# Summary

PNP Pincer Ligands in Late Transition Metal
Nitrido Chemistry and Gold Catalysis

The role of catalysts in modern day society can hardly be overestimated. They are essential to the production of many valuable and indispensable materials, such as pharmaceuticals, petrochemicals, agrochemicals and polymers. Catalysts enhance reaction rates, lower the required energy, can increase selectivity and reduce the production of waste for a chemical reaction. Because of these properties, catalysts can also reduce the environmental footprint of chemical processes. Homogeneous catalysts often consist of coordination complexes made of a (transition) metal center and coordinating ligands. Studying the coordination chemistry of these complexes can contribute to the understanding of homogeneous catalysts and is therefore of interest for research. A broad palette of spectroscopic methods is available to characterize these compounds, that can have a well-defined structure.

Pincer ligands are characterized by a tridentate coordination mode and a propensity for a *meridional* configuration. This coordination mode usually results in high stability of the metal-pincer complex. This allows them to be used as catalysts for highly endothermic reactions and for fundamental reactivity studies. In **Chapter 1** an overview is provided on the development of monoanionic diarylamine phosphine (PNP) pincer ligands and their application in late transition metal complexes. Examples of the coordination chemistry of these compounds are presented as well as examples in which they function as catalysts for a variety of reactions. The aim and outline for the rest of this thesis are also discussed. The PNP^{iPr} ligand is relevant for all other chapters of this thesis as it is used in the transition metal complexes studied in this thesis.

In **Chapter 2** we present a study on the possibility of the formation of nickel-nitrido species, as well-characterized Group 10 nitrido species are still elusive. Such species may serve as models for intermediates in N_2-splitting or N-transfer reactions. A new Ni(PNP)N_3 complex is used as the starting point for this study. Azido groups (N_3^-) are widely recognized as entry to nitrido species, as activation leads to expulsion of N_2. The synthesis of the complex is described and a full spectroscopic characterization is given. We show that the Ni(PNP)N_3 complex is stable upon (electro)chemical oxidation and at high temperatures. Irradiation of a benzene solution of the complex on the other hand results in a compound in which nitrogen has inserted into a Ni-P bond and benzene C-H activation over the resulting Ni-N bond has taken place (Figure 1). DFT studies are presented and we propose a plausible reaction mechanism, wherein photochemical induced N_2 release leads to a transient nickel-nitrido species. The nitrogen then easily inserts into a Ni-P bond and the resulting coordinatively unsaturated Ni^{II} species can activate the C-H bond of benzene. This step can be thermal or photochemical. Formation of a (transient) nickel-nitrido thus seems feasible, although experiments to trap an 'intact' Ni-N fragment were not successful.
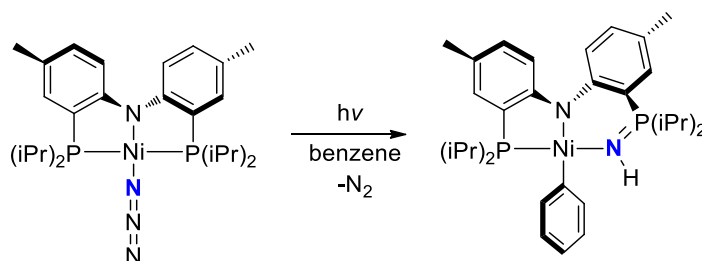
**Figure 1.** Irradiation of Ni(PNP)N_3 ultimately leading to N-insertion and solvent C-H activation

In **Chapter 3** we explore the activation of a Co(PNP)N_3 complex. We compare our studies to previous reports on the activation of Group 9 metal azide complexes, which were shown to result in either intra- or

intermolecular reactivity of the resulting (transient) cobalt nitrido fragments. We also investigate the possibility to detect a cobalt nitrido species with EPR spectroscopy by performing low temperature irradiation experiments. Both thermal and photolytic decomposition of the azide group lead to the same new product. X-ray structure determination shows insertion of one azide N into a Co-P bond, indicating intramolecular reactivity. Different from the nickel analogue, dimerization of two Co compounds takes places, generating a Co_2N_2 core (Figure 2). Also, solvent activation is not observed under photolytic conditions. Monitoring the photolysis with EPR spectroscopy at low temperature does not result in definitive proof for the existence of a transient cobalt-nitrido species. DFT calculations do however indicate that this is a likely intermediate in the reaction. Preliminary reactivity studies indicate that the dimeric product is active for bond activation of phenol and phenylacetylene, generating the corresponding mononuclear four-coordinate species. This is also supported by isolation of the Co(PNPN)Cl species upon reaction of the dimer with HCl.
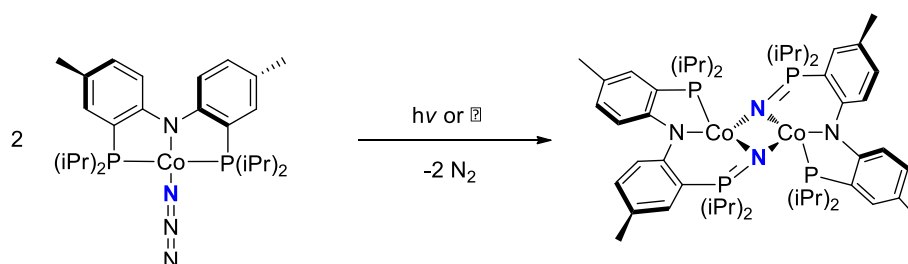
Figure 2. Azide activation by thermolysis or photolysis, leading to a dimeric product.

In **Chapter 4** we use the PNP ligand to prepare a dinuclear $(PNP)Au_2Cl_2$ complex. Selective two-electron oxidation leads to a $(PNP)Au^IAu^{III}$-compound (Figure 3). We describe that this mixed-valent species undergoes a remarkable reaction in the presence of silver salts or $GaCl_3$. The product of the complex reaction sequence is a new bisgold(I) carbazole complex. We use the new $(PNP)Au^I_2$-compounds to investigate the concept of ligand enforced σ,π-activation by preorganization of two gold centers onto the PNP ligand for subsequent activation of alkynes. Previous reports have shown that this dual-activation mode can invoke different selectivity in Au-catalysis as compared to traditional π-activation by mononuclear $[Au]^+$-catalysts. The heterocyclization of a urea-alkyne is selected as a proof-of-principle reaction. We demonstrate that ligand enforced proximity of two Au-centers results in high selectivity towards the product of σ,π-activation, even at low catalyst loadings. Furthermore, we show that this approach is not suitable for other forms of dual-activation.
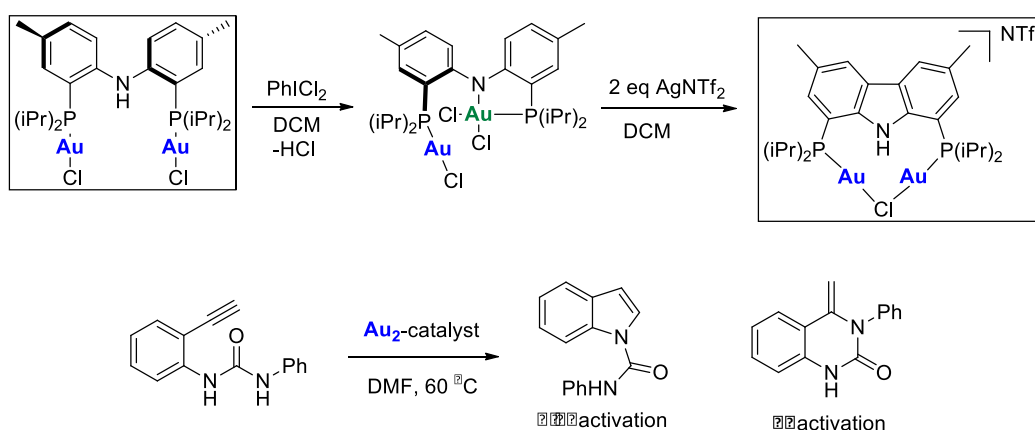
Figure 3. Top: Synthesis of $(PNP)Au_2$-complexes. Au^I in blue, Au^{III} in green. Bottom: Au-catalyzed proof-of-principle reaction with products of different activation-modes.

The mechanism behind the reaction we describe in Chapter 4 involving the Ag^+-induced conversion of a mixed-valent $(PNP)Au^IAu^{III}$ compound to a carbazole $(PNP)Au^I_2$ complex (depicted in Figure 3) is subject of further

investigation in **Chapter 5**. This reaction is of specific interest because of the new type of *ortho* redox reactivity exhibited by the PNP ligand. We show that it is possible to break this transformation down in a set of efficient stoichiometric reactions. Addition of a halide abstracting agent initially leads to a tetragold complex with the scavenging element sequestered between two Au_2 units. A Brønsted acid induced disproportionation reaction results in a Au^IAu^I and a $Au^{III}Au^{III}$ species (Figure 4). The latter forms the carbazole product when a proper two-electron reductant is added, while the former can be converted into the $Au^{III}Au^{III}$ compound in a four-electron oxidation reaction. The combined information gathered from the stoichiometric reactions results in the proposal of a mechanism for the scrutinized reaction.
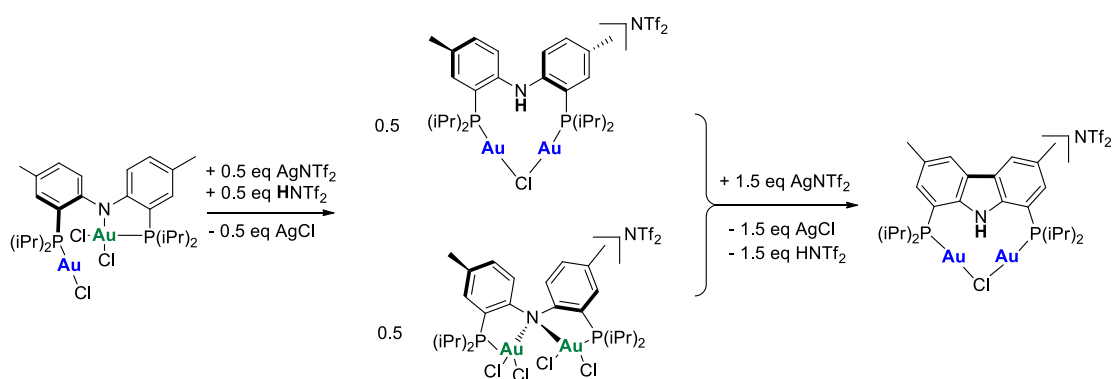
Figure 4. Part of the reaction mechanism described in Chapter 5.

With the research described in this thesis two new examples of transient Co- and Ni-nitrido complexes have been identified. This has (further) established the accessibility of such species. This research can therefore serve as a foundation for future investigations into Co and Ni complexes with multiple bonded ligands (N, O or S). Spectroscopic characterization of the proposed species remains elusive and still requires attention in future studies. Substituting the phosphine atoms in the ligand for other donor atoms (such as N) could be an interesting strategy to prevent the internal entrapment of the transient nitrido and offer a way for characterization of these species. The same strategy may be applied to achieve intermolecular reactivity with substrates for N-transfer chemistry, using the transient metal nitridos as terminal oxidants.

Au(I) catalysis by σ,π-activation can be used to obtain different product selectivity compared to mononuclear gold chemistry. In this thesis we have introduced a new concept to enforce this activation mode through ligand preorganization of two Au(I) centers. Finding the exact reason for the different selectivity of σ,π-activation compared to π-activation would be a useful basis for future studies. These studies should focus on expanding the substrate scope and the development of more active catalysts.