

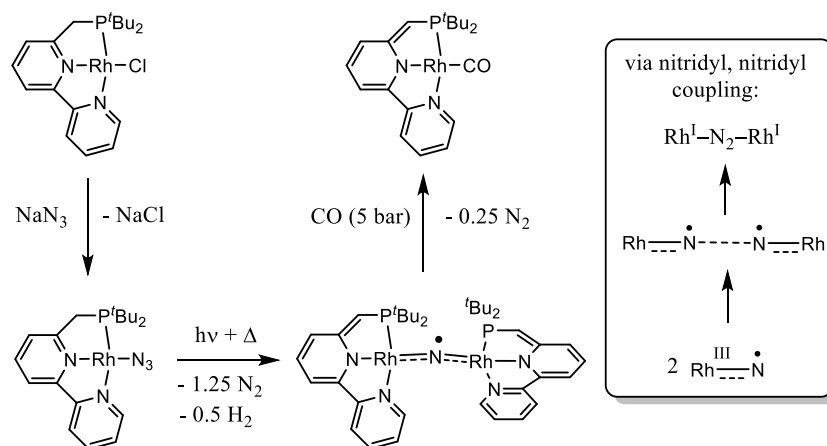
Summary

The Radical-type Chemistry of Rhodium and Iridium Complexes with 'non-innocent' Nitrido and PNN Pincer Ligands

In this Thesis our efforts to synthesize and study group 9 nitrido and nitridyl radical complexes are described. Several new complexes have been isolated and/or characterized by (inter alia) X-ray diffraction, multinuclear NMR and IR spectroscopy, electrochemistry and mass spectrometry and supported by DFT calculations.

In **Chapter 1** we give a brief introduction in the field of catalysis, followed by a more in-depth analysis of dinitrogen fixation. We then discuss the role of metal nitrido complexes ($M\equiv N$) in the field of dinitrogen fixation. The characteristics and bonding of nitrido complexes is described, and we discuss the difficulties in obtaining $M\equiv N$ complexes of late transition metals. Both isolated examples as well as reactive intermediates of $M\equiv N$ (and $M=N\cdot$) are presented and discussed. Furthermore, we give an overview of tridentate pincer ligands in the field of catalysis, followed by an introduction of the ligands applied in the research conducted in this Thesis, namely the PNNH (-di-(*tert*-butyl)phosphinomethyl-2,2'-bipyridine) and PNP (2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) ligand.

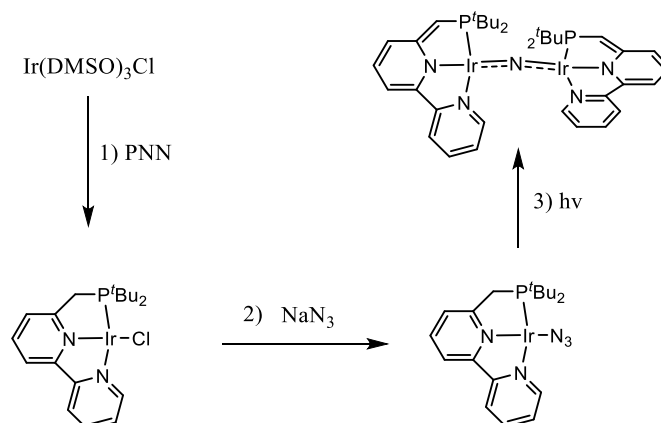
In **Chapter 2** we demonstrate that photochemical activation of $[Rh(N_3)(PNNH)]$ produces the paramagnetic ($S = 1/2$) $[(PNN)Rh=N\cdot-Rh(PNN)]$ (PNN^- = methylene-deprotonated PNNH), which could be crystallographically characterized. Spectroscopic investigation of $[(PNN)Rh=N\cdot-Rh(PNN)]$ indicates predominant bridging nitridyl radical ($\cdot N^{2-}$) character, which is confirmed computationally. This nitridyl complex reacts selectively with CO, producing two equivalents of $[Rh^I(CO)(PNN)]$, presumably by nitridyl radical N–N-coupling (Scheme 1).



Scheme 1. Synthesis of $[(PNN)Rh=N\cdot-Rh(PNN)]$ and its reactivity with CO.

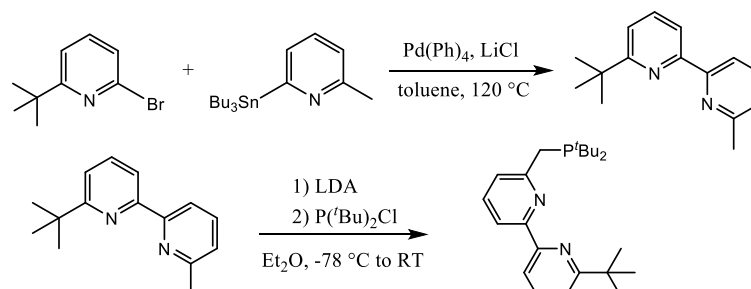
In **Chapter 3** we build on the results described in Chapter 2. The Chapter describes our efforts to investigate the effect of replacing rhodium by iridium, as well as the application of a new PNN ligand on the formation of bridging nitridyl species. Photochemical activation of $[(Ir(N_3)(PNNH)]$ produces the paramagnetic ($S = 1/2$) species $[(PNN)Ir=N\cdot-Ir(PNN)]$ from an analogous reaction as its rhodium congener (Scheme 2). Spectroscopic investigations indicate that $[(PNN)Ir=N\cdot-Ir(PNN)]$ has predominant bridging nitridyl radical ($\cdot N^{2-}$) character, which is confirmed computationally. Like its rhodium congener, $[(PNN)Ir=N\cdot-Ir(PNN)]$ reacts selectively with CO producing two equivalents of

$[(\text{Ir}^{\text{I}}(\text{CO})(\text{PNN}))]$, presumably by nitridyl radical N–N coupling. Hence, changing the metal from rhodium (Chapter 2) to iridium (Chapter 3) does not result in large differences in reactivity.



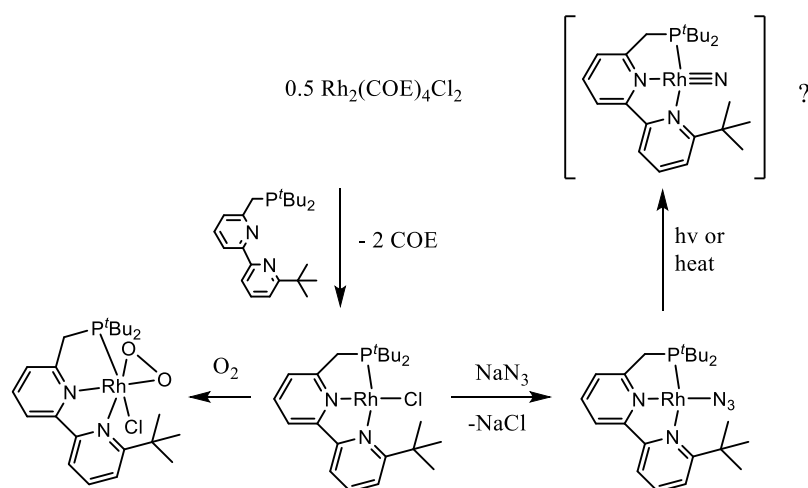
Scheme 2. Synthesis of $[(\text{Ir}(\text{Cl})(\text{PNNH}))]$, $[(\text{Ir}(\text{N}_3)(\text{PNNH}))]$ and $[(\text{PNN})\text{Ir}=\text{N}\cdot\text{Ir}(\text{PNN})]$.

In an attempt to synthesize a mononuclear rhodium nitridyl complex with a reduced tendency to undergo nitridyl radical N–N coupling, we describe the synthesis of a bulky analog of the bipyridine-based PNNH ligand used in Chapter 2, bearing a *tert*-butyl group at the 6'-position of the bipyridine moiety. This new bulky ${}^t\text{Bu}_3\text{PNNH}$ ligand is accessible via a three-step synthetic route, involving a selective nucleophilic substitution step, followed by a Stille coupling and a final hydrophosphination step to afford the desired 6-(*tert*-butyl)-6'-((*di-tert*-butylphosphino)methyl)-2,2'-bipyridine (${}^t\text{Bu}_3\text{PNNH}$) ligand (Scheme 3).



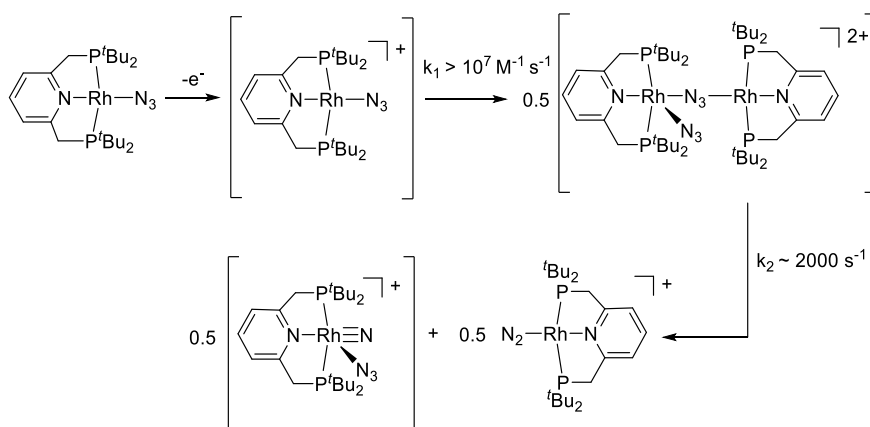
Scheme 3. Synthetic scheme toward the new ${}^t\text{Bu}_3\text{PNNH}$ ligand.

This newly developed ${}^t\text{Bu}_3\text{PNNH}$ ligand is used for the synthesis of sterically protected rhodium(I) azido complex $[\text{Rh}(\text{N}_3)({}^t\text{Bu}_3\text{PNNH})]$ (Scheme 4). Photolysis and thermolysis of this complex are investigated in an attempt to synthesize a mononuclear rhodium complex with a terminal nitrido moiety (Scheme 4). Unfortunately, characterization of the reaction product(s) using multinuclear NMR, cold-spray HR ESI-MS and EPR spectroscopy turns out to be inconclusive, leading to questions regarding the composition of this newly formed species, which is both EPR- and NMR-silent. Interestingly, data obtained by MS spectrometry reveal a dinuclear complex of which the structure could not be precisely determined. Unfortunately, despite several attempts, we have been unable to grow crystals suitable for X-ray diffraction studies. As a result, the molecular structure of this paramagnetic complex remains unknown.



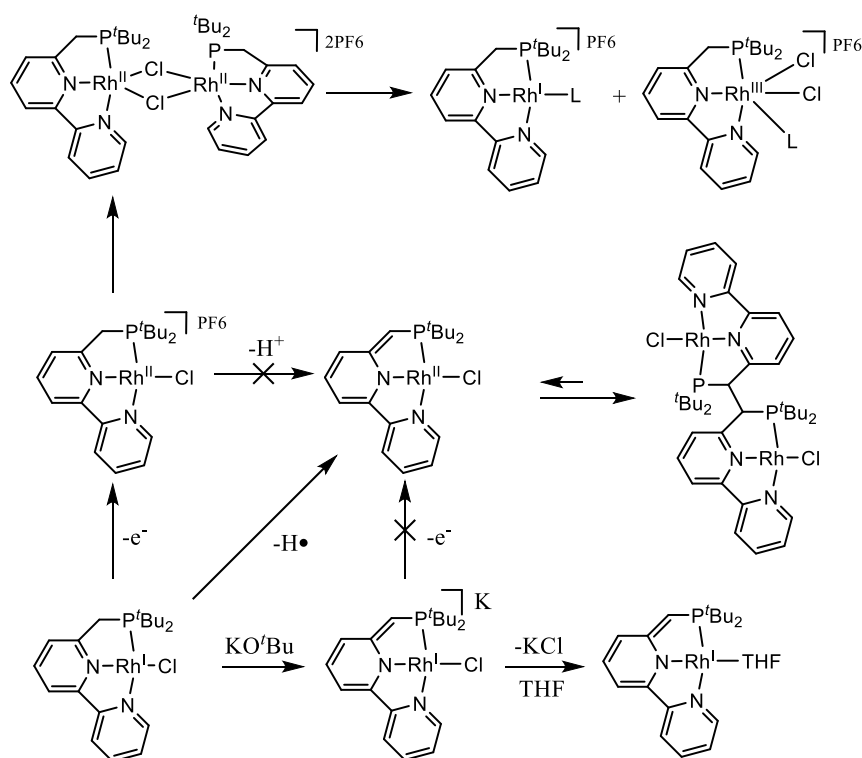
Scheme 4. Synthesis of $[\text{Rh}(\text{N}_3)(\text{tBu}_3\text{PNNH})]$ and the attempts to synthesize a terminal rhodium nitrido.

In **Chapter 4** we describe our efforts to investigate the effects of replacing the PNN rhodium complexes as described in Chapters 2 and 3 by a PNP rhodium complex on the reactivity of azido and nitrido/nitridyl species. As such we explore the reactivity of a $[\text{Rh}(\text{N}_3)(\text{PNP})]$ complex (Scheme 5), with the aim of synthesizing and characterizing a rhodium nitrido/nitridyl complex. One-electron oxidation of the rhodium(I) azido complex $[\text{Rh}(\text{N}_3)(\text{PNP})]$ leads to instantaneous and selective formation of the mononuclear rhodium(I)-dinitrogen complex $[\text{Rh}(\text{N}_2)(\text{PNP})]^+$. Interestingly, the $[\text{Rh}(\text{N}_3)(\text{PNP})]$ complex also acts as a catalyst for electrochemical N_3^- oxidation in the presence of excess azide at a substantially lower potential ($E_p \sim -0.23 \text{ V vs. Fc}^{+/0}$) than direct oxidation at a Pt-electrode ($E_p \sim +0.19 \text{ V vs. Fc}^{+/0}$). Cyclic voltammetry in the presence of an excess of tetrabutylammonium azide $[\text{N}(\text{nBu})_4]^+\text{N}_3^-$ reveals that electrocatalytic N_3^- oxidation occurs at roughly the same potential as the first oxidation wave of the $[\text{Rh}(\text{N}_3)(\text{PNP})]$ complex. The mechanism of azide oxidation is not straightforward. Unlike expected direct N_2 -loss from $[\text{M}^{\text{II}}(\text{N}_3)(\text{PNP})]^+$, followed by dinuclear N–N coupling of two nitridyl species, as was reported in related earlier work with neutral complexes ($\text{M} = \text{Rh}, \text{Ir}$), the cationic rhodium(II)-azido $[\text{Rh}(\text{PNP})(\text{N}_3)]^+$ seems to react via a different pathway. IR spectroelectrochemistry, CV simulations, EPR spectroscopy and supporting DFT studies all point to a route involving the coupling of two $[\text{Rh}(\text{PNP})(\text{N}_3)]^+$ complexes to produce the mixed-valent dinuclear $[(\text{PNP})\text{Rh}^{\text{I}}(\mu-(1,3)\text{-N}_3)\text{Rh}^{\text{III}}(\text{N}_3)(\text{PNP})]^{2+}$, which fragments via N–N bond splitting to form $[\text{Rh}^{\text{I}}(\text{N}_2)(\text{PNP})]^+$ and $[\text{Rh}^{\text{V}}(\text{N})(\text{N}_3)(\text{PNP})]^+$. Subsequent intramolecular azide attack at the terminal nitrido moiety of the formally rhodium(V) intermediate $[\text{Rh}^{\text{V}}(\text{N})(\text{N}_3)(\text{PNP})]^+$ then produces a second equivalent of $[\text{Rh}^{\text{I}}(\text{N}_2)(\text{PNP})]^+$ (Scheme 5). This mechanism deviates substantially from the mechanisms described in Chapters 2 and 3, and shows that replacing the PNNH/PNN⁻ ligand system by a neutral PNP ligand has a profound effect on the reactivity of the corresponding rhodium azido and nitrido/nitridyl complexes.



Scheme 5. Proposed reaction pathway after oxidation of $[\text{Rh}(\text{N}_3)(\text{PNP})]$, including the formation of transient azido-nitrido intermediate $[\text{Rh}^{\text{V}}(\text{N})(\text{N}_3)(\text{PNP})]^+$. Rate constants estimated from CV simulations and supporting DFT calculations.

In **Chapter 5** we describe our efforts to explore the chemical non-innocence of the PNNH ligand on the reactivity of the corresponding rhodium complexes. Hydrogen atom abstraction of $[\text{Rh}(\text{Cl})(\text{PNNH})]$ using with the 2,4,6-*tert*-butylphenoxy radical in toluene produces the diamagnetic dinuclear complex $[\text{Rh}(\mu\text{-Cl})(\text{PNN})]_2$ (Scheme 6). ^1H NMR, X-ray crystallography studies and supporting DFT calculations show that this diamagnetic dinuclear complex is held together by a slightly elongated C–C bond and π - π interactions of the bipyridine rings. At elevated temperatures the C–C bond can be broken, forming two mononuclear paramagnetic $[\text{Rh}(\text{Cl})(\text{PNN})]$ complexes. Upon cooling, these couple again to regenerate the diamagnetic dimer. The mononuclear $[\text{Rh}(\text{Cl})(\text{PNN})]$ complex reacts with water, after which $[\text{Rh}(\text{Cl})(\text{PNNH})]$ is formed, together with an unidentified product, which is presumably the corresponding hydroxide complex.



Scheme 6. Synthesis of $[\text{Rh}(\mu\text{-Cl})(\text{PNN})]_2$ by hydrogen atom abstraction from $[\text{Rh}(\text{Cl})(\text{PNNH})]$, and the fate of the attempts to synthesize it via separate oxidation and deprotonation steps.

Two-step procedures to prepare $[\text{Rh}(\mu\text{-Cl})(\text{PNN})]_2$ out of $[\text{Rh}(\text{Cl})(\text{PNNH})]$ by separate deprotonation and oxidation steps do not result in formation of $[\text{Rh}(\mu\text{-Cl})(\text{PNN})]_2$. Oxidation of $[\text{Rh}(\text{Cl})(\text{PNNH})]$ leads to a disproportionation reaction in which Rh^{I} and a Rh^{III} species are formed. Deprotonation of $[\text{Rh}(\text{Cl})(\text{PNNH})]$ with potassium *tert*-butoxide results in precipitation of KCl from the solution with selective formation of a new, neutral product, containing a methylene-deprotonated PNN^- ligand. HR ESI-MS reveals coordination of THF as the ancillary ligand. Moreover, $[\text{Ir}(\text{PNN})(\text{THF})]$ was synthesized as well and both $[\text{M}(\text{PNN})(\text{THF})]$ complexes ($\text{M} = \text{Rh}, \text{Ir}$) have been tested as catalysts for the coupling of amines with alcohols, and for the acceptorless dehydrogenation of alcohols. Complex $[\text{Ir}(\text{PNN})(\text{THF})]$ is slightly active as an alcohol dehydrogenation catalyst, but overall performance is worse than earlier established systems.

In conclusion, this thesis describes the first two examples of isolated nitridyl radical complexes. The unique combination of the right amount of steric congestion and the redox activity of the *PNNH* ligand allows the formation of these bridging nitridyl species. Different ligand systems with more steric congestion give rise to different reactivity of the azido complexes, such as an intramolecular reaction between an azido and the nitrido groups. Although the field of late transition metal nitride/nitridyl complexes has been significantly expanded, a well-characterized $\text{Rh}\equiv\text{N}$ complex (or its nitridyl analog) stable at room temperature, is still elusive. In the future, efforts could be made in subtly changing the electronic and steric parameters of the ligand system, perhaps allowing such a species to be stable enough for X-ray diffraction studies. Such follow-up studies might also enable application of $\text{Rh}\equiv\text{N}$ species (or their nitridyl analogs) in catalysis.

The chemical non-innocence of the *PNNH* ligand has been established as well. Hydrogen atom transfer reactivity leads to a partially carbon-centered radical complex that can reversibly dimerize by forming a C–C bond. Such complexes, which store an electron pair, could be applied in reversible generation of ‘ligand radicals’, rhodium(II) metallo-radicals and/or in ‘molecular batteries’.