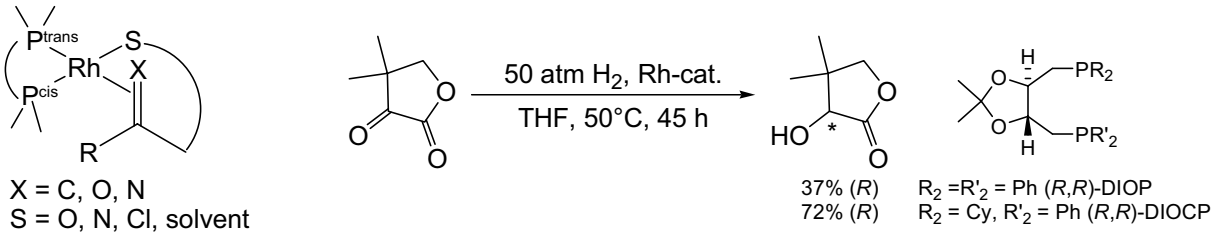
Figure 1.2: Orbital interactions in transition metal complexes

Transition metal complexes play an important role in homogeneous catalysis. Coordination at the metal center brings the reactants in close proximity and thus accelerates the reaction. Sometimes reaction can only take place when one or both reactants are activated through coordination. For example, coordination of a substrate to the metal can facilitate nucleophilic attack at the substrate. If the catalyst is chiral, *e.g.* through coordination of a chiral ligand, it can allow enantioselective syntheses through asymmetric induction. Normally, the metal component activates the reactants, while the chiral ligand is responsible for enantiocontrol.

1.2 Important Ligand-Classes

For a long time, the dominating ligands in asymmetric catalysis were C_2-symmetric.[4] C_2-symmetric ligands lead to fewer isomeric metal complexes in comparison to non-symmetric ligands, and thus to fewer transition states in catalysis. That renders them favourable objects for the determination of reaction mechanisms and the elucidation the origin of the observed asymmetric induction.

However, more recently nonsymmetrical ligands have found increasing attention. In fact, efficient nonsymmetrical ligands were in some reactions superior to C_2-symmetric ligands. This was well illustrated for rhodium-catalyzed asymmetric hydrogenation, where the intermediates in the catalytic cycle are nonsymmetrical (Scheme 1.1, left).[5]



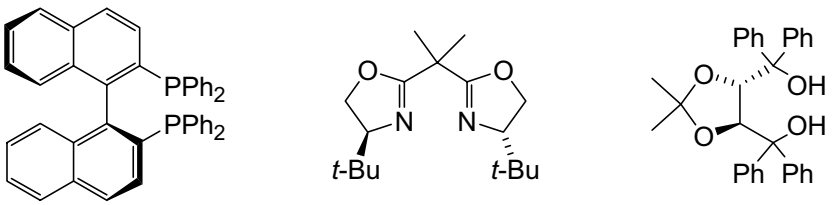
Scheme 1.1: Desymmetrized diphosphine in rhodium-catalyzed hydrogenation

In consequence the two phosphine groups interact with the substrate in a different manner. Since electronic effects are delivered preferentially to the *trans*-coordinated ligand, P^{trans} executes mainly an electronic effect. P^{cis}, in contrast, exerts mainly steric interactions with the substrate. Indeed, DIOCP ligand was more effective than DIOP in the asymmetric hydrogenation of ketopantolactone (Scheme 1.1, right).

1.2.1 P,P-Ligands: Diphosphines

Following several decades of developments, the use of asymmetric catalysis allows nowadays the enantioselective synthesis of numerous biologically active molecules or natural products.[6,7] The first breakthroughs in asymmetric catalysis have been carried out in the field of rhodium-catalyzed homogeneous hydrogenation. The use of C_2-symmetric phosphines as chiral inducers led to the formation of products with significant enantiomeric excesses. Kagan's work using the tartrate-derived diphosphine DIOP, and Knowles', using the P-chiral diphoshine DIPAMP, are the most salient pioneering examples of such catalytic systems (compare 2.1).[8,9]

The most prominent ligand among the diphosphines is probably BINAP **1**, an axially chiral ligand that was developed by Noyori *et al.* in 1980.[10] Being a so-called "privileged" ligand (Figure 1.3),[11] BINAP is used in numerous asymmetric catalytic reactions, such as hydrogenation, Diels-Alder reaction, Mukaiyama aldol reaction, *etc.*, where excellent results are obtained.[12,13,14]



BINAP **1** BOX **2** TADDOL **3**

Figure 1.3: Some "priviledged" ligands

1.2.2 N,N-Ligands: Semicorrins and Bisoxazolines

Chiral C_2-symmetric semicorrins were introduced as ligands in asymmetric catalysis by Pfaltz *et al.*.[15] These ligands were inspired by corrinoid and porphinoid metal complexes, which are known as biocatalysts. The flexibility of the semicorrin ligand framework is restricted by the inherent π-system and the two five-membered rings. The substituents at the two stereogenic centers shield the metal center from two opposite directions. They are expected to strongly influence the reaction taking place in the coordination sphere. Semicorrins were found to give

excellent results in copper-catalyzed cyclopropanation of olefins and cobalt-catalyzed conjugate reduction of α,β-unsaturated carboxylic acid derivatives.[16]

A related structural motive is found in bisoxazoline (BOX) ligands **2**, which were reported independently by several research groups.[17] BOX ligands are especially attractive, because they are easily accessible from amino alcohols which are derived from natural amino acids in enantiomerically pure form. This allows facile structural modification for different applications. More recently, related ligands (borabox, azabox) were developed, which are bearing heteroatoms in the bridge that connects the two oxazoline rings.[18,19]

1.2.3 P,N-Ligands: Phosphinooxazolines

Pfaltz, Helmchen[20] and Williams[21] developed independently a new class of ligands, the phosphinooxazoline (PHOX) ligands **4**. The combination of a P-ligand part and a chiral N-ligand part is another way to build up non-C_2-symmetric, chelating ligands, wherein the two ligand parts are more fundamentally distinguished, compared to the modified diphosphine ligands mentioned in 1.2. Here, the "soft" P-ligand exhibits π-acceptor properties, while the "hard" N-ligand is dominantly acting as a σ-donor. The beneficial effect of the combination of two ligands with different electronic properties is well illustrated in the palladium-catalyzed allylic alkylation (Figure 1.4, left). Crystal structure and NMR data confirmed that palladium-allyl-PHOX complexes exhibit a strong electronic differentiation of the allylic termini, and it was observed that these complexes are predisposed to be attacked at the allylic carbon atom trans to the phosphino group.[20,22] Electronic differentiation of this type has also been calculated by Ward[23] and demonstrated by Moberg *et al.* using *pseudo*-C_2-symmetric ligands (*e.g.* **5**), *i.e.* with sterical symmetry and electronic asymmetry (*e.g.* Figure 1.4, right).[24]

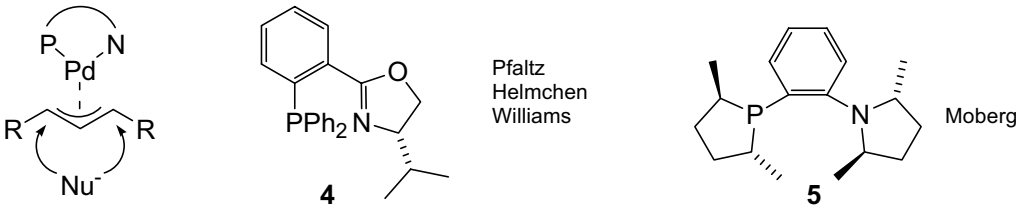


Figure 1.4: Regioselectivity in palladium-catalyzed allylic alkylation (*left*), different P,N-ligands **4** and **5**.[15,24]

PHOX ligands are modularly constructed and can be synthesized in few steps. This enables a relatively easy variation and allows to tailor the ligand according to its application. Apart from allylic alkylation, PHOX ligands were also applied in other metal-catalyzed processes, including Heck reactions,[25] silver-catalyzed 1,3 dipolar cycloaddition,[26] and iridium-

catalyzed hydrogenation.[27] The latter reaction was tested with numerous PHOX analogues, which are able to hydrogenate unfunctionalized aryl- and alkyl-substituted unfunctionalized and functionalized olefins, with high enantioselectivities and at low catalyst loadings.

1.2.4 C-Donor Ligands: *N*-Heterocyclic Carbenes

N-Heterocyclic carbenes (NHCs) were developed independently by Wanzlick[28] and Öfele in 1968.[29] However, it took about twenty years until an adamantyl-substituted carbene was isolated by Arduengo,[30] and only in the mid 1990s NHCs were finally introduced in asymmetric catalysis by Enders[31] and Herrmann.[32] Since then, the scope of catalytic reactions has largely expanded, and NHCs are now applied in a variety of metal-catalyzed asymmetric reactions, such as olefin-metathesis, allylic alkylation, transfer hydrogenation, 1,4-addition and others.[33,34,35,36]

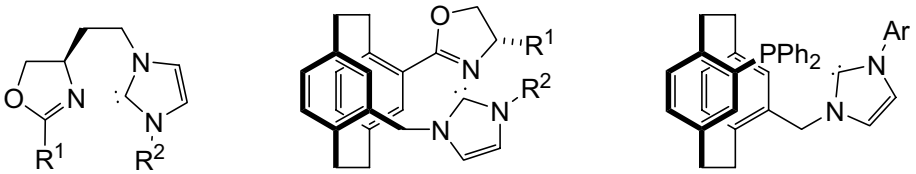


Figure 1.5: Oxazoline-NHC ligand **6** and paracyclophane based NHC chelating ligands **7** and **8**[37,38]

More recently, NHCs were incorporated in chelating P,C- and N,C-ligands, such as **6**-**8** (Figure 1.5), and tested in iridium-catalyzed hydrogenation. Burgess *et al*. reported high enantioselectivities for a range of olefins using a bidentate oxazoline-NHC ligand **6**.[38]

1.3 Objectives of this Work

Although many studies are carried out in order to design new catalysts on a rational basis, finding new selective ligands is also a matter of luck and intuition. Laborious screening is still the major way in obtaining taylor-made catalyst systems for a specific substrate.

Iridium-complexes derived from P,N-ligands represent a highly active class of catalysts for asymmetric hydrogenation. We were interested to extend our library of P,N-ligands (Figure 1.6), and to investigate the influence of a smaller ring-chelate **10**, since most previously tested ligands form six-ring-chelates. Another objective was to examine the effect of a strong π-accepting and planar phosphorus-moiety, as is found in λ^3-phosphinines **11**.

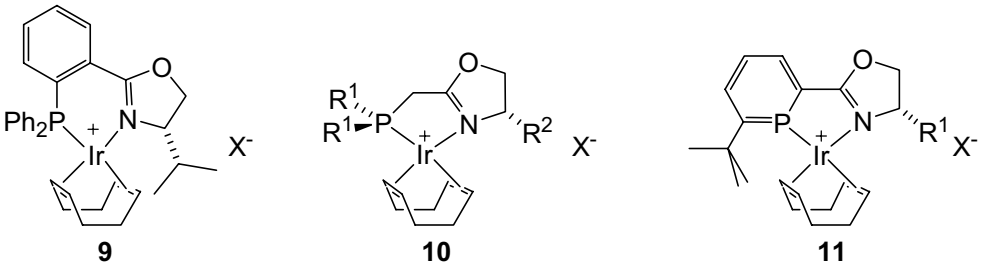
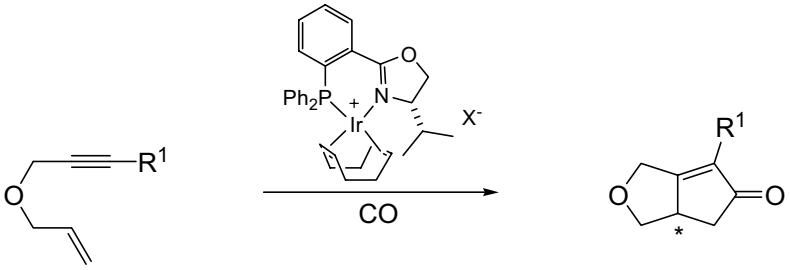


Figure 1.6: Cationic iridium-PHOX complexes

In addition, we were interested in the scope of iridium-PHOX complexes in other catalytic reactions. Initial studies towards the application of this system in asymmetric catalytic Pauson-Khand reaction have shown promising results (Scheme 1.2). The studies were to be completed regarding pressure influence, reproducability and the influence of the counteranion on the enantioselectivity of the reaction.



Scheme 1.2: Iridium-catalyzed asymmetric intramolecular Pauson-Khand reaction

The popularity of NHCs raised the question why their group 14 heavier analogues have not experienced the same attention in catalysis to date.[39] Although Fürstner *et al.* have published the application of a silylene-palladium complex **12** in Suzuki cross-coupling,[40] the actual catalytically active species remains unknown. No further attemps of using silylenes (Figure 1.7) in catalysis have been reported.

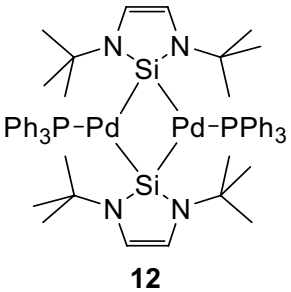


Figure 1.7: Dinuclear palladium-silylene complex **12**[40]

Inspired by the recent success of NHCs in the iridium catalyzed hydrogenation, we envisioned the synthesis of silylene containing iridium- and rhodium-complexes, suitable for hydrogenation studies.