# Summary

Many homogeneous and heterogeneous catalyst systems contain one or more transition metals. The widespread employment of these metals as catalysts is ascribed to their accessible *d*-orbitals to activate chemical bonds, and the ability to undergo metal-based oxidation state changes to facilitate desirable chemical transformations. The fine-tuning of homogeneous catalyst systems is commonly achieved by the coordination of (spectator) ligands, which can vary greatly in steric bulk or electron-donating ability. For such ligands the energy required for oxidation or reduction of the ligand is much bigger than that needed to change the oxidation state of the metal. Accordingly, the redox changes required for bond making and breaking processes typically occur at the metal center. Redox-active ligands have more energetically accessible levels for reduction and/or oxidation upon coordination to a metal. As a result, either solely ligand-centered redox processes can occur, with the metal center remaining in the same oxidation state, or more diffuse scenarios, wherein both the ligand and metal change oxidation states in a synergistic fashion. Although initially thought of as a spectroscopic curiosity, redox-active ligands are nowadays recognized for their ability to induce new reactivity at metal centers. In **Chapter 1** an overview is provided how these ligands can be used in stoichiometric and catalytic chemical transformations. Within this thesis we present new avenues for redox-active ligands that allow to expand upon a late transition metal's "common" reactivity.

In **Chapter 2** we introduce a new tridentate *o*-aminophenol-derived redox-active pincer ligand (**NNO**$^{\text{H2}}$). Coordination to Pd$^{\text{II}}$ under aerobic and basic conditions leads to a paramagnetic PdCl(**NNO**$^{\text{ISQ}}$) complex bearing an unreactive ligand-centered radical (Scheme 1, top). Notably, this complex can undergo fully reversible ligand-based one-electron reduction and oxidation events without changing the formal oxidation state of Pd. The one-electron reduced [PdCl(**NNO**$^{\text{AP}}$)]$^-$ is a highly reactive diamagnetic compound that can induce odd-electron reactivity on Pd$^{\text{II}}$. Utilizing a concept coined "intramolecular ligand-to-substrate single-electron transfer", reactive substrate-centered radicals can be generated (Scheme 1, bottom). To demonstrate the proof-of-principle reactivity using this ligand-based electron transfer concept, the intramolecular *sp*$^3$ C−H amination of an alkyl azide to generate a pyrrolidine species is demonstrated. A combined experimental and computational study showed that the redox-active **NNO** ligand dictates single-electron reactivity onto Pd$^{\text{II}}$, enabling radical-type pathways using a metal that is normally disposed to facilitate two-electron processes.
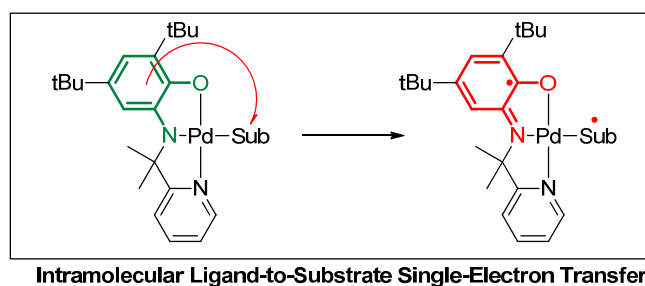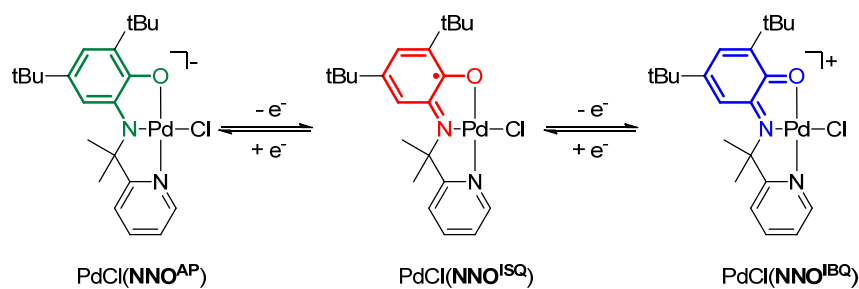
**Scheme 1.** Top: Redox states of Pd$^{II}$-coordinated **NNO** ligand. Bottom: Concept of intramolecular ligand-to-substrate single-electron transfer.

A simple methodology to prepare two unique mono-atomic bridged dinuclear palladium diradical species with either a chlorido or 1,1-azido bridgehead is described in **Chapter 3** (Scheme 2). The mononuclear species PdCl(**NNO$^{ISQ}$**) apparently has the tendency to form dinuclear systems upon halide abstraction in the absence of an exogenous ligand, which is the driving force behind the formation of the dinuclear diradicals. The respective solid state structures of the chlorido or 1,1-azido bridged species illustrate how the bridging motif affects the overall geometry of the dinuclear constructs. Most prominent is the difference in the Pd-X-Pd angle of 93° (X = Cl) and 120° (X = 1,1-N$_3$). The short Pd---Pd distance in the chlorido complex allows for an intramolecular $d^8$-$d^8$ interaction, which is supported by DFT calculations. Moreover, combined solid state and solution EPR spectroscopy as well as SQUID magnetometry data demonstrate how a subtle variation of the bridging ligand can have a significant effect on the electronic spin state of these mono-bridgehead dinuclear diradicals. The chlorido bridgehead allows for moderate spin-exchange coupling ($J$ = -62.9 cm$^{-1}$) and a singlet ($S$ = 0) ground state in the solid state, whereas for the 1,1-azido-bridged complex two independent $S$ = ½ spin carriers are observed that do not show a magnetic interaction. In solution, both complexes behave as systems with two independent $S$ = ½ spin carriers, due to unhindered rotation around the M-X-M linkage.
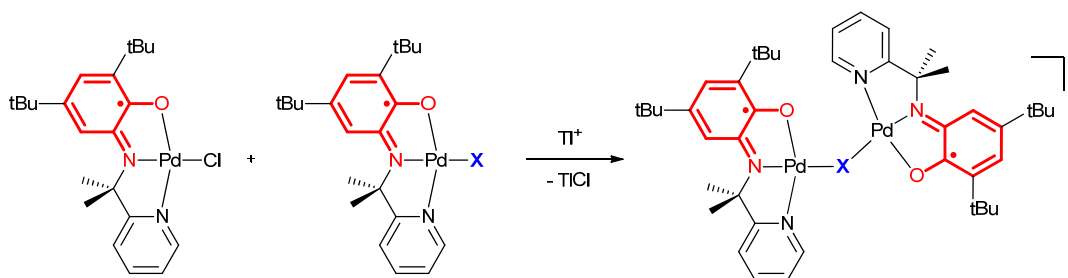
**Scheme 2.** Synthesis of monoatomic bridged dinuclear diradical Pd complexes (X = Cl or $N_3$) derived from mononuclear building blocks upon halide abstraction and consecutive trapping of Pd[($NNO^{ISQ}$)]$^+$.

As a follow-up of the work described in Chapter 3, a new rigid dinucleating redox-active ligand ($L^{H4}$), bearing two redox-active NNO-binding pockets and a triazole linker between both ligand fragments, is described in **Chapter 4**. Coordination of $L^{H4}$ to Pd resulted in the formation of a dinuclear paramagnetic Pd complex with a $\kappa^2$-*N,N'* bridging triazole and a single bridging chlorido ligand (Scheme 3). The latter is easily exchanged for a bridging 1,1-azido ligand. A combined crystallographic, spectroscopic, electrochemical and computational study confirmed Robin-Day Class II ligand-based mixed valence with little influence upon changing the secondary bridging anionic ligand. Selective one-electron oxidation allowed for isolation of the corresponding cationic diradicals. SQUID measurements of these compounds have revealed weak antiferromagnetic spin exchange between the two ligand radicals and an overall singlet ground state in the solid state, which is supported by DFT calculations. The limited influence of the secondary X-type ligand on the intramolecular electronic communication is attributed to the rigid nature of the dinucleating ligand framework.
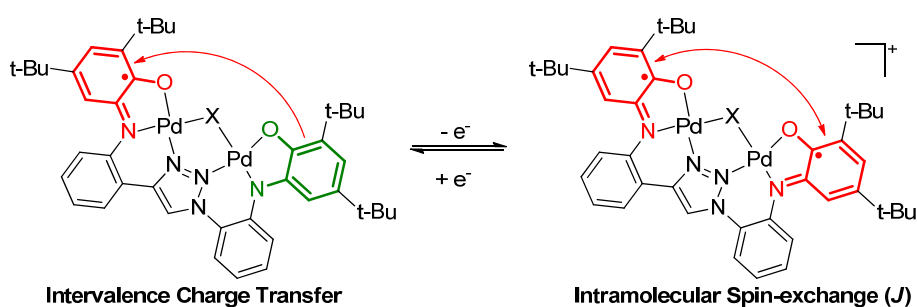


**Scheme 3.** Structure of the ligand-based mixed valent dinuclear Pd complexes, which exhibit an intervalence charge transfer band, and the corresponding one-electron oxidized diradical species, displaying intramolecular antiferromagnetic coupling. X = Cl or $N_3$.

Inspired by the recent progress in the generation of (transient) late transition metal nitrido- and nitridyl complexes, we decided to investigate the mono- and dinuclear azido complexes described in Chapter 3 towards azide decomposition, which is described **Chapter 5**. Upon one-electron oxidation of the mononuclear complex PdN$_3$(**NNO$^{ISQ}$**), the corresponding dinuclear 1,1-azido bridged diradical species, previously prepared via the route in Scheme 2, was cleanly generated. The exact mechanism, which includes the evolution of N$_2$, remains unclear but likely involves a reactive radical intermediate, as the presence of an H-atom donor impedes the reaction. Irradiation of the 1,1-azido bridged dinuclear diradical complex with high intensity UV light leads to the corresponding amido bridged dinuclear diradical species, which was crystallographically characterized (Figure 1). The proposed mechanism, which is based on DFT calculations, involves the formation of a nitridyl radical upon loss of N$_2$ by intramolecular ligand-to-nitrido electron transfer and two H-atom abstraction steps. Isotopic labeling experiments indicate that the source of H-atoms is likely adventitious water present in the reaction mixture. Future research is required to gain insight into the exact mechanism of the decomposition of these azido complexes.
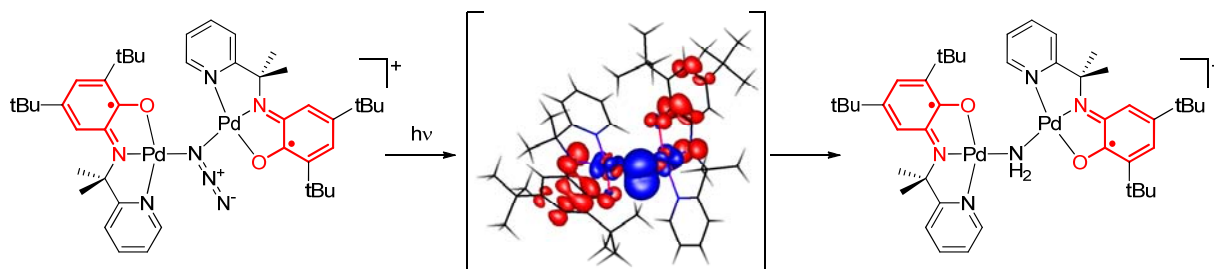


**Figure 1.** Photolysis with high intensity UV light of 1,1-azido-bridged dinuclear diradical results in the formation of a transient nitridyl radical complex, which upon two H-atom abstractions results in the formation of a bridged amido species.

The first example of a phosphine ligand appended to an redox-active aminophenol framework is described in **Chapter 6**. This **PNO$^{H2}$** pincer ligand can coordinate to Pd$^{II}$ as a neutral, radical monoanionic or dianionic scaffold, as supported by spectroscopic, X-ray diffraction and computational data. Cyclic voltammetry and spectroelectrochemistry demonstrate fully reversible ligand-based single-electron redox-events for complex PdCl(**PNO$^{ISQ}$**). There is a subtle but significant change in the redox potentials upon switching from **NNO** to **PNO**. The bulky phosphine arm and the relatively rigid backbone enforce considerable steric crowding around the Pd center compared to the **NNO** analogue described in Chapter 2. One-electron reduction generates complex [PdCl(**PNO$^{AP}$Pd**)]$^-$, which upon chloride abstraction is a competent reagent for homolytic bond activation of disulfides via ligand-to-substrate single-electron transfer (Scheme 4). The resulting dinuclear Pd-species contains a monothiolate bridgehead and an interesting mixed-valent ligand set, with one **PNO$^{ISQ}$** and one **PNO$^{AP}$**

unit. The presence of the flanking phosphine group in the **PNO**^H2 ligand could allow for expanding the concept of ligand-induced electron-transfer and radical-type reactivity to "softer" low-valent noble metals.
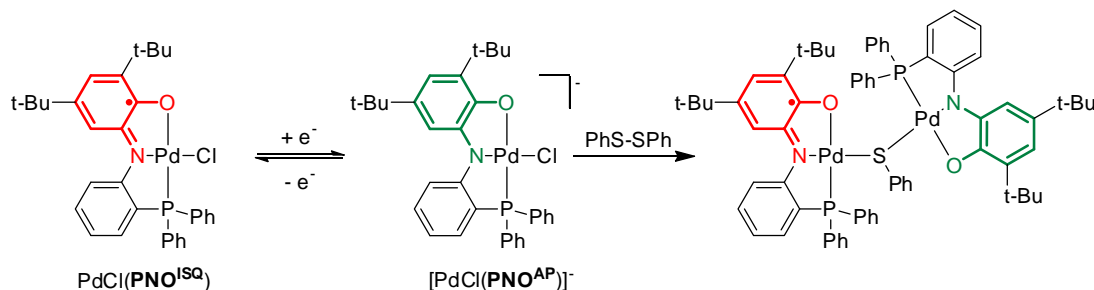


**Scheme 4.** The PdCl(**PNO**^ISQ) species that upon one-electron reduction is capable of homolytic disulfide activation to form a ligand-based mixed valent dinuclear Pd complex with a bridging thiolate.

In **Chapter 7** we utilized the difference in Lewis basicity of the three donating atoms in the **PNO**^H2 ligand to prepare unique diamagnetic trinuclear $Au^I$-$Ni^{II}$-$Au^I$ and dinuclear $Au^I$-$Ni^{II}$ complexes (Figure 2). A combination of spectroscopic, X-ray diffraction and computational data shows that both complexes contain two antiferromagnetically coupled ligand-centered radicals as well as intramolecular $d^8$-$d^{10}$ interactions between the $Ni^{II}$ and $Au^I$ atoms. Both complexes show rich electrochemistry, but only the trinuclear complex is able to electrocatalytically activate carbon-halogen bonds with subsequent C-C bond formation. It appears that the nature of the nickel-gold interaction in these heterobimetallic species plays an important role in facilitating the electrocatalytic activity. A preliminary computational study shows that two-electron reduction results in the weakening of the intramolecular $d^8$-$d^{10}$ interaction in the trinuclear complex whereas it is strengthened in the dinuclear complex. Future research is required to elucidate and understand this phenomenon and to rationalize why only the trinuclear species engages in carbon-halogen bond activation.
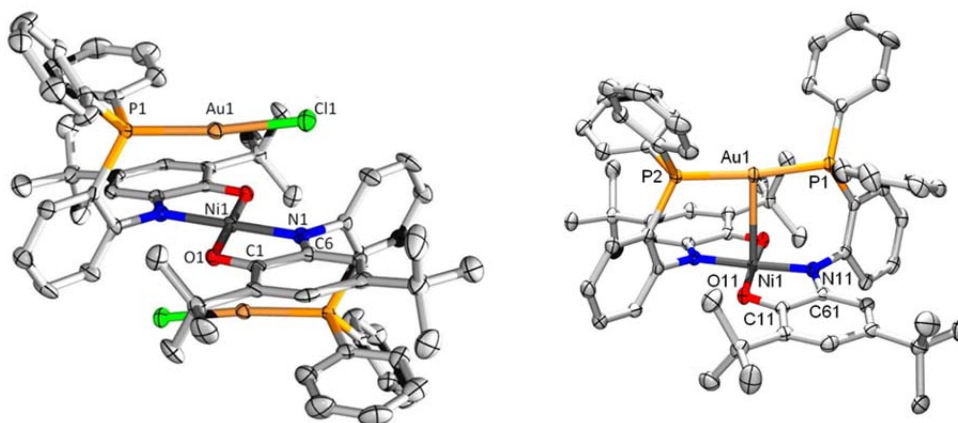


**Figure 2.** Displacement ellipsoid plots (50% probability level) of the trinuclear Au-Ni-Au and dinuclear Au-Ni complexes.

Throughout this thesis we have shown that *o*-aminophenol derived architectures can give fascinating spectroscopic properties upon coordination to late transition metals. Moreover, these ligands can expand upon a metal's "common" reactivity by actively taking part in intramolecular redox processes. We have demonstrated that intramolecular single-electron transfer processes can facilitate homolytic bond cleaving reactions and the generation of reactive nitrogen-centered radicals. Further development of these new concepts should allow for facilitating unprecedented chemical transformations.