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

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

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Vincent Vreeken

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Chapter 1

Rigid Diarylamine Phosphine (PNP)-ligands Applied In Late Transition Metal Chemistry – an Introduction
1.1 Catalysis in societal context

The decreasing availability of fossil fuels and minerals, combined with the ever-growing world population and perhaps plain morality, call for sensible use of resources. Catalysis offers ways to achieve this and, thus, advances in this research field can have a high economic impact for the chemical industry and benefit society. Nature employs (metallo)enzymes as catalysts, which have been perfected in many ways. Catalysts can decrease the energy requirement to perform reactions (convert substrates into products), increase the overall rate of reactions and enhance selectivity (and hence lower waste production) or facilitate new reactivity. Synthetic catalysts are applied in numerous industries (e.g. production of petrochemicals, polymers, medicine, agricultural chemicals, etc.) and as such provide for utilities essential in present-day society. In this context and in view of the current transition towards more sustainable and green societies, improving current and development of new catalysts remains an important point of interest in academic and industrial research.

Homogeneous catalysis is a major branch in the field of catalysis. The term “homogeneous” relates to the equal phase in which catalyst and substrate reside (usually dissolved in an organic or aqueous medium). The absence of phase-boundaries often allows for high and unique selectivity which can be achieved by proper design of these systems. Furthermore, ease of modification, a well-defined nature and a wealth of spectroscopic methods give the possibility to study these catalysts and the reactive intermediates in detail. The emergence of computational chemistry has provided additional tools for this. Transition metal (TM) coordination compounds dominate the category of homogeneous catalysts. Therefore, they attract interest for studies related to both applied (catalytic) and fundamental research.

TM coordination compounds consist of a metal core and ligands appended to this metal. The ligands in these complexes mostly constitute main group elements and range from being simple and one-atom in size to extensive, large frameworks. Traditionally, ligands are used to influence the steric and electronics of TM complexes. Concepts involving ligand cooperativity and construction of a second coordination sphere are relatively new. Because ligands have a great effect on the properties, stability and the reactivity of coordination compounds, choosing one from the extensive existing toolbox or designing a new scaffold is a fundamental step in coordination chemistry and homogeneous catalysis research.

Throughout the research described in this thesis, monoanionic diaryl-based PNP pincer ligands are used as supporting scaffold for all late transition metal complexes. A short review on these pincer ligands and their coordination compounds is therefore considered a valuable introduction. Also, it will provide insight into the versatile possibilities for stoichiometric and catalytic reactivity involving the ligand. For these reasons, this
Chapter will focus on the design and coordination chemistry of PNP ligands with transition metals and recent advances regarding their application in catalysis will be discussed. For this overview, we will focus on late TM complexes (Group 9-11) for the following reasons: 1) reports on compounds with these metals have dominated the literature the last decade (for reviews covering early- and mid-transition metal-PNP complexes, see ref 5 and 6);[5,6] 2) complexes with these metals are most relevant for the contents of this thesis; 3) in terms of reactivity, these metals can be active in C-H activation reactions. This type of reactivity attracts considerable attention and will also be the subject of later chapters.

1.2 Pincer ligands

Amongst the classes of tridentate ligands, pincer ligands are well-known scaffolds that coordinate to adjacent coplanar sites of a metal center, usually in a meridional configuration. Because of the extended chelate effect, these ligands in general give rise to very stable coordination compounds. Pincer complexes typically exhibit relatively good thermal stability and “offer a convenient framework for studies of [e.g.] square planar compounds in which only one coordination site is intended to be the “reactive” site.”[7] Besides square planar geometries, also square pyramidal and octahedral arrangements are commonly encountered.

The first pincer-type complexes were developed in the late 1970’s by groups of Shaw[8] and van Koten[9] and consisted of cyclometalated PCP- and NCN-ligands, respectively (Figure 1A). These ligands are highly modular: alterations of the neutral donor sites, the linkers or the central aryl ring can greatly affect the properties of the metal center.[10] The chemistry of ECE-type (E = two-electron donor) pincer complexes and their application in catalysis have been extensively studied in the past decades.[11–13] Nowadays, the definition of pincer ligands has widened such that they need not necessarily be of the ECE-type. Substitution of the central carbanion for other donor atoms (e.g. nitrogen (vide infra), phosphorus,[14] silicon[15]) and of the flanking donor atoms has led to new varieties. Although traditionally centered around monoanionic ligands by virtue of a central anionic moiety, the current pincer chemistry ranges from cationic to trianionic scaffolds.

The development of monoanionic PNP pincer ligands was pioneered by Fryzuk and later extended on by Caulton (Figure 1B). Intended as a “hybrid” ligand to generate a new electronic and steric environment, this chelating P\textsubscript{Si}N\textsubscript{Si}P scaffold paired soft phosphine donors with a hard central amido functionality.[16,17] This approach ensured compatibility with both early and late transition metals, resulting in versatile coordination chemistry.[18] In comparison with the carbanion donor in ECE-type ligands, the amido unit is a stronger π-donor, exhibits a weaker trans influence and is probably better comparable with a Cl
The monoanionic PNP ligand is therefore more similar to the meridional Cl(PR$_2$)$_2$ motif.$^5$ Remarkable reactivity can be achieved with the P$^{\text{Si}}$N$^{\text{Si}}$P ligand. For example, N$_2$-activation and –reactivity mediated by a Zr(PNP) complex has been observed by Fryzuk et al.$^{19}$ However, scission of the N-Si bond and the Si-C bond of the backbone was evidenced under various circumstances and the Si-atoms in the backbone are susceptible to attack by oxygen-containing reagents.$^{20-24}$ Furthermore, the scaffold is rather flexible and therefore not only lacks specific preference for a meridional or facial configuration, but also may lead to phosphine dissociation.$^{11,25}$

To circumvent these issues, attempts were made to develop more robust PNP ligands. The groups of Liang, Mayer/Kaska and Ozerov independently developed the class of diarylamido phosphine ligands (Figure 1E).$^{26-28}$ The aryl rings in this monoanionic ligand provide a more rigid framework. Also, imine formation through β-H elimination is effectively prevented by ortho-functionalization of the phenyl rings. For PNP ligands with an aliphatic backbone (Figure 1C) imine formation is known to occur. Still, these ligands have been applied successfully in coordination chemistry and in catalysis. Functionalization of this ligand by oxidation of the backbone to the enamido and dienamido analogues has also been reported. The coordination chemistry of this ligand has recently been reviewed.$^{29}$ The pyrrolyldiphosphine system, independently developed by Mani, Tonzetich and Gade, is another recent example of a PNP scaffold (Figure 1D).$^{30-32}$ Because neither ligand 1C nor ligand 1D are subject to further study in this thesis, their coordination chemistry is regarded to be beyond the scope of this overview and will be excluded from this Chapter.

![Figure 1](image.png)

**Figure 1.** Monoanionic ECE- and PNP-pincer type ligands.
1.3 Synthesis and characteristics of diaryl-based PNP ligands

The synthesis of the diaryl $\text{PN}^\text{H}P$ ligands can be divided in two parts: 1) preparation of the diarylamine backbone and 2) construction of the C-P bond. This allows for a modular synthesis and alterations that may greatly affect the properties of the ligand (vide infra) can be made in either stage. The diarylamine building block is in some cases commercially available, depending on the desired substituents. For other diarylamines, Buchwald-Hartwig amination provides a convenient synthetic route (Figure 2).

Especially the para-position of the aryl rings ($X$ in Figure 2) has been used to modify the backbone. Amongst the introduced functionalities are Me,$^{[33]}$ OMe,$^{[34]}$ F$^{[33]}$ and t-Bu.$^{[35]}$ Recently, the synthesis of a PNP ligand with disubstituted aryl rings (Me at X- and Y-position in Figure 2) was achieved by Buchwald-Hartwig coupling. The ortho methyl groups induce a high barrier of rotation around the C(Ph)-N bond, resulting in an atropisomeric ligand.$^{[36]}$ The two aryl rings have also been connected together by the introduction of a CH$_2$-CH$_2$ linker, creating a strained backbone $\text{StrPNMeP}$. This results in a ligand that is effectively bulkier and shows detectable differences in reactivity compared to unstrained analogs.$^{[37]}$ Prior to the C-P bond construction stage, the amine can also be methylated to generate $\text{PNMeP}$, although this may impede coordination as a monoanionic tridentate unit.$^{[38]}$

Formation of the C-P bond is achieved either by using a nucleophilic phosphine reagent in combination with electrophilic C-positions,$^{[26]}$ or by generating nucleophilic sites at the aryl rings and electrophilic phosphine reagents, such as ClPR$_2$ (Figure 2).$^{[27,28]}$ Both approaches require halogenated diarylamines. Unsymmetrical PNP ligands have been prepared by constructing the two P-C bonds stepwise, employing different ClPR$_2$ sources.$^{[39,40]}$
The anionic PNP framework has been shown to exhibit redox non-innocent behavior in several M(PNP) complexes.\textsuperscript{[41–44]} Mindiola and coworkers described the oxidation of a Ni(PNP)Cl complex with FcOTf. A combination of spectroscopic techniques such as XRD, EPR, UV-vis, and multi-edge XAS confirmed that the electron hole resides mainly at the PNP ligand in complex 1 (Figure 3). DFT calculations established that 32\% of the spin density resides on the N and 37\% on the aryl rings.\textsuperscript{[43]} The redox chemistry of Mn(PNP)(CO)\textsubscript{3} and Re(PNP)(CO)\textsubscript{3} complexes was studied by Ozerov and Nocera. X-ray crystallography, IR and EPR measurements suggested that one-electron oxidation is dominated by ligand-centered events. DFT calculations indeed predicted around 50\% of spin density to be found on the N of the ligand and 36\% (for Mn complex 2) or 43\% (for Re complex 3) on the aryl rings.\textsuperscript{[44]} Peters \textit{et al.} found a strong contribution from the PNP ligand to the redox chemistry of [Cu(PNP)]\textsubscript{2} complex 4 using a combination of XAS and DFT techniques.\textsuperscript{[42]} The observed participation of the PNP ligand in the oxidation chemistry of these described complexes can probably be explained by strong contributions of high-lying N \textit{p}-orbitals to the highest occupied molecular orbital (HOMO) of these complexes.\textsuperscript{[41]}
The influence of the aryl ring X-substituents and of the phosphine donor R-groups (Figure 2) on the electronic properties of the ligand was recently investigated by the group of Ozerov.\footnote{34} For this purpose, a number of Rh(PNP)CO and Pd(PNP)Cl complexes was prepared and cyclic voltammograms (CV) and IR spectra were acquired (Figure 4). The authors note that oxidation of the Pd(PNP) compounds is mainly ligand-centered. For this reason, CV measurements could be a good indicator for “electron-richness” of the ligand (lower oxidation potential means electron richer ligand). IR stretching frequencies of CO are often used as a measure for the “electron-richness” of a metal center and hence for the donating capabilities of the ligand.\footnote{34}

It was found that variation of the X-substituents results in relatively large changes in the oxidation potential and small changes in the $\nu_{\text{CO}}$ (Figure 4, top). Hence, these substituents mainly affect the electronics of the diarylamine backbone, but not necessarily the donating properties of the ligand. On the other hand, alterations of the R-groups on the P-donor have a strong effect on both the $\nu_{\text{CO}}$ frequency and the oxidation potential (Figure 4, bottom).\footnote{34} The results indicate that independent influence on the electronics of the ligand backbone and of the metal center is only possible to a limited extent.
Figure 4. Influence of X-substituents (top) and donor groups (bottom) on $v_{CO}$ and $E_{1/2}$ of Rh(PNP)CO and Pd(PNP)Cl complexes. Adapted from ref 34.

1.4 Group 9 PNP-complexes

1.4.1 Cobalt

The PNP ligand has been employed widely with Group 9 metals, especially for Rh and Ir chemistry. However, examples of cobalt complexes are scarce. In 2006, Mindiola and coworkers reported a number of reactive Co(PNP$^{iPr}$) complexes with different oxidation states (Figure 5).\textsuperscript{45} Preparation of Co(PNP)Cl complex 5 was achieved by a salt-metathesis reaction between CoCl$_2$ and [Li(PNP)]. The obtained square planar Co$^{II}$ complex was then chemically reduced in THF under an atmosphere of N$_2$ with excess NaC$_{10}$H$_8$, resulting in dianionic Co$^{-}$-dinitrogen complex $\{Na_2(thf)_3\}Co(N_2)_2$ 6.

Reduction of 5 with $t$BuLi under argon atmosphere resulted in $\{\{\mu_2-PNP\}Co\}_2$ complex 7. The PNP ligand has adopted a bridging coordination mode in this complex with the amido moieties situated between two Co$^{I}$ centers, which results in a Co$_2$N$_2$ diamond core. This unusual structure is believed to be a masked form of the coordinatively unsaturated Co$^{I}$-species 7a. The rearrangement of this unsaturated species to form 7 probably prevents the occurrence of metal or ligand disproportionation reactions. The dimeric species was shown to bind CO and N$_2$ and to be reactive towards ClCPh$_3$ to form (CPh$_3$)$_2$, likely via intermediacy of 7a.$^{45}$
In a different contribution of the Mindiola group, a Co(PNP\textsuperscript{iPr})(O\textsuperscript{t}Bu) complex was used to study B-B bond cleavage via a σ-bond metathesis pathway. Formation of Co(PNP)[B(pin)] compound 8 was shown to be feasible, but no further reactivity with this complex was reported.\textsuperscript{46} The group of Sun recently reported on the coordination chemistry of Co(PNP\textsuperscript{Ph})(PMe\textsubscript{3})\textsubscript{2} complex 9.\textsuperscript{47} In this complex, the PNP ligand adopts a facial configuration, which is in contrast to the Co\textsuperscript{I} complexes reported by Mindiola.

1.4.2 Rhodium

Rh(PNP) complexes were initially reported by Kaska and coworkers.\textsuperscript{27} They showed that PN\textsuperscript{H}P\textsuperscript{Ph} ligands can be coordinated to rhodium in two ways. Deprotonation of the amine prior to addition of a Rh\textsuperscript{I} precursor led to Rh\textsuperscript{I} complex 10 (Figure 6). Direct addition of the same Rh\textsuperscript{I} precursor to the neutral ligand led to oxidative addition of the N-H bond and formation of Rh\textsuperscript{III} complex 11. Ozerov \textit{et al.} showed that this methodology can be extended to N-methylated PN\textsuperscript{H}P\textsubscript{iPr} ligands. Upon reaction of PN\textsuperscript{Me}P\textsuperscript{Pr} with
[\text{COD} \text{Rh(u-Cl)}]_2$, initial formation of complex 12 was observed. Heating of either solid state samples and solutions of 12 resulted in the oxidative addition of the N-C bond to generate Rh$^{III}$ species 13 (Figure 6). Prepositioning of the N-H or N-C bond close to the Rh center is thought to contribute to the ease of the oxidative addition.$^{[37,38]}

**Figure 6.** Oxidative addition of N-H and N-C bonds in Rh$^I$(PNP) complexes.

Rhodium(II) complexes may be of interest for metalloradical chemistry. Hence, Ozerov and coworkers prepared an open-shell Rh$^{II}$ center supported by a PNP$iPr$ ligand. Rh$^{II}$ complex 15 was readily obtained by H-atom abstraction from trivalent 14 (Figure 7). In an alternative route, Rh$I$ complex 17 was oxidized with AgOTf, resulting in 18. Given the interest in the redox non-innocent properties of the ligand, spin densities of open-shell complexes 15 and 18 were calculated. For both compounds the spin density was found to mainly reside on the Rh-center (0.72 for 15 and 0.65 for 18). Still, a significant contribution from the ligand was found and a lack of hyperfine coupling in the EPR spectrum of 18 was attributed to this contribution.$^{[48]}

Interestingly, when 15 and 18 were reacted with an excess of H$_2$, Rh$^{III}$ compounds 16-Cl and 16-Tf were obtained, respectively. Both products show protonation of the N, indicating that the amido lone pair can participate in heterolytic splitting of H$_2$.$^{[48]}$ The PNP ligand also participates during the oxidative addition of TiCl$_4$ or ZrCl$_4$ to 17 to form heterobimetallic complexes 20-Ti and 20-Zr (Figure 7). The amido bridge is thought to be crucial for a tight interaction between the early and the late metal center.$^{[49]}$
Figure 7. Formation of Rh\textsuperscript{II} complexes (in boxes) and their reactivity towards H\textsubscript{2} and oxidative addition of TiCl\textsubscript{4} and ZrCl\textsubscript{4} to a Rh\textsuperscript{I}(PNP) complex.

Rh\textsuperscript{I}(PNP) complexes have been shown to be active in carbon-halide oxidative addition reactions and in carbon-carbon reductive elimination reactions, fields commonly dominated by Pd chemistry. The group of Ozerov showed that reaction of 13 with PhLi results in the unstable complex 20, which was characterized in situ (Figure 8). Reductive elimination forming PhMe is thought to result in three-coordinate species 21. This species then quickly reacts with aryl halides to form 22.\textsuperscript{[50]} By using rhodium(I) starting complexes of masked forms of 21, such as 17 or 23, it was possible to avoid the addition of PhLi. C-H oxidative addition products were also observed in some cases.\textsuperscript{[51,52]} The transient complex 21 is also thought to play a role in the oxidative addition of silyl halides, forming species such as 23.\textsuperscript{[53]} Tilley et al. established Si-H oxidative addition in the reaction of 24 with SiR\textsubscript{3}H to generate 25.\textsuperscript{[54]} The rigid PNP ligand allows for tolerance of a diversity of oxidative addition, reductive elimination and ligand exchange reactions by Rh(PNP) complexes.\textsuperscript{[53]}
Figure 8. Oxidative addition of aryl halides and silyl halides and reductive elimination of C-C bond.

Rh(PNP) complex 26 and its strained analogue 27 are active in alkyne dimerization catalysis. This reaction can in principle lead to three isomers (Figure 9). Both catalysts show a preference for the formation of the E-head-to-head coupling product for a broad selection of alkynes. Interestingly, it was found that 27 is more active and much more selective than its unstrained analogue 26. As the catalysts are electronically very similar, it was concluded that this superiority must arise from steric differences.\[^{[55]}\] Still, neither catalyst was found to be particularly fast. This, and strenuous synthesis of 27 gave rise to the development of catalyst 28. As discussed above, the two methyl groups ortho to the central amido create a strained atropisomeric ligand, while less synthetic effort is needed compared to 27. Nevertheless, 28 was found to perform more similarly to 26: “ sluggishly and not selectively.”\[^{[36]}\] In general, it was found that Rh(PNP) compounds catalyze the dimerization more slowly than comparable Rh-catalysts bearing other pincer ligands.\[^{[36]}\]

Figure 9. Rh-catalyzed dimerization of alkynes.
1.4.3 Iridium

Ir(PNP) complexes can be obtained in comparable ways as their second-row analogues. Complex 29 was prepared by Ozerov et al. through combination of [(COD)Ir(µ-Cl)]_2 and PN^HPr^PiPr and subsequent oxidative addition of the N-H bond (Figure 10). Formation of complex 30 on the other hand proved to be less selective, as the desired product constituted merely 30% of the final mixture. Tilley and coworkers reported the reaction of PN^HPr^Ph with [(COD)Ir(µ-Cl)]_2. Interestingly, no N-H oxidative addition was observed in this case and 31 was isolated. This is attributed to the decreased electron-richness of the iridium center as an effect of the less electron-donating phenyl-substituted phosphine donors. Addition of base rendered the desired complex 32 (Figure 10).

![Figure 10. Reactions of free PNP ligands with Ir-precursors and oxidative addition of (halo)benzene.](image)

Ir(PNP) has also been shown to oxidatively add C-H bonds. Reaction of 33 with norbornene in benzene cleanly produced the C-H activation product 35. It is proposed that this reaction follows a mechanism in which norbornene is first hydrogenated, leading to 14-electron species 34. This transient compound subsequently is able to react with benzene to produce 35 (Figure 10). 33 was also reacted with aryl halides. The product mixtures of these reactions contained small amounts of the thermodynamically favored C-halogen oxidative addition products 36. However, because of lower activation barriers, the C-H oxidative addition products were dominant in the final product mixtures.
Figure 11. Preparation of Ir(PNP) carbene complex 38 and its reactivity.

Grubbs et al. employed the PNP ligand in Ir\textsuperscript{I}-carbene chemistry. Through reaction of 33 with norbornene in the presence of methyl tert-butylether (MTBE), compound 37 was obtained, which gradually converted to the desired Fischer carbene 38 by two C-H activation reactions and expulsion of H\textsubscript{2} (Figure 11). A strong interaction was observed between the filled \textit{p}\textsubscript{π} orbital of the PNP amido donor and the empty \textit{p}\textsubscript{π} orbital of the carbene ligand.\textsuperscript{[57]} Reaction of the electrophilic carbene with CO\textsubscript{2}, CS\textsubscript{2} or isoelectronic reagents led to generation of thermodynamically stable complexes 39 and the corresponding (thio)formate esters.\textsuperscript{[58,59]} In contrast, reaction of 38 with CO afforded migratory insertion of the carbene ligand into the Ir-amido bond, leading to the formation of complex 40.\textsuperscript{[60]} In general, Ir(PNP) systems were found to behave differently and to be more active compared to Ir(PCP) systems in this carbene chemistry. Grubbs and coworkers were not able to achieve catalysis with complex 38. The use of organic azides, however, allowed for sequential processing. Addition of adamantyl azide to 38 afforded complex 41. Subsequent photolysis in the presence of norbornene and MTBE allowed for regeneration of 38. Four turnovers were realized in this way.\textsuperscript{[61]}

Tilley et al. have investigated the catalytic competence of Ir(PNP) in alkene hydrosilylation reactions. Cationic silylene complexes such as 43 were prepared as precatalysts in two steps. Addition of H\textsubscript{3}SiMes to a solution of 33 afforded silyl complex 42. This compound was then reacted with hydride abstracting agent [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}], resulting in cationic silylene species 43 (Figure 12). This complex was shown to be active in catalytic hydrosilylation of alkenes and was as such the second-known silylene catalyst to mediate this reaction. The catalysis was found to be regioselective and both aryl- and alkyl-substituted primary silanes could be used as substrates in combination with a variety
of unhindered alkenes. Competitive catalytic redistribution of silanes lowered the yield of the catalysis.\cite{62}

\textbf{Figure 12.} Formation of Ir(PNP) complex 43, Ir-catalyzed hydrosilylation of 1-hexene and the observed resting state of the catalyst (44).

A study of the mechanism of the catalyzed hydrosilylation reaction revealed that the PNP ligand may take part in the catalytic cycle. The reaction of H₃SiMes with 1-hexene catalyzed by 43 was monitored by NMR spectroscopy and showed the presence of 44 (Figure 12) as the main iridium-species. In this complex the silylene group has migrated to the ligand nitrogen atom. This species appears to be a resting state in the catalytic cycle and shows that the PNP ligand may be important by providing bond activation pathways that avoid high oxidation states and coordination numbers for the Ir-center.\cite{63}

Complex 33 has also been shown to be a competent catalyst for dehydrogenative borylation of terminal alkynes (DHBTA), Figure 13.\cite{64} The alkynyl boronate products of this reaction are versatile building blocks in synthetic chemistry. As a catalyst, 33 is outperformed by complex 45 that bears an unsymmetrical \( \text{iPrPNP}^{\text{Ph}} \) ligand. This may be related to the decreased steric bulk imposed by the phenyl substituents on the phosphine donor. Complex 45 was employed in a range of borylation reactions of alkyl, aryl and silyl-substituted alkynes, giving good to excellent yields under mild conditions and catalyst loadings down to 0.025 mol%. The mechanism behind this catalysis remains uncertain, but comparative studies with other pincer ligands suggest that an amido containing pincer ligand is crucial to provide an active DHBTA catalyst.\cite{64}
1.5 Group 10 PNP-complexes

1.5.1 Nickel

Coordination of PNP ligands to nickel has been achieved in various ways. Liang et al. showed that deprotonation of a prototypical PN\textsuperscript{12}P species with \textit{n}-BuLi followed by reaction with NiCl\textsubscript{2}(DME) results in formation of the Ni(PNP)Cl complex 46 (Figure 14).\textsuperscript{[26]} Alternatively, it is also possible to use zerovalent Ni\textsuperscript{0} precursors to enforce oxidative addition of the N-H bond and formation of the corresponding hydride complex 47 (Figure 14).\textsuperscript{[40,65]}

Figure 14. Coordination chemistry of Ni(PNP)Cl and Ni(PNP)H complexes.

Both chlorido complex 46 and hydrido complex 47 and their corresponding analogues provide entries into versatile coordination chemistry. The chlorido fragment of 46 has been substituted by salt-metathesis reactions\textsuperscript{[66,67]} and by treatment with Grignard reagents (Figure 14). Remarkably, no β-hydrogen elimination was observed in the ethyl,
$n$-butyl and isobutyl complexes, which is in contrast to related complexes bearing Fryzuk-type PNP ligands. The stability of the alkyl complexes is tentatively attributed to the rigidity and robustness of the diaryl-PNP ligand.\[26\] The robustness of the ligand is also reflected in the reaction of 47 with CO. This resulted in reductive elimination of the N-H bond and generation of zerovalent nickel carbonyl species, while Fryzuk-type PNP-ligands have been shown to undergo N,O-silatropic rearrangements.\[20,68\] Reaction of 47 with olefins (such as ethylene) resulted in olefin insertion in the Ni-H bond.\[40\] More interestingly, 47 was found to be active in intermolecular arene C-H activation. Addition of 1 equivalent AlMe$_3$ to a benzene solution of 47 was found to lead to the corresponding benzene C-H activation product (Figure 14). The conditions for this transformation were found to be very mild (room temperature, 4 hours reaction time) and, remarkably, full conversion could also be achieved employing substoichiometric amounts of Lewis-acid AlMe$_3$.\[69\]

Ni(PNP) complexes were found to be catalytically active in two different reactions. Ozerov et al. found that Ni(PNP)OTf complex 48 is a robust and easy to handle catalyst for the coupling of aldehydes with acetonitrile (Figure 15). The coupling proceeds smoothly for a range of aldehydes under mild conditions (45 °C) and with DBU as Brønsted base additive. The mechanism could not be fully elucidated, but the OTf in 48 can be substituted easily for acetonitrile. In the resulting complex, the cationic [Ni(PNP)]$^+$ likely functions as a Lewis acid and induces the reaction by increasing the C-H acidity of the acetonitrile.\[5,70\] Liang et al. reported that complex 46 (vide supra) is a potent catalyst for Kumada coupling reactions (Figure 15). Apart from aryl reagents it was shown that the catalysis was also compatible with alkyl Grignard reagents containing β-hydrogens. However, the exact mechanism was not fully elucidated.\[71\] Isoelectronic nickel complexes with diarylamine amine ligands (NNN) can outperform their PNP-analogues in this reaction, as demonstrated by Hu et al. The flanking amine donors are perhaps better suited to stabilize the higher oxidation states encountered in this reaction.\[72\]

![Figure 15](image_url)

**Figure 15.** Left: Ni(PNP)-catalyzed coupling of aldehydes and acetonitrile. Right: Ni(PNP)-catalyzed Kumada coupling.
Reduction of Ni(PNP)Cl complex 49 with KC₈ resulted in the formation of dinuclear Ni⁺-species 50, as reported by Mindiola et al. Comparable to its Cu-analogue 4 or Co-analogue 7, this dimeric structure possesses a diamanoid M₂N₂ core. However, it was found that the two Ni⁺-centers show only weak electronic coupling at low temperature, which decreased with increased temperatures. Hence, the system can be described as a diradical complex at room temperature. As such, 50 was subjected to homolytic H-X bond splitting reactions (X = H, OH, OCH₃, PHPh or B(catechol)), Figure 16. Equal amounts of divalent Ni(PNP)H and Ni(PNP)X complexes could indeed be formed. Also B-B bond splitting and homolytic S-S and Se-Se bond cleavage were shown to be feasible using 50.[73]

![Figure 16](image)

**Figure 16.** Reduction of Ni(PNP)Cl complex 49 forming ‘diradical’ species 50 and further reactivity.

The oxidation state of nickel can have a pronounced effect on the coordination geometry and reactivity of Ni(PNP) complexes. Lee and coworkers described that cationic Ni(II) carbonyl complex 51 adopts a square planar geometry. Reduction of this complex to 52 leads to a pyramidal geometry and further reduction to pseudotetrahedral Ni(0) species 53. The reactivity of these three complexes with MeI was investigated. Ni(II) complex 51 did not show any reaction, while Ni(0) compound 53 fully converted to the methyl species (Figure 17). Upon reaction of Ni(I) complex 52 with MeI, C-C coupling was observed (37%), along with the formation of a Ni(PNP)I complex (50%) and a small fraction of the Ni(PNP)Me product (13%). The authors speculate that this reaction could follow a radical pathway.[74] Complex 51 can be reacted with NMe₄OH to form a hydroxycarbonyl species. This process can be reversed by reaction with a strong acid.[75]
1.5.2 Palladium

Complexation of diaryl-based PNP ligands to palladium can be achieved by deprotonation of free PNHP ligand with a Pd(II) source.\textsuperscript{[65,76]} Complex 54 was prepared in this manner (Figure 18). Oxidative addition of the N-H bond of the ligand to a Pd(0) source, such as Pd\textsubscript{2}(dba)\textsubscript{3}, results in a Pd(PNP)H species.\textsuperscript{[28]}

Complex 54 and related analogues are highly effective catalysts for a variety of Heck coupling reactions (Figure 18).\textsuperscript{[28]} Turnover numbers up to 45 x 10\textsuperscript{6} were observed for the coupling of styrene with phenyl iodide.\textsuperscript{[76]} Complex 54 was also shown to be a viable catalyst for Sonogashira\textsuperscript{[77]} as well as for Suzuki coupling reactions. A number of functional groups was shown to be compatible for the latter and, noteworthy, the catalysis runs smoothly under aerobic conditions and even in the presence of water.\textsuperscript{[78]} For all coupling reactions, Hammett plots indicate that oxidative addition is not the rate-determining step. However, more details on the mechanisms are not known to date.\textsuperscript{[76–78]}
Figure 18. Complex 54 as catalyst for Heck (top), Sonogashira (middle) and Suzuki (bottom) coupling reactions.

Ozerov and coworkers have reported the chemistry of complex Pd(PNP)OTf (55) (Figure 19). This compound can be seen as masked [Pd(PNP)]^+ cation. The ability of 55 to perform heterolytic bond cleavage of H-X bonds over the Pd-N bond was probed. The oxidation state of the palladium center in the products of such reactions should stay unaltered. Bond splitting of H-X bonds (X = H, CCTol, SPh or SBr) indeed proved feasible (Figure 19). The mechanism behind this transition is not fully understood yet. DFT calculations suggested that the intermediacy of Pd^{IV} species is unlikely. It was therefore suggested that coordination of the H-X bond to the Pd-center is followed by triflate mediated proton transfer to the nitrogen of the ligand.\[79\] Heterolytic bond B-H cleavage proved to be unsuccessful with complex 55. This bond rupture could be achieved using complex 56, which features a more weakly coordinating anion (Figure 19).\[80\]

Figure 19. Heterolytic bond cleavage of E-H bonds over the Pd-N bond.

Pd(PNP)-alkyl compounds have been shown to be thermally stable species, but they are photolytically unstable. A nice example was given in a contribution of the Ozerov group in 2007. Exposure of solutions Pd(PNP)Et (57) to sunlight or UV-light (\( \lambda = 350 \text{ nm} \)) was
shown to result in the formation of Pd\textsuperscript{i}-Pd\textsuperscript{i} dimer 58 (Figure 20). Different from Ni\textsuperscript{i}-dimer 50, an unsupported metal-metal bond was found in the X-ray structure of 58. In solution these dimers can reversibly generate Pd\textsuperscript{i}(PNP) monomers.\textsuperscript{[81]}

![Diagram of Pd complexes](image)

**Figure 20.** Formation of 58 and its reactivity towards small molecules and ZnEt\textsubscript{2}.

Compound 58 has been shown to exhibit interesting reactivity (Figure 20). For example, activation of small molecules such as H\textsubscript{2}, H\textsubscript{2}O and even NH\textsubscript{3} leads to the rupture of the Pd-Pd bond and formation of two new monomeric structures via bimetallic oxidative addition. Whether these reactions require prior dissociation of 58 into the monomeric Pd\textsuperscript{i}(PNP) species is not clear.\textsuperscript{[81]}

Irradiation of 58 in the presence of ZnEt\textsubscript{2} led to the formation of a compound with two covalent Pd-Zn bonds.\textsuperscript{[82]} Furthermore, it has been shown that 58 is capable of reducing CO\textsubscript{2} to free CO using Me\textsubscript{3}SiOTf as oxygen acceptor.\textsuperscript{[83]} Stable superoxide complex 59 could be easily prepared by irradiation of Pd-dimer 58 in the presence of an excess of O\textsubscript{2}. With lower concentrations of O\textsubscript{2}, a bridging peroxo dimer was formed. The competence of 59 for catalytic O\textsubscript{2} activation was demonstrated by using it as a catalyst for the oxidation of PPh\textsubscript{3} to OPPh\textsubscript{3}.\textsuperscript{[84]}
1.5.3 Platinum

Platinum complexes bearing the PNP ligand can be obtained with the same strategies as used for the first and second row analogues, namely through oxidative addition of the N-H bond to a Pt$^0$-precursor or by deprotonation of the ligand and reaction with a Pt$^{II}$ source.$^{[65,85]}$ Reports on the reactivity or application of Pt(PNP)-complexes in catalysis are limited. Liang et al. reported on intermolecular C-H activation of benzene by Pt(PNP)OTf complex 60 in the presence of a base, such as Et$_3$N (Figure 21).$^{[85]}$ Ozerov et al. established similar behavior of closely related Pt(PNP)OTf complex 61. Stripping off the OTf ligand by K[BAr$_F^4$] in benzene led to generation of 62. Metal-ligand cooperativity of a [Pt(PNP)]$^+$ intermediate is postulated, similar to the Pd-analogue. Performing this reaction in dichloromethane led to Cl-abstraction. In the resulting trivalent complex 63 the ligand is likely oxidized, demonstrating its redox non-innocent properties.$^{[7]}$

![Figure 21](image-url)

**Figure 21.** Top: C-H activation by complex 60. Bottom: Metal-ligand cooperativity after OTf removal in 61 and Cl-abstraction from dichloromethane.
1.6 Group 11 PNP-complexes

1.6.1 Copper

Peters and coworkers reported on the preparation of \([\text{Cu}(\text{PNP})]\)\(_2\) species 4 (Figure 22).\(^{[14,42]}\) In these dimeric compounds, the ligand nitrogen atom bridges between two Cu-centers to form a diamond \(\text{Cu}_2\text{N}_2\) core, similar to the previously described \(\text{Co}_2\text{N}_2\) and \(\text{Ni}_2\text{N}_2\) cores. Complex 4 could be oxidized with two electrons, with the majority of the resulting spin density residing in the ligand. The steric bulk imposed by the tert-butyl groups is essential for stable oxidation, as substitution for hydrogens results in aryl-based reactivity.\(^{[42]}\) Compound 4 is highly emissive and has been applied in OLEDs.\(^{[86]}\)

![Figure 22. Emissive Cu2N2-compounds 4 (left). Synthesis of dimer [Ag(PNP)]2 (right).](image)

1.6.2 Silver

One example of a silver-PNP compound has been reported. Mindiola et al. showed that upon mixing of free PNP ligand with \(\text{Ag}_2\text{O}\), dimeric structure 63 is obtained (Figure 22). The PNP ligands also bridge between the two metal centers in this structure, but it differs from other described dimeric \(\text{M}(\text{PNP})\) structures, as no \(\text{Ag}_2\text{N}_2\) diamond core is observed. Complex 63 was used as a transmetalation agent for the formation of PNP complexes with Group 10 metals.\(^{[87]}\)

1.6.2 Gold

No examples of gold chemistry with diarylamino-diphosphine ligands are reported to date.
1.7 New avenues for PNP chemistry

1.7.1 Late transition metal nitrido chemistry

The examples provided in the previous sections illustrate that the diarylamine-based PNP ligand stabilizes complexes of late transition metals in a wide range of oxidation states and at elevated temperatures. Moreover, it has the tendency to form stable square planar compounds and has shown redox non-innocent behavior. Therefore, we reasoned that this ligand class could be used for research on late transition metal nitrido chemistry (Group 9-10). The nitrido ligand, formally a ‘naked’ nitrogen atom bound to a metal center, has been the subject of interest as it is proposed to be an intermediate in N₂ splitting and to be involved in N-atom transfer reactions.

The charge of a nitrido ligand is formally 3-. Oxidation of a metal-bound nitrido may generate a nitridyl or a nitrenido ligand in the coordination sphere of the metal center (Figure 23).[41] The formation of a ‘pure’ nitrido ligand is accompanied by high oxidation states of the metal complex and the strong π-donor character of the N³- ligand destabilizes complexes with a high d-electron count. This effect may be more or less pronounced, depending on the geometry around the metal center and the accompanying ligand field splitting. Tetrahedral or square planar geometries typically minimize overlap between filled metal d-orbitals and filled ligand p-orbitals (this will be further explained in Chapter 2), whereas an octahedral geometry is unsuitable for late TM nitrido complexes.[88,89]

Metal azido complexes are commonly a good entry to the formation of nitrido compounds, as activation of the terminal azido leads to release of N₂ (Figure 23). Such reactivity can be achieved by photolysis or, alternatively, by thermolysis or (electro)chemical oxidation, provided that decomposition of the complex does not occur first. Ligands should therefore afford stable complexes at elevated temperatures or oxidizing conditions.

The field of late TM nitrido chemistry has recently experienced important breakthroughs with reports of Group 9 metal nitrido complexes by the groups of Burger,[90,91] Schneider,[92,93] de Bruin[94] and Meyer.[95] Except for Meyer’s example, tridentate ligands were used in complexes with a square planar geometry. Only for iridium it was possible to isolate the nitrido complex, whereas for rhodium and cobalt this type of complex was merely a (proposed) intermediate.
1.7.2 Dinuclear gold catalysis

Catalytic systems relying on bimetallic approaches have been subject of much investigation recently.\[3,96\] For example, bimetallic complexes are utilized in CO2/epoxide copolymerization\[97\] and cooperative bimetallic catalysts have been reported for hydrogenation and hydroformylation reactions.\[98\] Furthermore, stereo-, chemo- and regioselectivity have been induced by bringing metals centers in close proximity.\[99,100\] In gold chemistry, bimetallic pathways have led to new types of reactivity and selectivity.\[101–105\] This dual-gold catalysis is dominated by the combined action of two mononuclear gold complexes. Studies on dinuclear gold catalysts in bimetallic pathways are very limited.\[106–108\] Nonetheless, using such dinuclear gold complexes as a way to enforce bimetallic reactivity may be an interesting concept for dual-gold catalysis.

The overview of PNP chemistry presented in this Chapter includes a number of dinuclear complexes. As the ligand contains two phosphine donors, it should be capable of coordinating two gold centers. Therefore, we thought it would be interesting to study the concept of enforced bimetallic gold catalysis using the PNP ligand as a supporting backbone.

1.8 Aim and outline of this manuscript

In the following chapters of this manuscript we report on 1) an investigation of the possibility of forming cobalt- and nickel-nitrido complexes by studying the activation of the corresponding metal-azido complexes, and 2) on an investigation into a novel, bimetallic approach to selectively promote the σ,π-activation mode in dual-gold AuI catalysis. The first goal requires a ligand that is capable of accommodating high-valent metal centers whilst being stable at elevated temperatures and under photolytic conditions. For the second goal a ligand capable of appending two gold centers is required, while a certain degree of rigidity is thought to be beneficial. Based on these requirements and the aforementioned properties of diarylamine-based PNP pincers, we selected this ligand class as the basis for our studies.
In Chapter 2 we describe the synthesis and photolysis of a Ni(PNP)N₃ complex in neat arenes. We demonstrate that this leads to decomposition of the azido group, to reactivity with the ligand and, ultimately, to solvent C-H activation. Using DFT calculations, a mechanism for this reaction is proposed, which involves the intermediacy of a transient nickel(IV)-nitrido species.

Chapter 3 describes the thermal and photolytic activation of a Co(PNP)N₃ complex. Herein, we show that this system leads to similar ligand reactivity as found for its nickel-analogue, although the follow-up coordination chemistry is strikingly different, resulting in formation of a bimetallic structure, with no solvent activation observed under photolytic conditions. Computational studies lead to the proposal of a mechanism, involving a transient cobalt-nitrido species. Low temperature EPR spectroscopy is used in an attempt to further confirm the existence of this intermediate, but definitive proof was not obtained.

In Chapter 4 we investigate the concept of enforced σ,π-activation in [Au]⁺-catalysis. We describe tethering of two Au¹-centers by a PNP ligand and show that this Au¹(PNP)-complex catalyzes the heterocyclization of a urea-appended alkyne, generating the product of σ,π-activation in high selectivity. Dilution studies are used to show the benefit of dinuclear Au-catalysts at low catalyst loadings. In this Chapter we also describe selective two-electron oxidation of one gold center leading to a mixed-valent Au¹Au³ complex. We establish that reaction of this complex with a Ag¹-salt leads to oxidative C-C bond formation in the ligand and two-electron reduction of the Au³-center.

In Chapter 5 we report on the individual steps that make up for the overall reaction sequence. We propose a mechanism of the reaction and confirm the plausibility of our proposal by the isolation and characterization of relevant intermediate species.
1.9 References


Chapter 2

C-H Activation of Benzene by a Photoactivated Ni^{II}(azide) – Formation of a Transient Nickel Nitrido Complex

* Part of this work has been published: V. Vreeken, M. A. Siegler, B. de Bruin, J. N. H. Reek, M. Lutz, J. I. van der Vlugt, Angew. Chem. Int. Ed. 2015, 54, 7055–7059.
2.1 Introduction

Transition metal complexes with terminal multiple bonds to main-group elements (e.g. C, O, N) play critical roles in various chemical and biological processes, including but not limited to nitrogen fixation, water splitting and metathesis.\cite{1} Ligands based on multiple-bonded heteroatoms (e.g. imido or nitrido) typically exhibit strong π-donor character. For stable multiple bonding to occur between a transition metal and a strong π-donor main-group element, one or more empty metal d-orbitals of suitable symmetry and matching energy levels should be available to accommodate the additional π-electron density.\cite{2} Hence, choosing a suitable geometry is particularly important when employing late transition metals, as relatively few d-orbitals are not anti-bonding (Figure 1). Nevertheless, even geometries featuring several non-bonding orbitals typically enforce high oxidation states of electron-rich metals. This explains why complexes with Group 9-11 metals featuring multiple-bonded E-fragments are either rare or elusive, a situation sometimes referred to as ‘the oxo-wall dilemma’.\cite{3} Notwithstanding the challenges associated with preparation of these species, their potential application in e.g. C-N bond formation\cite{4} or as intermediate in alternative routes for N₂ fixation warrant continued investigation, even when using ‘abiological’ non-Group 8 metals.

![Figure 1. Simplified qualitative orbital schemes for octahedral (left), tetrahedral (middle) and square planar (right) nitrido complexes.\cite{2,3}](image)

Metal azides offer access to the interesting chemistry of nitrido complexes, as thermal or photolytic activation or (electro)chemical oxidation may result in the expulsion of N₂. Progress in the generation of Group 9 nitrides and open-shell nitridyl radical analogues demonstrates the feasibility of this approach.\cite{5} However, these studies are dominated by the use of 2nd and 3rd row transition metals. Only recently the first low-temperature characterization of a cobalt nitrido intermediate was reported, which highlights the potential for late first-row transition metal nitrido chemistry.\cite{6} Still, studies on the activation of terminal metal azides to generate M≡N species with Group 10 metals are very scarce, particularly for nickel\cite{7,8,9} and no bona fide (transient) nickel nitrido has been reported to date.
Photo-, thermal or redox-induced release of $N_2$ would convert the monoanionic azido ligand into a trivalent nitrido ($N^3$) ligand, thereby raising the formal oxidation state of the metal center by two. Hence, stabilization of such (transient) species could potentially benefit from electron-donating or redox-active ligands. Terminal nitrido ligands on Group 9 metals are often too reactive to be isolated, and ‘trapping’ these sought-after transient species via intramolecular insertion into ligand C-H or metal-ligand bonds is an attractive strategy (Figure 2). However, well-defined reactivity of a ‘trapped’ nitrido-species toward intermolecular arene C-H bond activation has not been reported to date, to the best of our knowledge.

![Figure 2](image-url)

**Figure 2.** Schematic representation of reported Group 9 azide-activation chemistry.\[^{5,6,10}\]

As part of our ongoing program to utilize reactive ligands with (first row) late transition metals for bond activation,\[^{12}\] we decided to investigate the preparation of nitrido species for non-ligand C-H bond functionalization. Inspired by the recent examples with Group 9 metals,\[^{5,6}\] we wondered if such chemistry would be possible for the Group 10 congener nickel. The PNP\[^{\text{iPr}}\] (2,2’-di(isopropylphosphino)-4,4’-ditolylamide) ligand was selected as supporting tridentate scaffold. Similar to some of the previously reported Group 9 examples it contains electron-rich phosphine donors, while the redox non-innocent ditolylamino backbone\[^{13}\] could provide additional electronic flexibility to the system.

In this Chapter we address the question if a Ni(PNP)-nitrido complex is accessible via activation of an analogous azido complex. Next, we investigate if this nitrido complex is sufficiently stable to be characterized and/or to be trapped with suitable agents. The scope for further follow-up reactivity is also subject of our investigations.
2.2 Results and discussion

2.2.1 Synthesis and characterization of Ni(N₃)(PNP)

The previously reported chlorido complex Ni(Cl)(PNP) (1; PNP = 2,2’-di(isopropylphosphino)-4,4’-ditolylamide) was used as a starting point. This species cleanly reacted via salt metathesis with excess NaN₃ in THF to generate the green azido complex Ni(N₃)(PNP), 2, in high yield (Figure 3). The substitution was confirmed by a small shift in the ³¹P NMR spectrum (singlet δ 36.3 vs. 33.7 for 1) and by a new absorption stretch at ν 2051 cm⁻¹ in the IR spectrum, which is typical for a terminal azide group. The UV-vis spectrum of the complex shows strong absorption bands at λ 345 nm (ε = 32,000 L mol⁻¹ cm⁻¹) and at λ 316 nm (ε = 24,000 L mol⁻¹ cm⁻¹). The ¹H NMR spectrum of complex 2 indicates local C₂-symmetry, which is further confirmed by the X-ray structure of 2 (Figure 4). A ¹⁵N-labelled isotopomer of 2 was also prepared by using Na¹⁵N¹⁴N₂ as the azide source. It is important to note that only half of the enriched complex is labelled at the α-position in the -N₃ group, while the other half is labelled at the terminal N-position (Figure 3). The IR spectrum of ¹⁵/¹⁴N-2 shows a small red-shift for the azide stretch (ν 2040 cm⁻¹).

![Figure 3. Synthesis of 2 and ¹⁵/¹⁴N-2 by salt metathesis and 3 by one-electron oxidation](image)

Cyclic voltammetry experiments were performed to establish the stability of the azido complex upon oxidation. Complex 2 exhibited fully reversible one-electron oxidation chemistry, with an $E_{1/2}$ of 0.03 V vs. Fc⁰/Fc⁺ (in THF). In previous reports, DFT calculations showed that oxidation of chlorido-containing precursor 1 predominantly occurs at the nitrogen and aryl groups of the PNP backbone, making this a redox-active ligand. Oxidation of 1 takes place at a slightly milder potential than for 2 ($ΔE = -0.10$ V vs. 2), showing a small effect upon substitution of Cl for N₃. Chemical oxidation with...
AgBF$_4$ in acetone resulted in the blue cationic derivative \([\text{Ni}(\text{N}_3)(\text{PNP})]\)BF$_4$, 3 (Figure 3). IR spectroscopy of 3 indeed confirms preservation of the azide fragment. Surprisingly, the azide stretch of the oxidized species is found at the same wavenumber as for its neutral analogue (\(\nu 2051 \text{ cm}^{-1}\)). DFT calculations of the oxidized structure predict that also for this compound the spin density resides largely on the PNP ligand (Figure 4). The encountered stability of the oxidized azido species excludes one-electron oxidation as a way to activate the -N$_3$ group.

**Figure 4.** Left: ORTEP plot (50% probability level) for 2. Hydrogen atoms are omitted for clarity. Selected bond lengths (\(\text{Å}\)) and angles (°): Ni$_1$-P$_1$ 2.1956(4); Ni$_1$-N$_1$ 1.8970(8); Ni$_1$-P$_2$ 2.1988(4); Ni$_1$-N$_2$ 1.9004(10); N$_2$-N$_3$ 1.1826(17); P$_1$-Ni$_1$-P$_2$ 167.376(11); P$_1$-Ni$_1$-N$_1$ 83.82(4); P$_1$-Ni$_1$-N$_2$ 96.63(5); N$_1$-Ni$_1$-N$_2$ 177.08(6); Ni$_1$-N$_2$-N$_3$ 120.59(10); C$_6$-N$_1$-C$_{12}$ 121.97(9). Right: Calculated spin density plot of 3 (BP86, def2-TZVP).

As previously described,$^{[5a,b]}$ thermolysis is a well-known method for activation of azido groups. Species 2 proved to be thermally stable up to 200 °C and no sign of decomposition was observed after 5 days in refluxing toluene. Chemically induced decomposition of the azido group also did not provide any evidence for a (transient) nitrido species. Complex 2 cleanly converted to the isocyanato derivative when exposed to five bars of CO, as confirmed by NMR (\(^{31}\text{P}: \text{singlet } \delta 37.7\)) and IR spectroscopy (\(\nu_{\text{NCO}} 2240 \text{ cm}^{-1}\)). This reaction occurred both in the absence and presence of light, implying the direct (intramolecular) attack of CO on the azide with expulsion of N$_2$.$^{[15]}$ Intermediacy of a nitrido species therefore seems unlikely. Isocyanate species 4 [Ni(NCO)(PNP)] was also independently synthesized by reacting 1 with KNCO (Figure 5). Addition of PMe$_3$ or PPh$_3$ to a solution of 2 in THF did not result in any appreciable reactivity.
2.2.2 Irradiation experiments

Interestingly, in contrast to the thermal and oxidative stability of species 2, photolysis of a benzene-\textsubscript{d6} solution of 2 (10.4 mM) using a 500 W Hg/Xe lamp with a cut-off filter at 305 nm resulted in a clear color change from green to yellow. IR spectroscopy indicates complete conversion of the azide complex. Multinuclear NMR spectroscopy suggests the quantitative formation of a single well-defined diamagnetic species, denoted as 5\textsuperscript{D} (Figure 6). The structural characterization for this new compound will be discussed below.

The \textsuperscript{1}H NMR spectrum of 5\textsuperscript{D} (Figure 7) shows complete preservation of all hydrogen atoms within the ligand scaffold, hence excluding ligand-based intramolecular C-H activation as a potential reaction pathway. Furthermore, complete loss of the \textit{C}_2 symmetry is observed, with two signals for the –CH\textsubscript{3} groups of the ditolylamine backbone and eight non-equivalent –CH\textsubscript{3} signals from the PPr\textsubscript{2} groups present.
Notably, the $^{31}$P NMR spectrum contains two doublets at δ 45.9 and 48.5 with a small $J_{PP}$ coupling constant of only 6.4 Hz, excluding a direct trans-coordination of the P moieties (Figure 8). To confirm the presence of the azide Na-atom, the irradiation of a benzene-$d_6$ solution of the $^{15}$N-labelled isotopomer of $^{15/14}$N-2 was also studied. This resulted in two new doublets-of-doublets in the $^{31}$P NMR spectrum. Remarkably, both $J_{PN}$ coupling constants were found to be almost identical at 29.2 and 30.5 Hz, again with a $J_{PP}$ coupling constant of 6.5 Hz. This experiment not only established the presence of the azide Na-atom, but also show that the two P-atoms are chemically inequivalent and both couple to the $^{15}$N nucleus.
Figure 8. $^{31}$P NMR spectra of complex 2 (top) and the photolysis product $^{5}$D (bottom) in C$_6$D$_6$. The insert shows the doublet-of-doublets after irradiation of $^{15/14}$N-2.

We further analyzed the formed species $^{5}$D by coldspray ionization mass spectrometry (CSI-MS), which reveals the presence of a perdeuterophenyl fragment in the generated complex. Based on this observation, we decided to switch to C$_6$H$_6$ as the solvent for the photolysis reaction to form product 5. In line with the MS data, this resulted in the appearance of additional aromatic signals in the $^1$H NMR spectrum and, markedly, also a doublet at $\delta$ 0.22 with a $\it{J}$ value of 6.5 Hz (Figure 9). By selective $^{31}$P decoupling of the $^1$H NMR spectrum, this signal transforms into a singlet, supporting a P-H coupling interaction. The $^{15}$N-enriched material gave an additional splitting of the doublet with a large coupling constant ($\it{J}_{NH}$ 73.2 Hz), which suggests a direct bond between a hydrogen of the activated benzene and a nitrogen originating from the decomposed azide group. The existence of an N-H fragment was additionally confirmed by the appearance of a weak N-H vibration ($\nu$ 3365 cm$^{-1}$) in the IR spectrum. Closer inspection of the IR spectrum of $^{5}$D reveals the presence of an N-D vibration at $\nu$ 2493 cm$^{-1}$. In the corresponding $^{15}$N HSQC-NMR spectrum a triplet is observed at $\delta$ -365.
Figure 9. $^1$H NMR spectrum of photolysis product 5 in C$_6$D$_6$. Arrows pointing at new aromatic signals, inset shows the newly formed doublet. Traces of residual THF present.

Yellow-colored single crystals, suitable for X-ray diffraction, were obtained by slow evaporation of a dichloromethane-cyclopentane mixture. The X-ray structure of square planar Ni$^{II}$-complex 5 (Figure 10) confirms the formal insertion of an –NH fragment into the Ni$_1$-P$_1$ bond, thus creating a parent iminophosphorane, with a P$_1$-N$_2$ bond length of 1.5970(20) Å, typical for a P=N double bond.$^{[16]}$ The angles $\angle$N$_1$-Ni$_1$-N$_2$ (93.98(8)$^\circ$ vs. 83.83(4)$^\circ$ for $\angle$N$_1$-Ni$_1$-P$_1$ in starting material 2) and $\angle$N$_2$-Ni$_1$-P$_2$ (177.48(7)$^\circ$ vs. 167.38(1) for $\angle$P$_1$-Ni$_1$-P$_2$ in 2) illustrate the expanded coordination sphere around Ni upon transformation of the PNP-donor into a 5,6'-chelating PN$^m$N$^l$ donor in 5. Furthermore, C-H bond activation of benzene resulted in the introduction of a phenyl ligand, with hydrogen transfer to the nitrogen originating from the azide precursor.$^{[17]}$ Variable temperature NMR studies suggest that the phenyl ligand exhibits hindered rotation at r.t., causing the broadening of the ortho- and meta-H signals in the $^1$H NMR spectrum (Figure 9). Decreasing the temperature of a sample in toluene-$d_8$ to -20 °C gives rise to splitting of these broad signals into four well-defined peaks (see Appendix Figure 14).

Cyclic voltammetry of species 5 still displayed well-behaved redox-chemistry, with a reversible one-electron oxidation event occurring at $E_{1/2}$ -0.34 V vs. Fe$^0$/Fe$^+$, significantly more negative ($\Delta E$ -0.37 V) than for azide 2. DFT calculations show substantial spin density (66%) residing on the PN$^m$N$^l$-ligand, indicating that the structural modification imposed by N-insertion has little effect on the redox non-innocence of the ligand backbone.
Figure 10. Left: Formation of 5. Right: ORTEP plot (50% probability level) for 5. Hydrogen atoms are omitted for clarity, except for hydrogen on N$_2$ and hydrogens on exogenous phenyl ring.

Selected bond lengths (Å) and angles (°): Ni$_1$-N$_1$ 1.9770(17); Ni$_1$-P$_2$ 2.1259(6); Ni$_1$-N$_2$ 1.8923(18); Ni$_1$-C$_{27}$ 1.893(2); N$_2$-P$_1$ 1.597(2); P$_2$-Ni$_1$-N$_2$ 177.48(7); N$_1$-Ni$_1$-N$_2$ 93.98(8); N$_1$-Ni$_1$-P$_2$ 85.92(5); N$_1$-Ni$_1$-C$_{27}$ 177.74(8); Ni$_1$-N$_2$-P$_1$ 123.39(11); C$_6$-N$_1$-C$_{12}$ 117.99(17).

2.2.3 Computational studies

To obtain more insight into the mechanism of the formation of complex 5, DFT calculations were performed. For computational ease, a simplified model of complex 2 was used, with phenyl instead of tolyl rings for the backbone and Me-substituents at the phosphorus atoms. Routes involving different (excited state) spin states were investigated, both at the hybrid b3-lyp level (Figure 11) and the pure GGA BP86 DFT functional (see Appendix Figure 15). Open-shell singlet (OSS) configurations for all investigated stationary points could only be located at the hybrid b3-lyp level. At the BP86 level only closed-shell singlet (CSS) configurations were found (see Appendix for further considerations).

As a starting point the activation of the azide was investigated. The release of N$_2$ proceeds via a high-energy transition state TS1 on all calculated surfaces and is therefore considered as a non-thermal, photochemical step. The reaction pathway after N$_2$ loss from 2 can either follow photochemical or thermal steps or a combination thereof. The metastable ‘Ni$^{IV}$-nitrido’ intermediate B is most stable in its triplet configuration ($^3$B), both at the BP86 and at the b3-lyp level. The spin density predominantly resides at the N-atom (b3-lyp: 89%, BP86: 81%), resulting in significant nitridyl radical character (Figure 12), similar to previously reported systems.[5b,d,f][6] The unusual electronic structure of $^3$B is perhaps best described with contributions from the following resonance structures: Ni$^{IV}$(N$^-$) $\leftrightarrow$ Ni$^{III}$(N•$^-$) $\leftrightarrow$ Ni$^{II}$(•N•).
The CSS and the OSS configurations of singlet $^1B$ collapse via a virtually barrierless transition state $TS2$ to the coordinatively unsaturated Ni$^{II}$(PNPN) intermediate C, featuring two anionic N-donor atoms (i.e. the PNP-nitrogen and the ‘nitrido’ nitrogen). In fact, the barrier from $^1B$ to $^1C$ at the closed-shell singlet BP86 configuration is so low that $^1B$ converges spontaneously to $^1C$. Conversion of $^3B$ to $^3C$ on the triplet surface also has a quite low barrier (both at the BP86 and the b3-lyp level) and thus might well proceed thermally (although photo-excitation to the singlet surface cannot be excluded).

Figure 12. Spin density plot of triplet intermediate $^3B$ (b3-lyp, def2-TZVP) and a schematic representation of the nickel-nitrido $\pi$-bonding scheme.
The relative spin-state energies of intermediate C at the CSS, OSS and triplet surface are quite similar. While the triplet configuration of C is most stable at the b3-lyp level, the CSS configuration of C is most stable at the BP86 level. The reaction from C via TS3 to D may follow a thermal or photochemical pathway. Thermal conversion at the triplet surface has a prohibited high barrier at room temperature, but spin cross-over from the triplet to the CSS surface might facilitate the overall process. A pathway involving H-atom abstraction from benzene followed by a radical rebound reaction was found to be less likely, due to a higher energy barrier (see Appendix Figure 16). At the CSS and OSS surfaces, direct thermal conversion from $^1$C to $^1$D is energetically possible at room temperature. The alternative scenarios of outer-sphere C-H activation prior to the N-insertion step, with formation of a five-coordinate Ni(PNP)(NH)(Ph) imido-species intermediate, were also investigated but found to be less favorable.

2.2.4 Trapping attempts of postulated intermediates

Several attempts to trap the postulated intermediate B were undertaken. Photolysis of 2 in benzene was conducted in the presence of various additives that were hypothesized to react with B. The addition of Me$_3$NO might lead to formation of the corresponding nitrosyl complex Ni(NO)(PNP) and the presence of PMe$_3$ could lead to Ni(N=PMe$_3$)(PNP). However, neither of the expected trapping products were isolated, according to IR and NMR spectroscopic analysis. Performing the photolysis in pure 1,4-cyclohexadiene did not lead to the generation of Ni(NH$_2$)(PNP), nor did the use of H$_2$ as trapping agent. Most interestingly, however, the known Ni(H)(PNP) complex$^{[13]}$ was observed after the latter experiment. Furthermore, NH$_3$ was detected by $^{15}$N NMR spectroscopy ($^{14/15}$N-2 was used) and spectrophotometric assay analysis, while use of D$_2$ resulted in ND$_3$. It is possible that the NH$_3$ and the Ni-hydride originate from reaction of H$_2$ with the transient nitrido species B. Alternatively, light-induced reaction of 2 with H$_2$ to form Ni(H)(PNP) and HN$_3$ and subsequent decomposition of the latter generating NH$_3$ and N$_2$ is a likely scenario. Other pathways for the formation of the products can also not be excluded at this point. Nevertheless, it is clear that the nitrogen in the ammonia originates from the decomposed azido group.

2.2.5 Exploration of the scope of C-H activation

The (proposed) final step of the reaction is interesting as it involves C-H activation of benzene. Therefore, initial experiments were performed in an attempt to broaden the reactivity ‘scope’ of the trapped species C. Photolysis of 2 in toluene led to four sets of doublets according to in situ $^{31}$P NMR spectroscopy, suggesting that C($sp^2$)-H and C($sp^3$)-H bond activation may be competitive processes (see Appendix Figure 17). Photolysis of
2 in (2,3,4,5,6)-pentafluorotoluene seemed to confirm that C(sp\(^3\))-H bond activation is possible, as only one pair of doublets is present in the in situ \(^{31}\)P NMR spectrum (see Appendix Figure 18). However, the presence of a second species, a singlet that is likely attributable to a Ni(PNP)F complex, indicates other processes also occur. Photolysis of 2 in neat cyclohexane or heptane resulted in a myriad of unidentifiable species by \(^{31}\)P NMR spectroscopy. Due to the lack of selectivity, difficulty in the characterization of products and general impracticability of this method of C-H activation, further attempts were not made.

A kinetic isotope effect of 3.8 could be determined by performing the photolysis in a mixture of C\(_6\)D\(_6\) and C\(_6\)H\(_6\). An attempt to confirm this value by conducting the photolysis in 1,3,5-trideutero benzene was thwarted by trace amounts of chlorobenzene in the purchased solvent (detected by MS), culminating in the presence of two doublets at \(\delta\) 46.8 and 45.3 in the \(^{31}\)P NMR spectrum. These signals could be attributed to the chlorido-derivative of 5, NiCl(PNP\(^:\text{H}\)) (6). Irradiation of 2 in pure chlorobenzene resulted in formation of 1 and 6 after four hours, establishing that the chloride likely stems from this molecule. Complex 6 was also prepared independently by reaction of 5 with HCl (Figure 13) and fully characterized by NMR spectroscopy, mass spectrometry and X-ray diffraction. The structural parameters for the chlorido-derivative 6 are very similar to those observed for 5. We speculated that deprotonation of 6 with LDA in the presence of an arene might lead to C-H activation. However, conducting this experiment in benzene did not result in arene C-H activation.

**Figure 13.** Left: Synthesis of complex 6 by reaction with HCl. Right: ORTEP plots (50% probability level) for 6. Hydrogen atoms are omitted for clarity, except for hydrogen on N2. Selected bond lengths (Å) and angles (°): Ni1-N1 1.930(3); Ni1-P2 2.112(2); Ni1-N2 1.893(3); Ni1-Cl1 2.1951(11); N2-P1 1.587(3); P2-Ni1-N2 176.80(13); N1-Ni1-N2 94.05(13); N1-Ni1-P2 86.03(11); N1-Ni1-Cl1 173.74(9); Ni1-N2-P1 129.7(2); C6-N1-C12 116.8(3).
2.3 Conclusions

In conclusion, in this Chapter we have shown that a rare transient formal NiIV nitrido species can be accessed by activation of nickel-azido precursor 2. The activation of the azide can be achieved by irradiation, while other potential activation pathways (thermolysis, chemical oxidation) proved to be ineffective. The Ni-nitrido so far has resisted characterization or isolation, and trapping by external trapping agents (PMe3, Me3NO, CO and 1,4-cyclohexadiene) was not successful. Facile N-insertion into a Ni-P bond and subsequent intermolecular C-H activation of benzene lead to formation of 5. Hence, trapping of the nitrido is an intramolecular process. DFT calculations support the intermediacy of a Ni nitrido species with significant nitridyl radical character. The scope for further reactivity is limited. Other solvents appear to be activated by the trapped nickel nitrido intermediate (C) under photolysis conditions, but a lack of selectivity and the harsh experimental conditions render this method impractical for more generally applicable arene C-H activation. The obtained PNPNH scaffold might however be interesting for cooperative catalysis, given the short distance between the P=NH site and the metal center.

2.4 Acknowledgements

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2.5 Experimental Section

2.5.1 General methods

All reactions were carried out under an atmosphere of argon or dinitrogen using standard Schlenk techniques. With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. (PNP)Ni(Cl) (I) was synthesized according to literature procedures. Toluene, THF, pentane and diethyl ether were distilled from sodium benzophenone ketyl. CH2Cl2 was distilled from CaH2. NMR spectra (1H, 1H{31P}, 13C{1H}, 31P{1H} and 15N (HSQC)) were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer at room temperature, unless noted otherwise. Infrared spectra were recorded
on a Thermo Nicolet Nexus FT-IR spectrometer. High resolution mass spectra were recorded on a JEOL AccuTOF LC, JMS-T100LP Mass spectrometer using cold spray ionization (CSI) and electron spray ionization (ESI) and on a JEOL AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer using field desorption (FD). A Shimadzu UV 2700 spectrophotometer was used to record UV-vis spectra. Elemental analyses were carried out by Mikroanalytisches Laboratorium Kolbe. Cyclic voltammetry measurements were performed in THF containing N(Bu)4PF6 (0.1 M) at room temperature under an argon atmosphere using a platinum disk working electrode, a platinum coil counter-electrode and a silver coil reference electrode. All redox potentials are referenced to Fc/Fc+. For the irradiation experiments a 500 W Hg/Xe lamp (Hamamatsu Photonics L8288) with a 305 nm cut-off filter was used.

**2.5.2 Computational details**

Geometry optimizations were carried out with the Turbomole program package\cite{18a} coupled to the PQS Baker optimizer\cite{18b} via the BOpt package\cite{18c,18d,e} both at the BP86\cite{18d,e} level, using the def2-TZVP basis set.\cite{18f,i} All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The nature of the transition states was confirmed by IRC calculations.

The geometries for the open-shell singlet (singlet biradical) minima and transition states were evaluated employing the broken-symmetry protocol. The ‘real’ energy $\varepsilon_S$ of the (multi-determinant) open-shell singlet species was estimated from the $\varepsilon_0$ energies of the optimized single-determinant broken symmetry solutions and the $\varepsilon_1$ energies from a separate unrestricted triplet ($m_s = 1$) calculations at the same geometries with the same functional and basis set, using the approximate spin correction formula proposed by Noodleman and Yamagushi: \cite{19}

$$\varepsilon_S \approx \frac{S_1^2 \varepsilon_0 - S_0^2 \varepsilon_1}{S_1^2 - S_0^2}$$

**2.5.3 Synthesis and characterization of new compounds**

*Synthesis of complex 2:*

```
\[ \begin{array}{c}
\text{Ni} \\
\text{(iPr)\_2P} \\
\text{N\_3} \\
\text{(iPr\_2P} \\
\text{Ni} \\
\text{(iPr)\_2P} \\
\end{array} \]
```

To a solution of 1 (750 mg, 1.43 mmol) in THF (15 mL) was added NaN3 (466 mg, 7.2 mmol). The dark-green mixture was stirred for 20 hours, resulting in a gradual fading of color from green to moss-green. Upon complete conversion, based on $^{31}$P NMR spectroscopy, the volatiles were removed *in vacuo*. The
product was extracted with toluene and filtered over Celite. Evaporation of toluene yielded the desired complex as a green-brown powder (749 mg, 99%). Single crystals suitable for X-ray diffraction were grown from a toluene/pentane mixture at -20 °C.

\[ ^1H \text{ NMR} (400 \text{ MHz, C}_6D_6, \text{ ppm}) \]: \( \delta 7.45 (dt, J = 8.6, 2.3 \text{ Hz}, 2H), 6.86-6.82 (m, 2H), 6.69 \text{ (dd, } J = 8.5, 2.0 \text{ Hz, } 2H), 2.19-2.12 (m, 4H), 2.10 (s, 6H), 1.47 (q, J = 8.8, 7.2 \text{ Hz, } 12H), 1.17 (q, J = 8.0, 7.2 \text{ Hz, } 12H). \]

\[ ^13C\{^1H\} \text{ NMR} (101 \text{ MHz, C}_6D_6, \text{ ppm}) : \delta 162.2 \text{ (t, } J = 13.0 \text{ Hz)}, 132.6 \text{ (s)}, 132.0 \text{ (s)}, 125.4 \text{ (t, } J = 3.2 \text{ Hz)}, 119.4 \text{ (t, } J = 19.5 \text{ Hz)}, 116.7 \text{ (t, } J = 5.4 \text{ Hz)}, 23.4 \text{ (t, } J = 11.4 \text{ Hz)}, 20.4 \text{ (s)}, 18.4 \text{ (t, } J = 2.5 \text{ Hz)}, 17.7 \text{ (s).} \]

\[ ^31P\{^1H\} \text{ NMR} (162 \text{ MHz, C}_6D_6, \text{ ppm) : 36.3.} \]

\[ \text{FT-IR (CH}_2\text{Cl}_2, \text{ cm}^{-1}): \nu 2040 \text{ cm}^{-1} (N_3, \text{ strong).} \]

**Synthesis of \( ^{15}N \) enriched complex \( ^{15/14}N-2 \):**

\( ^{15/14}N-2 \) was synthesized by adding Na\(^{15}\)N\(^{14}\)N\(_2\) (75 mg, 1.14 mmol) to a solution of 1 (150 mg, 0.29 mmol) in THF (10 mL). The mixture was stirred for 66 hours, during which the green color slightly faded. Completion of the reaction was confirmed by \( ^3P \) NMR spectroscopy, where after the volatiles were removed in vacuo. The resulting solid was extracted with toluene and filtered over Celite. Removal of solvent yielded the product as a green-brown solid, which was recrystallized from a toluene/pentane mixture at -20 °C.

\[ \text{FT-IR (CH}_2\text{Cl}_2, \text{ cm}^{-1}): \nu 2040 \text{ cm}^{-1} (N_3, \text{ strong).} \]

**Synthesis of complex 3:**

To a Schlenk charged with 2 (26.1 mg, 0.049 mmol) and AgBF\(_4\) (9.1 mg, 0.047 mmol) was added 2 mL acetone. The solution immediately colored intense blue and was stirred for 2 hours. The volatiles were then removed in vacuo. The residue was triturated with 2 \( \times 1.5 \) mL toluene and 2 \( \times 2 \) mL pentane. The desired complex was then dissolved in CH\(_2\)Cl\(_2\) and filtered by cannula. Evaporation of the solvent resulted in a dark blue/purple solid (28 mg, 97%).

\( \mu_{\text{eff}} \): 2.047 \( \mu_B \) (CDCl\(_3\), 25°C, Evans method). **HR-MS** (FD) calcd for [M]\(^+\) \( \text{C}_{26}\text{H}_{40}\text{N}_4\text{NiP}_2 \) \( m/z \): 528.20817; found: 528.20797. **FT-IR** (CH\(_2\)Cl\(_2\), \text{ cm}^{-1}): \nu 2051 (strong, N\(_3\) stretch)

**Synthesis of complex 4:**

\( \text{Method A:} \) A solution of 2 (3.0 mg, 5.7 \( \mu \)mol) in C\(_6\)D\(_6\) (0.6 mL) was charged to a J-Young NMR tube. The tube was pressurized with 5 bars of CO and then covered with aluminum foil. The reaction was complete after 18 hours, with a color change to bright-green. **Method B: To a Schlenk charged with 1 (104 mg,
0.20 mmol) and KNCO (161.4 mg, 1.98 mmol) was added THF (10 mL). The mixture was stirred for 68 hours. The color changed to bright-green during this period and completion of the reaction was confirmed by $^{31}$P NMR spectroscopy. The volatiles were evaporated and the residue was extracted with toluene and filtered over Celite. Toluene was removed in vacuo, yielding a green crystalline solid (98.1 mg, 93%).

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): δ 7.43 (dt, $J_1=8.6, 2.2$ Hz, 2H), 6.82 (q, $J_2=3.6$ Hz, 2H), 6.68 (dd, $J_3=8.7, 0.6$ Hz, 2H), 2.09 (s, 6H), 2.07 – 1.96 (m, 4H), 1.40 (q, $J_4=8.8, 7.6$ Hz, 12H), 1.13 (q, $J_5=7.6, 7.2$ Hz, 12H).

$^{13}$C{$^1$H} NMR (100.6 MHz, CD$_2$Cl$_2$, ppm): δ 162.0 (t, $J_1=13.2$ Hz), 132.3 (s), 132.1 (s), 125.9 (t, $J_2=3.3$ Hz), 119.2 (t, $J_3=19.6$ Hz), 116.5 (t, $J_4=5.6$ Hz), 24.0 (t, $J_5=11.6$ Hz), 20.3 (s), 18.5 (t, $J_6=2.1$ Hz), 17.9 (s).

$^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, ppm): δ 37.7 (s). FT-IR (CH$_2$Cl$_2$, cm$^{-1}$): ν 2240 (strong, NCO band).

HR MS (FD) calcd for [M]$^+$ C$_{27}$H$_{40}$N$_2$NiOP$_2$ m/z: 528.19693; found: 528.19819.

Synthesis of complex 5:

A J-Young NMR tube was charged with 2 (3 mg, 5.2 µmol) dissolved in benzene (0.5 mL). The dark-green solution was irradiated for 30 minutes, during which the color of the solution changed to yellow. Removal of volatiles in vacuo resulted in a yellow solid that was used for analysis in NMR experiments. Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH$_2$Cl$_2$/cyclopentane mixture.

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): δ 7.92 (br. s, 2H), 7.68 (dd, $J_1=8.6, 8.4$ Hz, 1H), 7.26 (dd, $J_2=8.4, 4.2$ Hz, 1H), 7.16 (s, 2H), 7.02 (t, $J_3=7.2$ Hz, 1H), 6.96-6.91 (m, 2H), 6.84 (d, $J_4=8.6$ Hz, 1H), 6.69 (dd, $J_5=12.0, 2.1$ Hz, 1H), 2.28-2.20 (m, 1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.11-1.97 (m, 2H), 1.85-1.75 (m, 1H), 1.54 (dd, $J_6=17.1, 7.1$ Hz, 3H), 1.39 (dd, $J_7=16.9, 6.9$ Hz, 3H), 1.21 (dd, $J_8=18.7, 7.3$ Hz, 3H), 1.00 (dd, $J_9=16.6, 7.3$ Hz, 3H), 0.94 (dd, $J_{10}=10.8, 6.9$ Hz, 3H), 0.65 (dd, $J_{11}=14.4, 6.9$ Hz, 3H), 0.56 (dd, $J_{12}=14.6, 7.1$ Hz, 3H), 0.33 (dd, $J_{13}=13.7, 7.1$ Hz, 3H), 0.22 (d, $J_{14}=6.5$ Hz, 1H).

$^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$, ppm): δ 164.4 (d, $J_1=22.0$ Hz), 158.1 (s), 156.6 (d, $J_2=44.7$ Hz), 139.3 (bs), 133.0 (d, $J_3=2.0$ Hz), 132.4 (d, $J_4=2.1$ Hz), 130.9 (d, $J_5=1.1$ Hz), 130.1 (d, $J_6=8.7$ Hz), 126.0 (bs), 124.5 (d, $J_7=5.4$ Hz), 123.7 (s), 123.6 (d, $J_8=4.7$ Hz), 122.2 (s), 120.9 (d, $J_9=36.3$ Hz), 118.4 (d, $J_{10}=10.0$ Hz), 115.3 (s), 114.3 (s), 27.9 (d, $J_{11}=58.5$ Hz), 22.2 (d, $J_{12}=19.2$ Hz), 21.4 (d, $J_{13}=33.2$ Hz), 21.3 (dd, $J_{14}=53.5, 3.0$ Hz), 20.8 (s), 20.7 (s), 19.7 (d, $J_{15}=6.3$ Hz), 17.8 (d, $J_{16}=4.7$ Hz), 17.0 (d, $J_{17}=1.2$ Hz), 16.9 (d, $J_{18}=1.3$ Hz), 16.7 (d, $J_{19}=2.8$ Hz), 15.7 (d, $J_{20}=6.9$ Hz), 15.7 (d, $J_{21}=1.8$ Hz), 15.4 (d, $J_{22}=1.0$ Hz).

$^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, ppm): δ 48.5 (d, $J_1=6.4$ Hz), 45.9 (d, $J_2=6.4$ Hz). FT-IR (CH$_2$Cl$_2$, cm$^{-1}$): ν 3365 (weaker, NH stretch). HR-MS (CSI) calcd for [M+H]$^+$ C$_{32}$H$_{46}$N$_2$NiP$_2$ m/z: 579.25679; found: 579.25263. El. Anal. Calc. for C$_{32}$H$_{46}$N$_2$NiP$_2$: C 66.22; H 8.16; N 4.83. Found: C 66.31; H 7.99; N 4.92.
Isotopic labelling experiments:

Enriched $^{15}/^{14}$N-5 was prepared by irradiation of a J-Young NMR tube charged with a solution of $^{15}/^{14}$N-2 in benzene. Photolysis for 30 minutes using a 305 nm cut-off filter yielded the 50% $^{15}$N-enriched product $^{15}/^{14}$N-5.

$^1$H NMR (500 MHz, C$_6$D$_6$, ppm): $\delta$ 7.91 (s, 2H), 7.66 (dd, $J$ = 8.6, 5.0 Hz, 1H), 7.24 (dd, $J$ = 8.5, 4.2 Hz, 1H), 7.16 (s, 2H), 7.01 (t, $J$ = 7.2 Hz, 1H), 6.93 (td, $J$ = 7.6, 6.7, 2.1 Hz, 2H), 6.84 (d, $J$ = 8.5 Hz, 1H), 6.70 (dd, $J$ = 11.8, 2.2 Hz, 1H), 2.32 – 2.19 (m, 1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.14 – 1.97 (m, 2H), 1.88 – 1.77 (m, 1H), 1.54 (dd, $J$ = 17.2, 7.2 Hz, 3H), 1.39 (dd, $J$ = 16.9, 6.9 Hz, 3H), 1.22 (dd, $J$ = 16.4, 7.3 Hz, 3H), 1.01 (dd, $J$ = 16.6, 7.2 Hz, 3H), 0.94 (dd, $J$ = 10.8, 6.9 Hz, 3H), 0.66 (dd, $J$ = 14.4, 7.0 Hz, 3H), 0.57 (dd, $J$ = 14.6, 7.2 Hz, 3H), 0.34 (dd, $J$ = 13.7, 7.1 Hz, 3H), 0.21 (d, $J$ = 6.4 Hz, 0.5H), 0.21 (dd, $J$ = 73.2, 6.4 Hz, 0.5H). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, ppm): $\delta$ 48.5 (dd, $J_{NP}$ = 30.5 Hz, $J_{PP}$ = 6.5 Hz), 48.5 (d, $J_{PP}$ = 6.5 Hz), 45.8 (dd, $J_{NP}$ = 29.2 Hz, $J_{PP}$ = 6.5 Hz), 45.8 (d, $J_{PP}$ = 6.5 Hz).

$^{15}$N{$^1$H} NMR (50.7 MHz, C$_6$D$_6$, ppm): $\delta$ -364.8 (t, $J$ = 30.2 Hz).

Deuterium-labelled 5D was prepared by dissolving 2 in C$_6$D$_6$. A J-Young NMR tube was filled with the solution and irradiated using a 305 nm cut-off filter. After 30 minutes the color had changed from green to yellow and the deuterium-labelled product 5D had formed.

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): $\delta$ 7.68 (dd, $J$ = 8.7, 5.0 Hz, 1H), 7.26 (dd, $J$ = 8.4, 4.1 Hz, 1H), 6.93 (td, $J$ = 7.9, 7.0, 2.2 Hz, 2H), 6.86 – 6.83 (m, 1H), 6.69 (dd, $J$ = 11.9, 2.1 Hz, 1H), 2.28 – 2.20 (m, 1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.13-1.95 (m, 2H), 1.86-1.73 (m, 1H), 1.54 (dd, $J$ = 17.2, 7.2 Hz, 3H), 1.39 (dd, $J$ = 16.8, 6.9 Hz, 3H), 1.21 (dd, $J$ = 16.3, 7.3 Hz, 3H), 1.00 (dd, $J$ = 16.6, 7.2 Hz, 3H), 0.94 (dd, $J$ = 10.8, 6.9 Hz, 3H), 0.65 (dd, $J$ = 14.4, 7.0 Hz, 3H), 0.56 (dd, $J$ = 14.6, 7.1 Hz, 3H), 0.32 (dd, $J$ = 13.6, 7.0 Hz, 3H). FT-IR (CH$_2$Cl$_2$, cm$^{-1}$): $\nu$ 2493.

Synthesis of complex 6:

A solution of 5 (10 mg, 17.3 µmol) in 2 mL THF was prepared. A small excess of HCl (1M in Et$_2$O) was added and the mixture was stirred for 2.5 h. During this period the color of the solution changed from yellow to green. All volatiles were removed in vacuo. The resulting solid was redissolved in pentane and filtered via cannula. After evaporation of the solvent a green powder remained as product (6.2 mg, 67%).

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): $\delta$ 7.50 (dd, $J$ = 8.8, 4.8 Hz, 1H), 6.97-6.90 (m, 2H), 6.81 (dd, $J$ = 8.8, 0.8 Hz, 1H), 6.70 (d, $J$ = 8.4 Hz, 1H), 6.61 (d, $J$ = 12 Hz, 1H), 2.40 (septet, $J$ = 7.2 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.07-1.95 (m, 1H), 1.86-1.71 (m, 2H), 1.74 (dd, $J$ = 15.2, 7.2 Hz, 3H), 1.63-1.53 (m, 6H), 1.28 (dd, $J$ = 16.0, 7.2 Hz, 3H), 1.07
(dd, $J = 13.8, 7.2$ Hz, 3H), 0.85-0.75 (m, 6H), 0.55 (dd, $J = 15.2, 7.2$ Hz, 3H), 0.35 (d, $J = 4.5$ Hz, 1H). $^{13}$C($^1$H) NMR (100.6 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 165.0 (s), 164.7 (s), 156.7 (s), 132.9 (d, $J = 2.3$ Hz), 132.5 (d, $J = 2.3$ Hz), 130.9 (d, $J = 1.0$ Hz), 130.4 (d, $J = 8.5$ Hz), 126.7 (d, $J = 12.3$ Hz), 126.2 (d, $J = 8.4$ Hz), 125.8 (d, $J = 5.9$ Hz), 120.6 (d, $J = 41.8$ Hz), 119.5 (d, $J = 11.0$ Hz), 28.0 (d, $J = 56.5$ Hz), 25.2 (d, $J = 20.3$ Hz), 23.1 (d, $J = 3.8$ Hz), 22.8 (s), 22.1 (dd, $J = 55.0, 3.2$ Hz), 20.7 (s), 20.3 (s), 19.0 (d, $J = 4.1$ Hz), 18.4 (d, $J = 1.8$ Hz), 18.1 (s), 17.4 (d, $J = 1.8$ Hz), 16.9 (s), 16.8 (s), 15.7 (d, $J = 1.0$ Hz).

$^{31}$P($^1$H) NMR (162 MHz, C$_6$D$_6$, ppm): $\delta$ 46.8 (d, 8.1 Hz), 45.3 (d, 8.1 Hz).

HR MS (FD) calcd for [M]$^+$ C$_{26}$H$_{41}$ClN$_2$NiP$_2$ m/z: 536.17807; found: 536.17904.

2.5.4 Irradiation experiments using other solvents

For a typical experiment, 3 mg (5.7 $\mu$mol) of 2 was dissolved in 0.6 mL of the chosen solvent. A J-Young NMR tube was charged with the solution. The solution in the NMR tube was irradiated until the starting material was completely converted, based on in-situ $^{31}$P NMR spectroscopy.

2.5.5 Irradiation experiments of 2 with nitrido trapping agents

Experiments were conducted in an attempt to trap the postulated nitrido intermediate B, by carrying out the photolysis of 2 in the following ways:

- In a J-Young NMR tube, 2 (4 mg) was dissolved in degassed 1,4-cyclohexadiene (0.5 mL) and irradiated in the usual manner. The reaction was monitored by in situ $^{31}$P NMR spectroscopy. When full conversion of the starting material was reached, all volatiles were removed in vacuo. The solid residue was dissolved in C$_6$D$_6$ and $^{31}$P and $^1$H NMR spectra were measured. The spectra showed no trace of Ni(NH$_2$)(PNP).

- In a J-Young NMR tube, 2 (4 mg, 7.6 $\mu$mol) was dissolved in C$_6$H$_6$ and 50 eq. of PMe$_3$ (39 $\mu$L, 380 $\mu$mol) were added. The mixture was irradiated in the usual manner. The reaction was monitored by in situ $^{31}$P NMR spectroscopy. When full conversion of the starting material was reached, all volatiles were removed in vacuo. The solid residue was dissolved in C$_6$D$_6$ and $^{31}$P and $^1$H NMR spectra were measured. The spectra showed no trace of Ni(N=PMe$_3$)(PNP).

- In a J-Young NMR tube, $^{15}$N enriched $^{15/14}$N-2 was dissolved in C$_6$D$_6$ and put under 5 bar H$_2$ pressure. The mixture was irradiated in the usual manner and when completion of the reaction was reached, $^{31}$P, $^1$H and $^{15}$N NMR spectra were measured. The spectra showed no trace of Ni(NH$_2$)(PNP). Instead, the main product was the known Ni(H)(PNP) complex.[14] The presence of NH$_3$ was confirmed by $^1$H NMR ($\delta$ -0.30, br s) and $^{15}$N HSQC-NMR (-385.1 ppm, t) spectroscopy. After NMR analysis the organic phase was washed with 1 mL of a 1M H$_2$SO$_4$ (aq) solution. The presence of NH$_3$ in the aqueous
phase was confirmed by the indophenol method\textsuperscript{[20]} and by a fluorometric ammonia assay.\textsuperscript{[21]} To exclude the involvement of 3 in the formation of NH\textsubscript{3}, 3 was irradiated in the presence of H\textsubscript{2}, which did not lead to formation of Ni(H)(PNP). To establish the origin of the hydrogen atoms in the formed NH\textsubscript{3} and Ni(H)(PNP), \textsuperscript{15}N enriched \textsuperscript{15/14}N-2 was dissolved in C\textsubscript{6}H\textsubscript{6}, put under 5 bar D\textsubscript{2} pressure and irradiated. The corresponding 2D NMR spectrum showed formation of ND\textsubscript{3} and Ni(D)(PNP).

- In a J-Young NMR tube 2 (3.3 mg, 6.2 μmol) and 18.7 eq. BPh\textsubscript{3} (28 mg, 116 μmmol) were dissolved in C\textsubscript{6}H\textsubscript{6}. The mixture was irradiated in the usual manner. After full conversion of the starting material, the \textsuperscript{31}P NMR spectrum of the solution showed a mixture of products, but the desired trapping product Ni(N-BPh\textsubscript{3})(PNP) could not be identified.

- In a J-Young NMR tube 2 (3.5 mg, 6.6 μmol) was dissolved in C\textsubscript{6}D\textsubscript{6} and the solution was saturated with Me\textsubscript{3}NO. The mixture was irradiated in the usual manner. After full conversion of the starting complex the \textsuperscript{31}P NMR spectrum showed a mixture of products. The IR spectrum of the resulting mixture did not show an indicative Ni-NO stretch.

### 2.5.6 X-ray crystallographic measurements details

For 2: Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) up to a resolution of (sin θ/λ)\textsubscript{max} = 0.71 Å\textsuperscript{-1} at a temperature of 150(2) K. Intensities were integrated using the SAINT software.\textsuperscript{[22]} Absorption correction and scaling based on multiple measured reflections was performed with SADABS\textsuperscript{[23]} (0.70-0.75 correction range). 9601 Reflections were unique (R\textsubscript{int} = 0.013), of which 9338 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using the program SHELXT.\textsuperscript{[24]} The crystal structure can be approximated in the higher symmetric space group P2/n (no. 13) with the metal complex on a twofold rotation axis and an inversion center in the crystal packing. The routine ADDSYM of the PLATON software\textsuperscript{[25]} calculates an 82% fit for the higher symmetry. Only the coordinated azide ligand and the non-coordinated toluene solvent molecule violate the higher symmetry, and force the structure to be in the lower symmetric space group Pn (no. 7). Refinement in space group Pn was done as an inversion twin, resulting in a twin fraction (Flack parameter\textsuperscript{[26]}) of 0.496(5). The SHELXL-97 software\textsuperscript{[27]} was used for the least-squares refinement against F\textsuperscript{2} of all reflections. No correlation matrix element was larger than 0.5. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference-Fourier maps and refined with a riding model. 373 Parameters were refined with 2 restraints (floating origin restraints). R1/wR2 [I > 2σ(I)]: 0.0204 / 0.0554. R1/wR2 [all refl.]: 0.0215 / 0.0561. S = 1.054. Residual electron density between -0.22 and 0.37
e/Å³. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[25]

For 5: All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu Kα radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2013S18 and was refined on F² with SHELXL-2013 (Sheldrick, 2013). Analytical numeric absorption corrections based on a multifaceted crystal model were applied. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times Ueq of the attached C atoms. The H atom attached to N2 was found from difference Fourier map, and its coordinates and isotropic temperature factor were refined freely. The structure is ordered. Prior to the final refinement, the occupancy factor of N2 was refined freely, and its value refines to 0.9983(99), which unambiguously shows that the atom type for N2 has been correctly assigned. In the final refinement, one residual electron density peak of ca. 1.80 e− Å⁻³ was found at 0.99 Å of Ni1, but has no chemical significance. A check for twinning was performed, but no applicable twin laws could be detected from Fobs/Fcal analysis.

For 6: X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å). Diffraction data were collected at 150(2) K using a CMOS Photon 50 detector. Intensity data were integrated with Bruker APEX2 software.[29] Absorption correction and scaling was performed with SADABS.[23] The structures were solved using direct methods with SHELXL-13.S18 Least-squares refinement was performed with SHELXL-2013S18 against F² of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Heteroatom bound hydrogen atoms were refined freely with an isotropic displacement parameter, all other hydrogen atoms were included at calculated positions using a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[25]
2.6 Appendix

Figure 14. Stacked $^1$H NMR spectra of complex 5 at different temperatures from 203 K (bottom) to 273 K (top) ($\text{C}_7\text{D}_8$, 298 K, 500 MHz).

DFT calculations, mechanistic considerations:

The b3-lyp functional as well as the BP86 functional was used for the geometry optimizations. The b3-lyp functional was used to enable optimization of geometries in the open-shell singlet (OSS) state. Although the calculated reaction pathway was found to be similar in the calculated for either functional (loss of N$_2$, insertion of N into a Ni-P bond, concerted C-H activation of benzene) discrepancies were found in the relative stability of the spin states (CSS and triplet) of several geometries. As a result, clear statements on the most stable spin states of intermediate and transition state structures in the envisioned mechanism are not possible. Furthermore, the CSS state of intermediate B could only be isolated using the b3-lyp functional, attempts with the BP-86 functional resulted in direct insertion into the Ni-P bond. A short discussion on the proposed pathway calculated using each will be given (*vide infra*).

Using the b3-lyp functional (Figure 11): the starting azide complex A is most stable in its closed-shell singlet (CSS) state, as expected. Attempts to optimize an open-shell singlet (OSS) state resulted in convergence to the CSS state, while the triplet (T) state was found to be 12.3 kcal mol$^{-1}$ higher in energy. Through (photochemical induced) expulsion of N$_2$...
in TS1 intermediate B is formed, which is most stable in its triplet state. Insertion of the N into the Ni-P bond through TS2 leads to the low-energy intermediate C. Energies of the different spin states of C are very similar, with the triplet state being slightly preferred. Two scenarios were considered for the activation of benzene: a concerted pathway via TS3 involving a spin cross-over from the triplet to the singlet surface (see Figure 11) or a hydrogen atom abstraction on the triplet or open-shell singlet surface via TS3*. (Appendix Figure 16). The concerted mechanism is deemed more likely because of the lower energy barrier TS3 poses opposed to TS3*. As expected, the product species D was found to be most stable in the CSS state.

Using the BP86 functional (Appendix Figure 15): starting complex A was found to be most stable in the CSS state. Expulsion of N₂ in TS1 is followed by a barrierless insertion of N into a Ni-P bond in the CSS state leading to intermediate C. In the triplet state however intermediate B involving a ‘Ni-nitride’ could be isolated. A subsequent insertion of this ‘nitride’ into the Ni-P bond then also leads to intermediate C. A concerted C-H activation of benzene over the Ni-N moiety trough TS3 leads to final product D.

**Figure 15.** DFT calculated free energy profile (ΔG°₂⁹₈K in kcal mol⁻¹) of the proposed pathway from the starting azide complex A to the product of the photolysis D (BP86, def2-TZVP).
Figure 16. DFT calculated free energy profile ($\Delta G_{298}^{0}$ in kcal mol$^{-1}$) for the alternative activation step of benzene via a hydrogen atom abstraction pathway (b3-lyp, def2-TZVP).

Figure 17. $^{31}$P$\{^1$H$\}$ NMR spectrum of an irradiated toluene solution of 2 (CD$_2$Cl$_2$, 298 K, 162 MHz), * = doublet for chlorinated complex (6), probably due to presence of traces HCl in CD$_2$Cl$_2$. HR MS (CSI) calcd for [M]$+\ C_{26}$H$_{41}$ClN$_2$NiP$_2$ m/z: 592.26462; found: 592.26839.
Figure 18. $^{31}$P($^1$H) NMR spectrum of an irradiated solution of 2 in (2,3,4,5,6)-pentafluorotoluene (298K, 162 MHz).
2.7 References


[8] Tetraedral Ni4(BP3)3(N3) complex was reported to be unreactive upon irradiation, while thermolysis led to a myriad of products. N-atom transfer using dbab (dbab = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]-hepta-2,5-diene) was also not successful. See: C. E. MacBeth, J. C. Thomas, T. A. Betley, J. C. Peters, *Inorg. Chem.* 2004, 43, 4645 – 4662.


Activation of CuH₂ by a Ni(PNP)-hydride species has been reported, but AlMe₃ is required to promote this reaction: L.-C. Liang, P.-S. Chien, Y.-L. Huang, *J. Am. Chem. Soc.* **2006**, *128*, 15562 – 15563.


Chapter 3

Thermal and Photolytic Activation of a (PNP)Co-Azido Complex
3.1 Introduction

Preparation, characterization and reactivity of transition metal complexes featuring multiple bonded nitrido (M≡N) ligands have attracted increased interest of chemists recently, as such fragments are proposed to play important roles in N$_2$ splitting, N-atom transfer reactions and in biochemical processes. Nitrido complexes with early and mid transition metals are well-known and have been well-studied.[1–4] However, moving to later TMs (Group 9-11), detectable bona fide M≡N complexes are still rare. This can be rationalized by considering the mismatch between the strongly π-donating N$_3^-$ ligand and the increasingly electron-rich metal centers, leading to the filling of antibonding π-orbitals and overall destabilization of the M-N bonding in these complexes. The resulting elusiveness of octahedral oxido complexes beyond Group 8 has been referred to as the “oxo-wall dilemma” (as a similar situation exists for O$_2^-$ ligands, that were previously investigated).[5–7]

The first examples of rhodium and iridium complexes bearing nitrido/nitridyl[8] ligands were reported recently.[9–14] Typically, M-azido (azido = N$_3^-$) complexes were used as precursors to generate the nitrido species, using either thermolysis, chemical oxidation or photolysis to activate the azido-group with release of N$_2$. Two Ir-nitrido compounds were actually isolated by the groups of Burger and Schneider,[9,10] while examples with Rh proved too reactive to be isolable and thus were only implied from follow-up reactivity. In one report, Schneider, de Bruin and coworkers suggested homocoupling of the characterized intermediate A, which bears significant spin density at the nitrido/nitridyl moiety, to form complex B. In the presence of N$_2$, C will be formed selectively (Figure 1, left).[13] In a different report, De Bruin et al. proposed coupling of nitridyl intermediate D forming dimeric species E. This compound can then be trapped again by D to form the isolated product F.[12]

![Diagram of complexes A to F](image)

**Figure 1.** Reactivity of intermediate rhodium nitrido/nitridyl species leading to homocoupled products.
In 2014, Meyer and coworkers described the first example of a characterized cobalt-nitrido intermediate. A Co(II)-azido precursor was subjected to photolysis at 10 K, whereafter a Co(IV)-nitrido complex was identified by EPR spectroscopy. At higher temperatures, migratory insertion of the nitrido into a metal-carbene bond (part of the ligand) and subsequent H-atom abstraction (from a sacrificial H-atom donor) resulted in the formation of a cobalt-bound imidazolin-2-imine fragment (Figure 2).[15] Earlier, the group of Chirik had reported on photolysis and thermolysis of bis(imino)pyridine cobalt azide complexes, leading to N-insertion into ligand C-H bonds. A putative transient cobalt-nitrido complex was proposed as the intermediate species, but no spectral evidence was provided (Figure 2).[16] It is clear that reactivity of the (proposed) nitrido is intramolecular in both cases and as such different from the Rh examples. Clearly, Group 9 nitrido chemistry is far from trivial. Interestingly, in contrast to the Rh and Ir examples, no cobalt-based nitrido chemistry has been reported for complexes bearing phosphine ligands.

In Chapter 2, the photolysis Ni(PNP)(N₃) (PNP = 2,2’-di(isopropylphosphino)-4,4’-ditolylamine) in a benzene solution was described.[17] The isolated product was characterized as the Ni(PNP'H)Ph complex (Figure 2). DFT-studies resulted in the proposal of a mechanism involving a transient Ni-nitrido complex, N-migratory insertion into a Ni-P bond and successive C-H activation of benzene to provide the final product. However, spectral characterization of the postulated Ni≡N complex was unsuccessful and the scope of C-H activation was limited to the solvent used during photolysis. Mindiola and coworkers reported on the thermolysis of Fe(PNP)(dbabh) (dbabh = 2,3:5,6-dibenzoz-7-azabicyclo[2.2.1]hepta-2,5-diene). This reaction led to release of anthracene and a dimeric [(PNP)Fe(μ₂-N)]₂ structure (Figure 2) in which N-insertion into the Fe-P bond had occurred. The formation of a transient Fe≡N species was proposed as a possible intermediate in this reaction.[18]
Figure 2. N-insertion products resulting from thermolysis and photolysis of first-row metal nitrido precursors. Example of Meyer et al.: Reprinted and adapted with permission from ref 15. Copyright 2014 American Chemical Society. Example of Chirik et al.: Reprinted and adapted with permission from ref 16. Copyright 2010 American Chemical Society.

With the described examples of Group 9 nitrido chemistry in mind and knowing the possibilities and limitations in the activation of Ni(PNP)(N$_3$)$_2$, we decided to investigate the activation of Co(PNP)(N$_3$)$_2$ complex 2. This Chapter revolves around the following central questions: i) how do the activation of 2 and the resulting (intra- or intermolecular) reactivity compare to the nickel analogue and other Group 9 examples, ii) can the paramagnetism of Co$^{II}$ be utilized to perform low temperature characterization of a possible nitrido intermediate with EPR spectroscopy, and iii) are intermediates or products of the azide activation interesting targets for follow-up chemistry.

3.2 Results and discussion

3.2.1 Synthesis and characterization of azido complexes

The (PNP)CoCl complex (1) is an easy synthetic starting point, as substitution of the chloride for different nucleophiles is expected to be facile. Following a modified literature procedure,$^{[19]}$ compound 1 was prepared in high yield by the addition of CoCl$_2$ to in situ prepared (PNP)Li (Figure 3). A subsequent efficient salt metathesis reaction between 1 and NaN$_3$ led to the desired (PNP)CoN$_3$ species (2) in 95% yield. A color change from blue to dark green accompanies the conversion to the azido complex. A $^{15}$N enriched analogue of 2 was prepared by reacting 1 with an excess of Na($^{15}$N$^{14}$N$_2$). The resulting 2-$^{15}$N is enriched at either the metal-bound ($\alpha$) position of the azide (50%) or at the terminal ($\gamma$) position (50%).
Figure 3. Preparation of complexes 1 and 2 by salt metathesis.

The CoII-complex 2 was characterized by a variety of spectroscopic methods and by single crystal X-ray diffraction studies. The $^1$H NMR spectrum ranges from 44 ppm to -25 ppm and shows broadened signals, indicative of a paramagnetic compound. Evans’ method was used to determine the magnetic moment of 2. At room temperature the $\mu_{\text{eff}}$ was found to be 1.77 $\mu_B$,\textsuperscript{[20]} suggestive of an $S = \frac{1}{2}$ spin ground state. X-band EPR spectroscopy gives $g_x$ and $g_z$ values of 2.008 and 1.950, respectively (Figure 4).\textsuperscript{[21]} The combined results suggest the formation of a divalent low-spin Co species in a square planar geometry.

Markedly different from the nickel analogue described in Chapter 2, azido complex 2 is extremely air-sensitive. Solutions of 2 that come into contact with air immediately change color from dark green to light brown. Presumably, the discoloration is caused by oxidation of the ligand. Single crystals acquired from attempts to crystallize 2 support this, as structures of the double oxidized free ligand and of the related homoleptic cobalt complex were obtained in several attempts (not shown). The preparation of 2 is therefore best performed inside a glovebox. The sensitivity towards oxygen hampered analysis by coldspray ionization (CSI) HR-MS. Although the presence of 2 was confirmed by MS analysis, (oxidized) free ligand was also present in the mass spectrum.

Figure 4. Left: solution IR spectrum of 2 (solid line) and 2-$^{15}$N (dashed line) recorded in THF. Right: EPR spectrum of 2. Experimental parameters: Frequency = 9.386576 GHz, T = 20 K, Modulation Amplitude = 4.0 G, power = 0.6 mW. Simulated (DFT) $g$ value and hyperfine couplings $A$ (MHz): $g_x$ 3.00 (2.363), $g_y$ 2.008 (2.111), $g_z$ 1.950 (2.080); $A_{\text{Co}x}$ = 270 (364), $A_{\text{Co}y}$ = NR (325), $A_{\text{Co}z}$ = NR (-132).
Solution IR spectroscopy of 2 provides extra evidence for the incorporation of the azido group. New absorption bands ($\nu_{N3} = 2052$ and $2025$ cm\(^{-1}\)) and a shoulder ($\nu_{N3} = 2043$ cm\(^{-1}\)) are in the expected region for metal-azido species (Figure 4). The presence of two peaks instead of one is different from the nickel azido analogue, but not unprecedented\([22]\) and likely stems from multiple accessible conformations of the azido complex in solution. The IR spectrum of 2-\(^{15}\)N shows small shifts of the azide bands ($\nu_{N3} = 2043$ and $2036$ cm\(^{-1}\)) and a shoulder at $2010$ cm\(^{-1}\)), in line with the expected changes upon introduction of the heavier isotope. The UV-vis spectrum of 2 (Figure 18, Appendix) shows an absorption band at $302$ nm ($\epsilon = 12100$ M\(^{-1}\) cm\(^{-1}\)) and a shoulder at $338$ nm ($\epsilon = 6800$ M\(^{-1}\) cm\(^{-1}\)).

Single crystals of 2 could ultimately be grown from a saturated benzene solution. X-ray diffraction analysis indicate that also in the solid state different conformations are accessible. In fact, the unit cell shows four complexes that can be divided in two conformations, A and B, with the N\(_3\) group bent more (A: Co1-N2-N3 128.5(4) °) or less (B: Co4-N14-N15 147.2(7) °) out of plane (Figure 5). This difference is also manifested in elongation of the Co-azide bond for A (1.898(5) Å vs 1.867(6) Å for B) and a small contraction of the N\(_\alpha\)-N\(_\beta\) bond (1.181(8) Å for A vs 1.120(9) Å for B).

Figure 5. Two selected ORTEP plots (50% probability level) for 2. Hydrogen atoms are omitted for clarity, selected bond lengths (Å) and angles (°), left A: N1-Co1 1.889(4), P1-Co1 2.205(2), P2-Co1 2.199(2), Co1-N2 1.898(5), N2-N3 1.181(8), N3-N4 1.161(8), P1-Co1-P2 172.28(6), N1-Co1-N2 176.4(2), Co1-N2-N3 128.5(4), N2-N3-N4 177.3(7), C7-C12-C6-C1 63(1), N1-Co1-N2-N3 63(3); right B: N13-Co4 1.882(5), P7-Co4 2.224(2), P8-Co4 2.211(2), Co4-N14 1.867(6), N14-N15 1.120(9), N15-N16 1.16(1), P7-Co4-P8 168.60(8), N13-Co4-N14 177.2(3), Co4-N14-N15 147.2(7), N14-N15-N16 180(1), C79-C80-C90-C85 65(1), N13-Co4-N14-N15 149(5).

The electrochemical stability of 2 was explored with cyclic voltammetry. A reversible one-electron oxidation event was found at -0.26 V vs. Fe\(^{0+/+}\) (Figure 19, Appendix) which is very similar to the value reported for parent complex 1 (-0.25 V vs. Fe).\([19]\) Chemical
oxidation of 2 with FcPF₆ generated complex 3 (Figure 6). Oxidation of 2 as a means to decompose the azido group can therefore be discarded. Complex 3 is NMR-silent in line with an open-shell (high-spin) state, instead of a closed-shell singlet state. The IR spectrum still contains assignable azide absorption bands (ν = 2045, 2025 (shoulder) cm⁻¹), but also a broad peak at 2091 cm⁻¹ (Figure 20, Appendix). Whether this also can be assigned to the presence of an azide group is not clear. The magnetic moment was determined with Evans’ method and found to be 6.27 μB. This value is high, even if a high-spin d⁶ complex with a tetrahedral geometry is taken into consideration. In the cyclic voltammogram of 3 a reversible reduction wave is observed at -0.26 V vs. Fc⁰/⁺, supporting the assignment of 3.

![Figure 6. Chemical oxidation of azido complex 2 with FcPF₆.](image)

### 3.2.2 Thermolysis of complex 2 and characterization of the product

As 2 proved to be stable after chemical oxidation, with no sign of azide activation, thermolysis was studied as an alternative way to decompose the azido group. This method may be preferred over photolytic activation as it should allow for easier scale-up of the reaction to obtain sufficient quantities of material. First, the behavior of complex 2 at increased temperatures was monitored using Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA measures changes in the mass of a sample as a function of temperature, while DSC can provide insight in the heat-flow during the reaction. The combination of these techniques is especially suited for reactions involving thermal decomposition of azides, as this is an exothermic event involving significant mass loss. The results of the TGA-DSC measurement of 2 are displayed in Figure 7. Examination of the scan reveals an endothermic event from 100 °C – 112 °C. This event can point at melting of the complex, although the loss of mass suggests that evaporation of water traces and of solvent residues (toluene, THF) may also take place. Subsequently, a clear exothermic event takes place starting at 169 °C. This event is associated with a mass change of -3.1 %, which is less than expected for pure N₂ release (-5.3 %). Despite this discrepancy, the combination of mass loss and energy release gives a valuable indication that decomposition of the N₃ group might take place around this temperature.
The difference between the expected and the found mass-loss can probably be explained by a combination of the extreme sensitivity of 2, affecting the purity of the compound measured (and hence the available azide), and a decreased accuracy of the machine at smaller quantities (<10 mg). Events at even higher temperatures likely involve other decomposition pathways of the complex.

![Figure 7. TGA-DSC measurement of 2 using 3K/min scanning speed.](image)

With this initial information in hand, 2 was subjected to solid state thermolysis on a larger scale. A J-Young type Schlenk was charged with 150 mg of the compound and sealed under a nitrogen atmosphere. Subsequently, the solid was heated in an oil bath. In line with observations from the TGA-DSC measurements, the complex started melting around a temperature of 110 °C. Further heating was uneventful until a temperature of 150 °C was reached. At this point bubbles in the dark green liquid became evident and a color change to dark red was clearly visible. The reaction appears to be very fast (completion within minutes), but the Schlenk can be left at a temperature of 180 °C for an hour without signs of product decomposition. The product of the reaction, complex 4 (Figure 8), can be extracted with pentane, in which it is remarkably soluble (124 mg was dissolved in 3 mL). Evaporation of the solvent yielded a dark red solid. The characterization of 4 will be discussed below.
Thermolysis of 2 resulting in N\textsubscript{2} expulsion, N-insertion and dimerization to form 4.

IR spectroscopy of 4 showed full consumption of the azide group. Much like the starting material, compound 4 is very air-sensitive in solution. Contact with air results in a color change from red to green. Despite the combination of this sensitivity and a markedly high solubility in apolar solvents, single crystals could ultimately be grown from a cooled pentane solution. The solid state structure of 4 was determined by X-ray diffraction analysis (Figure 9). Two cobalt centers have combined to form a centro-symmetric dimeric Co\textsuperscript{II}-species with two phosphiniminato units bridging both Co centers, comparable to the aforementioned iron analogue.\textsuperscript{[18]} Mindiola et al. have also reported on a Co\textsuperscript{I}\textsubscript{2}N\textsubscript{2} diamond core structure involving a PNP ligand, although in that case the ligand bridges both Co centers via the central amido group.\textsuperscript{[19]} The phosphiniminato unit likely has formed by insertion of a naked N-atom into a Co-P bond, resulting in the formation of an asymmetric dianionic PN\textsubscript{2}N ligand, similar to the nickel-azido photolysis product described in Chapter 2. The cobalt atoms have a formal oxidation state of II and have adopted a tetrahedral geometry, which leads to a curious orientation of the four phenyl rings in the complex. Two rings are directed away from each other and the Co\textsubscript{2}N\textsubscript{2} center. The other phenyl rings face each other and are in an almost perpendicular orientation with regard to the Co\textsubscript{2}N\textsubscript{2} center. This implies that π-stacking might take place, although the distance between the rings may be too large for any significant interaction (4.335 Å). The total reaction equation formally only shows loss of N\textsubscript{2}. 
Figure 9. ORTEP plots (50% probability level) of 4. Hydrogen atoms are omitted for clarity, selected bond lengths (Å) and angles (°): Co1-Co2 2.5680(6), Co1-N2 1.982(3), Co1-N4 1.928(3), Co2-N2 1.938(3), Co2-N4 1.989(3), Co1-P2 2.315(1), Co2-P4 2.331(1), P1-N2 1.580(3), Co1-N1 1.965(3), P3-N4 1.582(3), Co2-N3 1.976(3), Co1-N4-Co2 81.9(1), Co1-N2-Co2 81.8(1), N2-Co1-N4 98.0(1), N2-Co2-N4 97.4(1), C1-C2-C8-C7 65.4(7), C27-C28-C34-C33 63.1(7).

Complex 4 was further characterized by $^1$H NMR spectroscopy. The spectrum ranges from 25 to -5.5 ppm and shows relatively sharp signals that allow for integration and also some degree of multiplicity determination (Figure 10), which is very unusual for Co-based species. All CH$_x$ groups of the ligand framework are inequivalent, signifying overall asymmetry in the binding motif of the PN$_2$N skeleton. The $^1$H NMR chemical shifts for all signals are temperature dependent as indicated by VT-NMR. Some of them display strong anti-Curie behavior, whereas other signals show weak Curie-like behavior (Figure 11).

Figure 10. $^1$H NMR spectrum of 4 in C$_6$D$_6$. Insert displays two signals with assignable multiplicity. Minor impurities of residual toluene peaks (*)
The effective magnetic moment of 4 in THF at 20 °C of $\mu_{\text{eff}} = 5.97 \mu_B$, as determined by Evans’ method, implies an $S = \frac{5}{2}$ species, which is improbable for a Co$^{II}$ species. We therefore suspected temperature dependence of the solution magnetic moment. This was investigated by VT-NMR studies (Evans’ method). The $\mu_{\text{eff}}$ varied from 5.21 (173 K) to 6.21 $\mu_B$ (333 K) (Figure 11). This likely indicates an (incomplete) transition from a $S = 2$ to a $S = 3$ state taking place in this temperature range. The EPR spectrum of 4 (Figure 21, Appendix) exhibits two very weak signals at low temperature (30 K). Although these signals may stem from the high-spin compound, it is also possible that they result from minor impurities.

The sensitivity of complex 4 interfered with attempts to analyze this species using CSI HR-MS. A very weak signal was found for the expected mass of 4 but the main species in the mass spectrum are free, oxidized ligand ([P$^\text{V}$PN$^\text{H}$PN$^\text{H}$ + H]$^+$ calculated $m/z$: 461.2851, found 461.2917) and cobalt complexes with this phosphinoxide ligand. Depending on the flow and addition of acetonitrile other species became more prominent. The mass spectrum of the thermolysis product of 2-$^{15}$N confirmed the incorporation of azide-N into the ligand, as the O$^\text{P}$PN$^\text{H}$PN$^\text{H}$ fragment shifts with one atomic mass unit to $m/z$ 462.2613. This provides evidence for the azide being the source of the new P=N moiety.

3.2.3 Photolysis of compound 2

Having shown that Co(PNP)N$_3$ can be thermolyzed in solid state, we set out to investigate photolysis in arene solution. We were particularly interested to see whether this would invoke formation of 4 or arene C-H (or C-D) activation as described in Chapter 2. Irradiation of a J-Young NMR tube containing a C$_6$D$_6$ solution of 2 resulted in selective generation of 4, as deduced by $^1$H NMR spectroscopy. The photolysis experiment was
also conducted in a THF solution using a Schlenk cuvette, which led to 4 in a much less clean form. These results mark another difference in the chemistry of 2 compared to Ni(PNP)N₃: not only is it possible to perform thermolysis and generate 4, photolysis in the presence of solvent leads to the same dimeric product and not to solvent C-H activation.

### 3.2.4 Computational studies

A plausible reaction mechanism for the azide activation and N-insertion was studied using DFT calculations. Both the doublet and the quartet spin states were considered using the BP86 DFT functional (Figure 12). In accordance with the experimental data, starting material 2 is clearly most stable in the \( S = \frac{1}{2} \) state. The activation of the azide leading to \( \text{N}_2 \) release proceeds via transition state TS1 which is high in energy (30.0 kcal mol\(^{-1}\)), but much lower compared to the activation barrier calculated for Ni(PNP)N₃ in Chapter 2 (46.2 kcal mol\(^{-1}\)), in line with an accessible thermal activation pathway. Expulsion of \( \text{N}_2 \) results in nitrido structure B, which also is most stable in the doublet spin state. The spin density in B is distributed over the Co center (0.58) and the nitrido N atom (0.39) (Figure 13), giving the latter significant nitridyl character. The single occupancy of the anti-bonding \( d_{\alpha\pi} \)-orbital indicates a bond order of 2.5.

**Figure 12.** Proposed pathway for formation of C upon photolysis/thermolysis of 2 based on DFT calculations (BP86-d3, def2-TZVP). Energies in kcal mol\(^{-1}\) relative to \( S = \frac{1}{2} \) spin state of the starting material. Dimerization of C to form 4 is proposed to be an accessible step, but was not calculated.
The transition state TS2 involving insertion of the nitrido N into the Co-P bond that leads to the formation of species C is relatively low (6.9 kcal mol\(^{-1}\) for \(S = \frac{1}{2}\)). This T-shaped intermediate is equally stable in the doublet and quartet spin state, with at least one vacant coordination site to fulfill a square planar geometry. Dimerization of two species C to form final product 4 is therefore deemed a likely process. Indeed, the energy of 4 with \(S = 3\) was calculated to be -35.3 kcal/mol. Other spin states of 4 did not converge. The transition state from C to 4 was not calculated, but it is assumed to be accessible considering the unsaturated nature of C.

Alternative pathways for the formation of 4 can also be envisioned, but are considered less probable (Figure 14). Structure D may be generated as the initial step from two equivalents of 2. Activation of the bridging azido groups leading to expulsion of N\(_2\) would result in complex E. Insertion of the bridging nitrido atoms into the Co-P bonds would then deliver 4. However, this is not compatible with the activity observed in low temperature EPR experiments (\textit{vide infra}) and it seems unlikely that such a step should be preferred over direct activation of the azide in 2. It is also possible that compound E is formed by dimerization of two nitrido species B, but regarding the low activation barrier for intramolecular N-insertion to form structure C this is an improbable event (Figure 13). The same argument is valid for generation of F from B. In addition, F has been reported as an isolated structure\(^{19}\) and N\(_2\) splitting to form E therefore is highly unlikely.
3.2.5 Low temperature irradiation and EPR studies

We studied the reaction by performing the irradiation on a frozen solution of 2 at low temperature (20 K). The photolysis was carried out inside the cavity of an EPR spectrometer, which provided the possibility to monitor the reaction in situ (Figure 15). Unfortunately, the spectrum before irradiation contains a small impurity around 1060 G. After irradiating for 900 seconds, the signals of the starting material have significantly decreased and two new signals have appeared. One of these signals appears at low field, indicating a high-spin species. After prolonged irradiation a third new signal becomes visible. These different new signals and their non-aligned growth indicate a mixture of (at least) three species being formed. Taking into account the calculated pathway, these species may be $B^{S=1/2}$, $C^{S=1/2}$ and high-spin $C^{S=3/2}$. However, considering the quality of the spectra this remains speculative. Also, the seemingly overlapping signals hinder proper simulation of the spectra and comparison with DFT calculated EPR parameters.

Figure 14. Alternative routes towards final product 4
Figure 15. EPR spectra of an irradiated sample of 2 in toluene at 20K. Irradiation time given in seconds. Arrows indicate direction of evolving signals.

3.2.6 Preliminary reactivity studies of 4

Complex 4 can be viewed as two masked coordinatively unsaturated Co\textsuperscript{II} species with a pendant anionic phosphiniminato moiety. The presence of such an internal base in close proximity to the metal center can give the ligand bifunctional character. Therefore, the complex may be interesting in future studies aiming at heterolytic C-H or E-H (E = O, S, N) bond activation.\textsuperscript{[25]} To investigate the potential for such reactivity with 4, we performed a number of initial test-reactions.

Starting with an ‘easy substrate’, 4 was reacted with an equimolar amount of HCl. The addition of this reagent led to the formation of a light blue solid, while the liquid phase remained red. Work-up and subsequent analysis of the product, 5, indicated splitting of the dimer and formation of a Co-Cl structure. The IR spectrum exhibits an absorption band at $v = 3375$ cm\textsuperscript{-1}, which can be assigned to an N-H stretch. X-ray diffraction studies of single crystals confirmed the structure of 5 (Figure 16). This shows that it is indeed possible to heterolytically ‘split’ (strong) acids over the Co-N’ moiety. The observed blue solid is likely CoCl\textsubscript{2}. 
Figure 16. Left: reaction 4 with HCl to form 5. Right: ORTEP plot$^{[24]}$ (50% probability level) of 5. Hydrogen atoms are omitted for clarity, selected bond lengths (Å) and angles (°): Co1-Cl1 2.2549, Co1-N1 1.9584, Co1-N2 1.9520, N2-P1 1.6147, Co1-P2 2.3278, Co1-N2-P1 116.76, C1-C2-C8-C7 70.12.

We set out to expand the scope of this ‘activation’ by investigating less acidic bonds. Reaction of 4 with 2.1 equivalent phenol in C$_6$D$_6$ resulted in full conversion of the starting material as indicated by $^1$H NMR spectroscopy (see Figure 22, Appendix). The product(s) was not characterized by X-ray crystallography, but a new absorption band at 3372 cm$^{-1}$ in the IR spectrum and observation of the expected mass in the HR-MS spectrum are strong indications of successful O-H activation and presence of 6 in the product mixture (Figure 17).

Complex 4 was also reacted with 2.2 equivalent phenylacetylene in THF (Figure 17). Full conversion of the starting material was again observed. IR spectroscopy revealed an absorption band at 3365 cm$^{-1}$, again indicating formation of an N-H bond. Comparable to a known Co$^{II}$(CCPh) complex, an IR stretch is found at 2068 cm$^{-1}$.$^{[26]}$ This peak can be assigned to a C≡C stretch vibration and ascertains the presence of a phenylacetylide moiety in complex 7. The mass spectrum shows the expected mass, but also for 7+phenylacetylene, oxidized free ligand and some unknown species.
Reaction of 5 bar H$_2$ with 4 resulted in generation of several new signals in the $^1$H NMR spectrum, but 4 clearly remained the major species even after prolonged reaction time and heating. A reaction of 4 with 5 bar of CO led to formation of a new species. Analysis of the sample with IR spectroscopy reveals a strong CO peak at $\nu_{CO} = 1890$ cm$^{-1}$, which could indicate that strong $\pi$-acceptor ligands also invoke formation of monometallic species.

3.3 Conclusion

In this Chapter the synthesis and activation of Co(PNP)N$_3$ (2) have been studied. The chemistry of 2 is distinctly different to that of its nickel congener described in Chapter 2. This is reflected in the methods of activation of the azido group. Like its Group 10 analogue, 2 can be reversibly oxidized via both electrochemical and chemical pathways. Irreversible activation of the azido group concomitant with N$_2$ loss can be achieved both thermally and photolytically. The product of this activation is dimeric structure 4 that features a diamond Co$_2$N$_2$ core in which the azido-N has inserted into the Co-P bond; this results in an anionic phosphiniminato fragment that acts as bridging N-donor. This reactivity is comparable to other first-row metal examples and not to previously reported Rh and Ir complexes bearing phosphine ligands. Definitive proof for the intermediacy of a nitrido species could not be obtained by low temperature EPR measurements. DFT calculations do, however, show that this species is accessible and that trapping should be possible. Considering the importance of the amount of $d$-electrons for TM-nitrido chemistry, it is tempting to explain the distinction in reactivity between Ni(PNP)N$_3$ and
Co(PNP)N$_3$ in terms of difference between $d^8$ and $d^7$ metal chemistry. Preliminary reactivity studies with compound 4 show promising results in C-H and O-H activation reactions.

### 3.4 Acknowledgements

Lambert Baij is gratefully acknowledged for contributions to this work and for continued enthusiasm in the subject. Christophe Rebreyend is kindly thanked for help with VT EPR measurements and calculations to determine EPR parameters. Bas de Bruin is acknowledged for simulation of EPR spectra and advice regarding DFT computations. Ed Zuidinga is thanked for performing the mass spectrometry measurements.

### 3.5 Experimental

**General methods**

With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. All experiments were conducted under inert atmosphere, either by using Schlenk techniques or by using a Glovebox under N$_2$ pressure. PN$_2$P$_4$Pr$_2$ (bis(2-diisopropylphosphino-4-methylphenyl)amine)$^{[27]}$ was synthesized according to literature procedures. Toluene, tetrahydrofuran, diethylether and pentane were distilled from sodium benzophenone ketyl. CH$_2$Cl$_2$ was distilled from CaH$_2$. NMR spectra ($^1$H, $^1$H{$^{31}$P}, $^{13}$C{$^1$H}, $^{31}$P{$^1$H}) were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer at room temperature, unless noted otherwise. Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with a cryostat (Oxford Instruments). Irradiation inside the EPR cavity was conducted with a Honle Bluepoint ecocure 4 UV-lamp. High resolution mass spectra were recorded on a JEOL AccuTOF LC, JMS-T100LP Mass spectrometer using cold spray ionization (CSI) and electron spray ionization (ESI) and on a JEOL AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer using field desorption (FD). IR spectra were either recorded on a Thermo Nicolet Nexus FT-IR spectrometer or on a Bruker Vertex 70. UV/visible spectra were recorded on a Hitachi U-3300 spectrophotometer. Cyclic voltammetry measurements were performed in THF containing N(n-Bu)$_4$PF$_6$ (0.1 M) at room temperature under a nitrogen atmosphere using a platinum disk working electrode, a platinum coil counter electrode and a silver coil reference electrode. All redox potentials are referenced to Fc/Fc$^+$. For the irradiation experiments a 500 W Hg/Xe lamp (Hamamatsu Photonics L8288) was used.
Computational details

Geometry optimizations were carried out with the Turbomole program package\textsuperscript{28a} coupled to the PQS Baker optimizer\textsuperscript{28b} via the BOpt package\textsuperscript{28c} at the BP86\textsuperscript{28d,e} level. We used the def2-TZVP basis set\textsuperscript{28f,g} Dispersion corrections were applied.\textsuperscript{29} All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The nature of the transition states was confirmed by IRC calculations. Calculated EPR spectra were obtained with ORCA\textsuperscript{30} (DFT: b3-lyp, def2-TZVP), using Turbomole optimized geometries.

Synthesis and characterization of new compounds

Synthesis of complex 1

![Complex 1 structure](image)

The synthesis was performed according to a modified literature procedure.\textsuperscript{19} A solution of $\text{PN}^\text{H}^\text{Pr}$ (1.66 g, 3.89 mmol) in THF (20 mL) was prepared and cooled to -78°C. Subsequently, $n$-BuLi (1.71 mL of a 2.5 M solution in hexanes, 4.28 mmol) was added to the solution. Then, a suspension of anhydrous CoCl$_2$ (0.505 g, 3.89 mmol) in THF (50 mL) was added via canula and the reaction mixture was allowed to stir for 22h. The solvent was removed \textit{in vacuo} and the product was extracted with toluene (50 mL). After filtration over Celite, the filtrate was concentrated to approx. 5 mL and stored overnight at -20 °C, yielding complex 1 as a dark-blue crystalline solid (1.63 g, 80%). The product was identified by comparing the $^1$H NMR spectrum with the reported literature values.

Synthesis of complex 2

![Complex 2 structure](image)

A Schlenk flask was charged with 1 (500 mg, 0.96 mmol) and NaN$_3$ (624 mg, 9.6 mmol). THF (20 mL) was added and the resulting suspension was stirred for 22h during which the color of the mixture changed from dark blue to dark green. Then, volatiles were removed \textit{in vacuo}. The azido product was extracted with toluene and filtered over Celite. The filtrate was concentrated to approx. 5 mL and stored at -20 °C overnight, yielding a dark green solid 485 mg, 95%). Single crystals suitable for X-ray diffraction were grown from a saturated C$_6$D$_6$ solution. The $^{15}$N enriched azido complex 2-$^{15}$N was prepared according to the same method by using $^{15}$N-enriched sodium azide.

$^1$H NMR (400 MHz, C$_6$D$_6$, ppm): δ 43.28 ($\Delta\nu_{\parallel} = 24$ Hz), 37.02 ($\Delta\nu_{\parallel} = 39$ Hz), 29.72 ($\Delta\nu_{\parallel} = 270$ Hz), 25.85 ($\Delta\nu_{\parallel} = 250$ Hz), 12.29 ($\Delta\nu_{\parallel} = 50$ Hz), 4.79 (bs), 3.87 (bs), -24.92 ($\Delta\nu_{\perp} = 447$ Hz); $\mu_{\text{eff}} = 1.77 \mu_B$ (Evans’ method, 24°C, C$_6$D$_6$); EPR $g_{x,y} = 2.006$, $g_z = 2.73$ (toluene,
40K); HR-MS (CSI) calcd for [M]⁺ C_{26}H_{46}CoN_{4}P_{2} m/z: 529.2060, found 529.2032; FTIR (N₃ stretch): (THF) ν = 2052, 2025 (shoulder) cm⁻¹; (benzene) ν = 2052 (broad) cm⁻¹, for 2-^{15}N (THF): ν = 2044, 2037 (shoulder) cm⁻¹.

**Synthesis of complex 3**

To a stirring solution of 2 (243 mg, 0.46 mmol) in THF (20 mL) was added FcPF₆ (142 mg, 0.46 mmol) which led to a color change from green to dark-red. The resulting mixture was allowed to stir for 1 hour. Then, the solvent was removed under reduced pressure. The resulting solid was washed with pentane (3x 5 mL) yielding a dark red to brown powder (255 mg, 82 %). μₑffective = 6.27 μB; FTIR (N₃ stretch): (acetone) ν = 2045, 2025 (shoulder) cm⁻¹.

**Synthesis of complex 4**

**Thermolysis:** A J-Young type Schlenk was loaded with complex 2 (150 mg, 0.28 mmol). The solid was heated to 180 °C. Around 110 °C the green solid melted and around 150 °C bubble formation was visible. At this point, the color changed from green to red. The temperature was maintained at 180 °C for 1 hour. Subsequently, the product was allowed to cool down and then extracted with pentane. Evaporation of the solvent yielded a dark red solid (124 mg, 88%). Crystals suitable for X-ray diffraction studies were grown from a pentane solution at -20 °C.

**Photolysis:** A J-Young type Schlenk-cuvette was charged with a dark green solution of complex 2 (11 mg, 0.02 mmol) in THF (2 mL). While stirring, the mixture was irradiated for 1.5 hours. During this period the color changed to dark red. The solvents was removed in vacuo and the resulting red solid was analyzed with ¹H NMR confirming the presence of complex 4 as the major product.

¹H NMR (400 MHz, C₆D₆, ppm): δ 24.64 (s, 1H), 12.29 (s, 1H), 10.02 (d, J = 7.5 Hz, 1H), 9.47 (s, 1H), 9.45 (s, 1H), 8.65 (s, 1H), 8.47 (d, J = 6.6 Hz, 1H), 7.14 (s, 1H), 5.72 (s, 3H), 4.73 (s, 1H), 4.44 (s, 3H), 4.37 (s, 3H), 3.81 (s, 3H), 3.52 (d, J = 8.1 Hz, 1H), 3.30 (s, 3H), 3.15 (s, 3H), 0.31 (s, 3H), -1.84 (s, 3H), -2.70 (s, 3H), -5.26 (s, 3H); μeffective = 5.97 μB (Evans’ method, 20°C, THF-d₈); HR-MS (CSI) calcd for [M + H]^+ C_{52}H_{81}Co_{2}N_{4}P_{4} m/z: 1003.4076, found 1003.5360.
Synthesis of complex 5

In a J-Young Schlenk complex 4 (53 mg, 0.053 mmol) was dissolved in Et₂O (2 mL). To the red solution 2M HCl in Et₂O (53 μL, 0.106 mmol) was added, causing the formation of a light blue solid. The liquid phase remained dark red and was stirred for 1 hour. Then, the mixture was filtered and the solvent was evaporated. The crude solid was triturated with pentane and dried in vacuo, yielding 5 as a brown solid (32 mg, 56%). Red crystals suitable for X-ray analysis were obtained from a saturated Et₂O solution.

\(^1\)H NMR (400 MHz, C₆D₆, ppm): δ 43.85 (Δ½ = 24 Hz), 42.54 (Δ½ = 21 Hz), 34.73 (Δ½ = 25 Hz), 33.76 (Δ½ = 16 Hz), 24.62 (Δ½ = 40 Hz), 19.61 (Δ½ = 37 Hz), 3.25 (Δ½ = 55 Hz), -42.18 (Δ½ = 74 Hz); \(\mu_{\text{eff}} = 4.28 \mu_B\) (Evans’ method, 24°C, C₆D₆); HR-MS (ESI) calcd for [M]^+ C₂₆H₄₁Cl₁Co₁N₂P₂ m/z: 537.17655, found 537.17288. FTIR (DCM): \(\nu_{\text{NH}}\) 3375 cm\(^{-1}\).

Synthesis of complex 6

A J-Young type Schlenk was loaded with 4 (20 mg, 0.02 mmol) and phenol (4.0 mg, 0.042 mmol). The solids were dissolved in C₆D₆ and the light red solution was stirred for 30 minutes at 80 °C. The mixture was analyzed with \(^1\)H NMR and IR spectroscopy and with HR MS without prior purification.

\(^1\)H NMR (400 MHz, C₆D₆, ppm): δ 39.01 (Δ½ = 21 Hz), 33.78 (Δ½ = 27 Hz), 31.22 (Δ½ = 33 Hz), 27.11 (Δ½ = 17 Hz), 22.89 (Δ½ = 51 Hz), 15.65 (Δ½ = 42 Hz), -43.15 (Δ½ = 101 Hz); HR-MS (FD) calcd for [M]^+ C₃₂H₄₁Cl₁Co₁N₂O₁P₂ m/z: 595.2417, found 595.2451. FTIR (DCM): \(\nu_{\text{NH}}\) 3372 cm\(^{-1}\).

Synthesis of complex 7

Complex 4 (20 mg, 0.02 mmol) was charged in to a J-Young type Schlenk. Phenylacetylene (4.8 μL, 0.044 mmol) was added and the mixture was dissolved in THF (0.5 mL). The light red solution was stirred for 2 hours, then the volatiles were removed in vacuo. The product was analyzed with \(^1\)H NMR and IR spectroscopy and with HR MS without prior purification.

\(^1\)H NMR (400 MHz, C₆D₆, ppm): δ 35.32 (s), 28.20 (s), 20.49 (s), 19.92 (s), 18.23 (s), 16.27 (s), 11.08 (s), 5.18 (s), 4.91 (s), 4.21 (s), 0.96 (s), -0.87 (s), -1.05 (s), -4.86 (s), -11.58 (s), -12.73 (s), -14.70 (s), -19.56 (s); HR-MS (FD) calcd for [M]^+ C₃₄H₄₆Co₁N₂P₂ m/z: 603.2468, found 603.2477. FTIR (DCM): \(\nu_{\text{NH}}\) 3365 cm\(^{-1}\), \(\nu_{\text{CC}}\) 2068 cm\(^{-1}\).
X-ray Crystal Structure Determination of complex 2: X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.[31] Absorption correction and scaling was performed with SADABS.[32] The structures were solved using intrinsic phasing with the program SHELXT.[31] Least-squares refinement was performed with SHELXL-2013[33] against F² of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times Ueq of the attached C atoms.

X-ray Crystal Structure Determination of complex 4: All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu Ka radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7[34] and was refined on F² with SHELXL-2014/7.[34] Analytical numeric absorption correction using a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 Ueq of the attached C atoms. The structure is ordered.
3.6 Appendix

Figure 18. UV-vis spectra of 2 and 3 in THF.

Figure 19. Cyclic voltammograms of 2 and 3 recorded in THF (scan speed 0.1 V/s)
Figure 20. FT-IR spectrum of complex 3 in acetone.

Figure 21. EPR spectrum of 4 in Me-THF measured at 30 K.
Figure 22. $^1$H NMR spectra of 4 (top), after reaction with phenylacetylene (middle) and phenol (bottom).
3.7 References

[21] The DFT calculated $g_s$ value deviates strongly from the experimental data. This may be the result of a small HOMO-LUMO gap, affecting the precision of the calculations.
[23] The spin-only moment of a high-spin $d^6$ compound is 4.90. The deviation is possibly caused by a large contribution of the spin-orbital coupling or the orbital angular momentum. These terms are neglected in the calculation of the spin-only moment.
[24] Plot is derived from preliminary, partly refined X-ray crystallographic data.


[30] F. Neese, *ORCA: An ab Initio, Density Functional and semiemperical Program Package, version 2.7.0;* University of Bonn, Bonn, Germany, **2009**.


Chapter 4

Well-Defined Dinuclear Gold Complexes for Preorganization-Induced Selective Dual-Gold Catalysis

4.1 Introduction

Homogeneous gold catalysis has flourished over the past 15 years, enabling a wide range of transformations.\(^{[1]}\) More recently, the discovery of catalysis involving novel dual-activation mechanisms has led to a new range of possible transformations.\(^{[2]}\) Opposed to ‘conventional’ late transition-metal catalysts, gold complexes generally tend not to perform oxidative addition and reductive elimination reactions and do not cycle through different oxidation states during the catalysis. This is commonly explained by the large redox-couple between AuI/AuIII of ± 1.4 V.\(^{[3]}\) Nevertheless, recent advances show the feasibility of performing elementary reactions on gold complexes provided well-designed strategies are employed.\(^{[3c-e]}\) However, the field of gold catalysis is still mainly dominated by other forms of activation related to Lewis acid-type behavior.

‘Traditional’ mono-gold catalysis relies on \(\pi\)-activation of a substrate (alkyne, alkene, allene) by a cationic Au(I) center. The resulting electrophilicity allows for attack by an internal or external nucleophile and formation of a new bond (Figure 1). In one example the concept of \(\sigma\)-activation has been demonstrated as an alternative.\(^{[4]}\) This strategy allowed for terminal alkyne groups to perform an intramolecular nucleophilic attack in substrates bearing a sulfonate leaving group. Dual-gold catalysis typically involves both \(\sigma\)- and \(\pi\)-activation by two Au centers. Two separate functionalities (such as C≡C bonds) can simultaneously be activated to enhance both electrophilic and nucleophilic properties at the same time (\(\sigma^+ \pi\)-activation). In a different approach one functionality is activated simultaneously by two Au centers (\(\sigma, \pi\)-activation), which can lead to different reactivity and selectivity compared to \(\pi\)-activation (Figure 1).\(^{[5]}\) The prevailing strategy utilizes mononuclear Au(I) complexes to induce dual-activation, which sometimes have been developed specifically for this purpose.\(^{[6]}\) However, this strategy offers no handles to induce pre-organization of both Au-centers to specifically target well-defined \(\sigma, \pi\)-activation of e.g. unsaturated hydrocarbon C-C multiple bonds whilst avoiding \(\pi\)- or \(\sigma^+ \pi\)-coordination nor does it provide any control over the selective binding of bifunctional substrates (e.g. for heterocyclizations).

![Figure 1](image-url) Reported activation modes in gold(I)-catalysis. Red = nucleophilic site, Blue = electrophilic site
The synthesis and coordination chemistry of dinuclear Au(I) complexes is well-developed.\(^7\) Aiming at transformations involving the generation of chiral stereocenters, digold complexes have been employed in enantioselective catalysis.\(^8\) Furthermore, the proximity of both Au-centers has occasionally been credited to enhance reactivity.\(^9\) However, the competence of well-defined dinuclear \(\sigma,\pi\)-alkynide complexes in dual-gold catalysis has never been reported, to the best of our knowledge, despite the potential benefits of two pre-organized Au centers with respect to chemoselectivity and activity for this type of reactions.

The ditopic tridentate ligand \(\text{PN}^\text{HPr}^\text{Pr} (\text{L}^\text{H})\) and its congeners display versatile coordination chemistry to a wide range of transition metals,\(^10\) including Cu\(^\text{11}\) and Ag\(^\text{12}\) (Figure 2). Furthermore, chemistry related to the redox-active nature\(^13\) of \(\text{L}\) has been well-established in Ni, Mn and Re complexes,\(^14\) but ligand redox-activity with Group 11 metals is limited to one example with Cu(I), leading to dimerization on one of the para-positions of the PNP backbone.\(^11a\) Strikingly, no single complex of gold with this type of ditopic framework is known to date. New avenues for gold coordination chemistry and catalysis may become accessible by developing strategies to preorganize and stabilize multiple gold centers on suitable ligand platforms, such as the \(\text{PN}^\text{HPr}^\text{Pr}\) ligand. The ligand enforced proximity of Au-nuclei may result in selective binding and activation of bifunctional substrates in a \(\sigma,\pi\)-mode, which should have a beneficial effect particularly on dual-gold catalysis relying on this activation mode (Figure 2). Because of the forced proximity and the concomitant loss of flexibility, tethering of gold centers is not expected to have a positive effect on most other forms of dual-gold catalysis (\(\sigma+\pi\)-activation).

**Figure 2.** Reported Group 11 TM-complexes containing a monoanionic PNP ligand (left). Concept of enforced \(\sigma,\pi\)-activation (right).

In this Chapter we aim to investigate the potential of the \(\text{PN}^\text{HPr}^\text{Pr}\) ligand in dinuclear Au\(^1\) catalysis. We address the question whether using this ligand to preorganize two gold centers is a viable strategy to enforce dual-gold catalysis involving a \(\sigma,\pi\)-activation. We will therefore first describe exploratory studies on the versatile coordination chemistry of
gold with the redox-active ditopic $\text{PN}^{\text{HPr}}$ ligand. This will be complemented by studies demonstrating the catalytic abilities of the described dinuclear Au$^1$ complexes.

### 4.2 Results and discussion

#### 4.2.1 Synthesis and characterization

The straightforward reaction of $\text{PN}^{\text{HPr}}$ with AuCl(SMe$_2$) in a 1:2 ratio provided complex 1 as a white solid (Figure 3). The $^{31}$P NMR spectrum shows a slightly broadened singlet at $\delta$ 40.9 and the $^1$H NMR spectrum suggests a $C_2$ symmetric species. White single crystals of 1 were grown by slow diffusion of pentane into a THF solution. X-ray structure determination resulted in molecular structure A$^{[15]}$ of 1 (Figure 4, left), which displays Au-P and Au-Cl distances that are within the range for typical Au$^1$-phosphine complexes. The orientation of the PNP backbone results in a dihedral angle between the two phenyl rings of 99.7(5)$^\circ$, with both phosphine donors on the same side of the ligand backbone. This allows for an intramolecular Au1---Au2 distance of 3.2379(17) Å, which indicates an aurophilic $d^{10}$-$d^{10}$ interaction exists in the solid state.$^{[16]}$

![Figure 3. Synthesis of complexes 1 and 2.](image)

Crystals of 1 were also obtained by slow diffusion of pentane into a CDCl$_3$ solution of the complex. Surprisingly, these crystals were colored purple. X-ray diffraction studies gave polymorph structure B$^{[15]}$ of 1 (Figure 4, right). Interestingly, the Au1-Au2 distance in this structure is much longer (5.5345(6) Å) which precludes the possibility of aurophilic interactions. Presumably, this is a result of increased twisting of the ligand backbone, as indicated by the greater dihedral angle (140.1(6)$^\circ$). The purple color of the crystals is likely explained by a minor impurity that was detected in the crystal. The data quality of this structure is low, but indicates the presence of a Au$^1$Au$^{III}$ complex, vide infra.
Figure 4. Displacement ellipsoid plots (50% probability level) of two polymorphs of 1. Hydrogen atoms, except those on N1, not shown for clarity. Selected bond lengths (Å) and angles (°), for polymorph A\(^{[15]}\): Au1-P1 2.2495(8); Au2-P2 2.2478(8); Au1-Cl1 2.3010(7); Au2-Cl2 2.3003(8); Au1–Au2 3.23791(17); C6-N1 1.396(4); C12-N1 1.403(4); P1-Au1-Cl1 173.45(3); P2-Au2-Cl2 168.13(3); C6-N1-C12 126.3(3); C1-C6-C12-C7 99.7(5). For polymorph B\(^{[15]}\): Au1-P1 2.2350(11); Au1-Cl1 2.2866(11); Au1–Au1’ 5.5345(6); C1-C6 4.401(6); C6-N1 1.417(5); P1-Au1-Cl1 178.53(4); C6-N1-C6’ 119.0(5); C1-C6-C6’-C1’ 140.1(6).

To assess the possibility of selectively abstracting a single chloride from the complex, 1 was reacted with one equivalent of AgNTf\(_2\). Selective formation of compound 2 was indeed observed (Figure 3), as indicated by a singlet at \(\delta\) 40.6 ppm in the \(^{31}\)P NMR spectrum and slightly shifted signals in the \(^1\)H NMR spectrum as compared to the starting material. Field desorption (FD) mass spectrometry of 2 only shows signals for a ‘monomeric’ dinuclear species, while cold-spray ionization (CSI) also shows signals corresponding to a tetranuclear ‘dimer’. Single crystals of 2 were grown from a DCM-pentane mixture. X-ray diffraction studies established the presence of a centro-inverse tetranuclear Au\(^{\ddagger}\) structure featuring two \(\mu\)-Cl bridges (Figure 5). The angle \(\angle\text{Au-Cl-Au}\) in 2 is around 97°, while the general orientation of the PN\(^{\ddagger}\)PiPr backbone is very similar to polymorph A of 1. Notably, the ‘dimeric’ form of 2 in the solid state contrasts the ‘monomeric’ species observed in mass spectrometry. Two-dimensional Diffusion Ordered Spectroscopy (DOSY) NMR indicates that 2 exists as a dinuclear monomer in solution.
Figure 5. Displacement ellipsoid plots (50% probability level) of 2. NTf₂ counterions and hydrogen atoms, except for those on N1, not shown for clarity. Selected bond lengths (Å) and angles (°): Au1-P1 2.2630(12); Au1-Cl1 2.3732(11); Au1---Au2 3.2882(4); P1-Au1-Cl1 170.33(4).

The residual Au¹Au³ structure found in the crystal lattice of polymorph B of 1 is intriguing, as it signifies an entry into mixed-valent Au¹Au³ species. In an attempt to selectively generate such a species, colorless 1 was reacted with one molar equivalent of dichloro-λ³-(iodanyl)benzene (PhICl₂) in dichloromethane. Addition of this oxidant led to instantaneous formation of an intensely purple colored solution with a strong UV-vis absorption at λ 573 nm (ε = 1.1 × 10³ L mol⁻¹ cm⁻¹). Furthermore, two signals were present in the ³¹P NMR spectrum at δ 105.3 (P1) and 44.3 (P2) for complex 3. The chemical shift for P2 is similar to that for 1, but the strongly downfield shifted signal for P1 supports coordination to a Au³ center via site-selective two-electron oxidation of one of the Au(I) centers. The ¹H NMR spectrum, which is also indicative of an asymmetric compound, contains one remarkably upfield shifted aromatic signal at δ 5.90 ppm but no –NH signal could be identified (Figure 6). Mass spectrometry supports formation of a single dinuclear gold species with only three chlorido ligands.

X-ray structure determination confirmed the formation of mixed-valent Au¹-Au³ species 3, with the deprotonated central secondary amine of PNP coordinating to the square
planar AuIII center as an amide, together with two chlorido ligands and P1 (Figure 6). The PNP ligand backbone is severely twisted, with a dihedral angle between both phenyl rings of approximately 75°. This distortion relates to the upfield shifted aromatic signal in the 1H NMR spectrum, which corresponds to the shielded C(6)-H hydrogen that is positioned on top of the second phenyl ring. The orientation of the PNP backbone induces an intramolecular Au–Au distance of ± 4.641 Å that excludes any aurophilic d8–d10 interaction.

Figure 6. Left: Displacement ellipsoid plots (50% probability level) of complex 3[15]. Hydrogen atoms, except for H6, are not shown for clarity. Selected bond lengths (Å) and angles (°): Au1-P1 2.2655(21); Au1-N1 2.041(7); Au1-Cl1 2.354(2); Au1-Cl2 2.3039(22); Au2-P2 2.2401(23); Au2-Cl3 2.2948(24); Au1–Au2 4.641; P1-Au1-Cl1 178.39(8); P1-Au1-N1 84.51(19); N1-Au1-Cl2 172.66(20); P1-Au1-Cl1 176.30(11); C1-N1-C7-C12 75(1). Right: 1H NMR spectrum (top) and 31P NMR spectrum (bottom) of 3.

Generation of a vacant coordination site on a gold-halide precursor is generally, but not always,[94] a prerequisite for Au-catalysis. This can be achieved by halide abstraction with e.g. Ag+ salts or a suitable Lewis acid. With the mixed-valent AuI–AuIII species 3 in hand, we wondered about the ensuing reactivity of this species toward halide abstraction bearing multiple chlorido fragments. Addition of one equivalent of AgNTf2 as halide abstracting agent to 3 led to a mixture of species, according to 31P NMR spectroscopy. However, addition of two equivalents of this reagent (or other Ag+ salts or Lewis acid GaCl3) led to rapid decoloration of the reaction solution and generation of a single product with a signal at δ 40.4 in the 31P NMR spectrum, suggesting the formation of AuI-phosphine fragment(s). Furthermore, the 1H NMR spectrum indicates the formation of a symmetric species, with only one methyl signal for the ditolylamine backbone and chemically identical isopropyl groups at phosphorus. Most notably, only two aromatic
hydrogen signals for the PNP backbone are observed instead of the anticipated three (given the symmetry of the molecule), together with a downfield signal at δ 10.53. This signal integrates for one hydrogen and can be attributed to an –NH fragment. ESI-MS data suggests that the dinuclear complex remains intact during this transformation, with only one Cl ligand present in the complex.

The structure for complex 4 was elucidated by X-ray structure determination using single crystals grown from CH2Cl2-pentane (Figure 7). Halide abstraction has resulted in reduction of the AuI-AuIII mixed-valent species to a AuI-AuI species, concomitant with formal two-electron oxidation of the ligand backbone. This has generated a new C-C bond from the two C-H groups ortho to the central nitrogen, forming a carbazole framework. Furthermore, the nitrogen in this ligand scaffold has been reprotonated and both gold centers are bridged by a single chlorido ligand, leading to an acute $\angle$Au1-Cl1-Au2 of 81.74(4)$^\circ$. Relative to complex 1, featuring the non-oxidized ligand backbone, the intramolecular Au---Au distance is shortened by approximately 0.16 Å. At first glance this may seem counter-intuitive, considering the larger natural bite angle of the carbazole diphosphine.$^{[17]}$ We believe that the shorter distance relates to the positioning of the phosphine lone pairs and the loss of rotational freedom around the C-N-C axle. To the best of our knowledge, this is the first report of redox-chemistry occurring at the ortho C-H positions of the diphenylamine framework within the coordination sphere of a transition metal.

![Figure 7](image_url)

**Figure 7.** Left: Displacement ellipsoid plot (50% probability level) for the cationic part of 4. The NTf2 counterion, lattice solvent molecules and hydrogen atoms, except for the one on N1, are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) for 4: Au1-P1 2.2500(12); Au2-P2 2.2500(12); Au1-Cl1 2.3484(12); Au2-Cl1 2.3522(11); Au1-Au2 3.0758(3); C2-C8 1.449(7); C1-N1 1.381(7); C7-N1 1.382(7); P1-Au1-Cl1 178.53(4); Au1-Cl1-Au2 81.74(4); P2-Au2-Cl1 176.27(4). Right: Reaction scheme for selective transformation of 3 into 4 with 2 eq. AgNTf2

The existence of a single chlorido bridgehead between two AuI centers is relatively rare.$^{[18]}$ Notably, no single example exists of an intramolecular Au-Cl-Au bridge stabilized by a dinucleating ligand. Furthermore, we are not aware of any studies
regarding the substitution reactivity of chlorido-bridged dinuclear gold species. It would be interesting to explore whether the Au-Cl-Au entity could be disrupted to release a masked Au(I)-cation. Reaction of 4 with an excess of phenylacetylene led to broadening of the $^{31}$P NMR signal and appearance of an additional singlet at $\delta$ 43.3, which fully converted to single product 5 upon addition of one equivalent of either AgNTf$_2$ or K$_2$CO$_3$. No signal corresponding to the terminal CH of the alkyne was observed for this species by $^1$H NMR spectroscopy, suggestive of Au(acetylide) formation. The overall symmetry of the complex appears to be retained during this transformation, which may point to rapid exchange of the phenylacetylide between the two gold centers in solution.$^{[19]}$ Single crystal X-ray structure determination corroborated the dual interaction of the -C≡CPh ligand with the Au$^1$-Au$^1$ complex, i.e. $\sigma$-coordination of the terminal phenylacetylide carbon C(15) to Au(1) and $\pi$-coordination of the triple bond system to Au(2) (Figure 8). This is the first crystallographically characterized example of an intramolecular dinuclear gold $\sigma,\pi$-acetylide complex with a diphosphine ligand. Treatment of complex 2 with AgNTf$_2$ in the presence of phenylacetylene resulted in the very similar complex 5'. Although crystallization attempts were unsuccessful, the complex was fully characterized with NMR and mass spectroscopy. The observation that dinuclear complexes 4 and 2 engage in well-defined $\sigma,\pi$-activation of C-C triple bond systems encouraged us to investigate the catalytic abilities of the dinuclear gold complexes, which are described in the next section.
4.3.2 Catalytic studies

To probe the idea of ligand enforced dual-gold catalysis with our dinuclear Au\textsuperscript{I} complexes, we selected three known and one new substrate that give rise to different products depending on the mode of activation - \(\pi\), \(\sigma^+\pi\) or \(\sigma,\pi\) - of the C\(\equiv\)C-fragment (Figure 9). Substrate 9 was prepared as a thiourea analogue of urea-6. We assumed that analysis of product mixtures and determination of the ratio between mono- and dual-activation products would give an indication of the propensity of our digold complexes.
to perform dual-catalysis. Reaction conditions were used as reported in the literature and not further optimized.

The heterocyclization (intramolecular hydroamination) of urea-functionalized alkyne 6 was selected as proof-of-concept reaction for \( \sigma,\pi \)-activation. This reaction was found to be particularly suitable because Markovnikov addition to generate a 6-membered ring (8) involves \( \pi \)-activation by a single Au-species, while dinuclear \( \sigma,\pi \)-activation results in anti-Markovnikov addition to give a 5-membered ring (7) (Figure 10).\(^{[5a]}\)

**Figure 9.** Middle: selected substrates 6, 9, 13 and 16 for Au\(^{1}\)-catalysis. Left: reported products of mono-gold \( \pi \)-activation. Right: reported products of dual-gold activation.

**Figure 10.** Au\(^{1}\)-catalyzed heterocyclization of 6 via different activation modes resulting in indole 7 or quinazoline 8.
Performing an experiment using 2.5 mol% of 4 in DMF at 60 °C for 5 hours led to full conversion and high regioselectivity to the five-membered indole 7 (85%), in accordance with a selective σ,π-acetylide mechanism (Table 1). Use of external base (K₂CO₃) resulted in catalyst deactivation. On the other hand, addition of one equivalent AgNTf₂ with respect to the catalyst provided slightly higher regioselectivity to 7 (90%). Presumably this is due to faster generation of the σ,π-acetylide species. The bis(chlorido)-bridged tetranuclear complex 2 displayed similar preference to form 7 without additives (Ag⁺ or base). The addition of K₂CO₃ as base again proved to be detrimental for the conversion. Complex 1 was ineffective as catalyst in the absence of additives, as can be expected due to the lack of vacant sites. Full conversion and high regioselectivity was achieved by addition of two equivalents of AgNTf₂.

Table 1. Au¹-catalyzed heterocyclization of 6[^a][^c]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Au-catalyst</th>
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<th>8 (%)</th>
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<td>2.5 mol% K₂CO₃</td>
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<td>2</td>
<td>4</td>
<td>-</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>2.5 mol% AgNTf₂</td>
<td>90</td>
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<tr>
<td>4</td>
<td>1</td>
<td>-</td>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>2[^d]</td>
<td>2.5 mol% AgNTf₂</td>
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<td>12</td>
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<td>1</td>
<td>5 mol% AgNTf₂</td>
<td>94</td>
<td>6</td>
</tr>
</tbody>
</table>

[^a]: conditions: [6] = 1.0 × 10² mM, [cat] = 2.50 mM, 0.5 mL DMF, t = 5h, T = 60 °C, full conversion was obtained unless stated otherwise. [b] Calculated ratios 7/8 from ¹H NMR spectroscopy. [c] conversion below detection limit. [d] [cat] = 1.25 mM (2 is considered as a tetragold complex).

To attain the σ,π-activation of substrate 6, complexes 2 and 4 require dissociation of the bridging chloride. In the absence of a suitable halide abstracting agent, the terminal alkyne group of the substrate is likely deprotonated to generate hydrogen chloride. In order to assess whether the chloride indeed is released, a stoichiometric mixture of 4 and 6 in DMF was prepared. Mass spectrometry of the mixture shows signals corresponding to the mass of 4 and, mainly, of the mass of 4 and 6 combined minus HCl (Figure 11). This is another indication that 6 is indeed activated in a σ,π-mode, similarly to the phenylacetylide moiety found in complex 5. A minor signal at \( m/z = 1911 \) is observed that could indicate π-activation involving a tetranuclear complex.
The high regioselectivity achieved using dinuclear catalysts 2 and 4 to generate product 7 is attributed to the ligand-enforced proximity of both Au(I) centers. Dilution studies to investigate the effect of decreased catalyst loadings on the level of regiocontrol in the conversion of 6 to 7 and 8 clearly validate this hypothesis, as the high regioselectivity for the formation of 7 with catalyst 3 is independent on the catalyst concentration (Figure 12). In contrast, dilution experiments with mononuclear AuCl(PtBu3) – reported as the best catalyst to form product 7 via σ,π-activation[5a] – resulted in a drop in selectivity. These results demonstrate the benefits of well-defined preorganization of two gold centers to enforce selective σ,π-activation and to mediate highly regioselective dual-gold catalysis with functionalized alkynes, even at low catalyst loadings.

Figure 11. Mass spectrum 5 minutes after mixing 4 and 6 in a 1:1 ratio in DMF.

Figure 12. Comparison of regioselectivity to indole 7 obtained with dinuclear catalyst 4 vs. mononuclear benchmark AuCl(PtBu3) under dilution conditions (DMF, 60 °C, 20 h).
Several reasons can be envisioned to explain the different selectivity arising from dual $\sigma,\pi$-activation compared to mono $\pi$-activation. The latter is likely accompanied by $\eta^2\rightarrow\eta^1$ slippage of the cationic Au center toward to terminal carbon, which results in enhanced electrophilicity at the $\beta$-carbon position, enabling nucleophilic attack to form a 6-membered ring.\(^{[20]}\) In the case of $\sigma,\pi$-activation, the presence of a gold center at the terminal position might invert the favored direction of the $[\text{Au}]^+$-slippage, leading to a reversed polarization of the alkyne bond (Figure 13). Nucleophilic attack to form a 5-membered indole ring is then preferred over $N$-attack to from a 7-membered ring. The inversion of the gold-slippage direction likely stems from electronic rather than steric reasons, as the steric bulk of ligands is too far to be of influence. Medio-Simón et al. have proposed a (3c-2e) gem-diaurated species as the transition state in fast exchange of the acetylide between the two gold centers (Figure 13). The same research group showed that $\sigma$-activation alone does not lead to cyclization.\(^{[5a]}\)

![Figure 13. Proposed $\eta$-slippage in mono- and dual-activation mechanism (top). Exchange of $\sigma$- and $\pi$-Au fragments via a gem-diaurated transition state as proposed by Medio-Simón (bottom).\(^{[5a]}\)](image)

We sought to expand the scope of the selective heterocyclization by preparing substrate 9 bearing a thiourea instead of an urea group. The compound was successfully synthesised by reacting $o$-ethynylaniline with phenyl isothiocyanate. First complex 4 was employed as catalyst for the heterocyclization without additives and under the same conditions as used for substrate 6. Analysis of the product mixture with $^1$H NMR spectroscopy indicated 94% conversion and high selectivity (82%) toward a species tentatively assigned to product 11 (Figure 14, product signals were compared to known $^1$H NMR spectra of 7 and 8, no further characterization was done). The mixture contained only a
minor fraction (7%) of product 10 and a small fraction of product 12 resulting from S-attack (11%). The same reaction in the presence of AgNTf2 and 4 resulted in a comparable product mixture. We furthermore found that AgNTf2 also acted as catalyst for the heterocyclization of thiourea 9, leading to a similar product ratio. Heating a DMF solution of substrate 9 at 60 °C for 5h resulted in low conversion (16%) to form products 12 (88%) and 11 (12%). These results show that the selectivity obtained from preorganization and σ,π-activation in the heterocyclization of urea 6 is not necessarily easily translated to other substrates.

Figure 14. Heterocyclization of alkyne thiourea 9 and the possible ring-closed products.

Substrate 13 was selected as a model substrate for σ+π-activation involving two alkyne bonds. Its reactivity was reported by the group of Hashmi in 2012.[24] It was found that activation of this compound by 5 mol% Au(IPr)(NTf2) led to a mixture of naphthalene products a-15 and b-14 (in a 2:1 ratio). The formation of a-7 was proposed to follow π-activation by a mono-gold species, a ring-closing step (Figure 15), then attack by benzene and protodeauration. For the conversion to b-8 a dual-activation mechanism was proposed. Initially, two gold complexes are σ,π-coordinated at one terminal alkyne moiety. The reaction is initiated by intramolecular transfer of one [IPrAu]+ to the second alkyne bond (σ+π-activation, Figure 15). Subsequent ring-closing and -expansion reactions, benzene attack and catalyst transfer lead to the final product.[21] It is clear that the gold centers need to be able to move freely. Use of a σ,π-precatalyst almost selectively provided b-8 (ratio a-7:b-8: 2:98).[6]
As discussed in the introduction, tethering of two gold centers in one catalyst, as in 4, was not expected to be beneficial for most catalytic reactions with \( \sigma+\pi \)-activation mechanisms. Indeed, we found that reaction of a benzene solution of 13 and 2.5 mol\% 4 results in small amounts of naphthalene product \( \alpha-15 \) and \( \beta-14 \) in a 85:15 ratio, as detected by \(^1\)H NMR spectroscopy. Broad signals in the spectrum of the crude mixture pointed towards polymerization processes as side reaction, while starting material was still present. Addition of base has been shown to enhance the formation of dual-activated substrate and hence the formation of \( \beta-14 \).\(^{[2d]} \) The reaction was therefore repeated with 7.5 mol\% NEt\(_3\) as base. The selectivity to \( \beta-14 \) was only slightly raised (\( \alpha:\beta \), 80:20).

The Au-catalyzed reaction of diphenylacetylene 16 with phenol was reported by Nolan \textit{et al.} in 2013. The initially proposed mechanism also involves dual-activation in a \( \sigma+\pi \)-mode.\(^{[2f]} \) DFT studies provided more insight into the catalytic cycle.\(^{[22]} \) The precursors to the catalytically active complexes are two monogold compounds bridged by a hydroxide (Figure 16). The hydroxide-anion functions as an internal base for deprotonating the phenol, resulting in a Au\(^{I}\)-phenoxy and a \( \pi \)-activated diphenylacetylene. Nucleophilic attack by the \( \sigma \)-activated phenoxy ultimately leads to the hydroxyphenoxylation product.

Despite this being a \( \sigma+\pi \)-reaction, we speculated that enforced proximity of the Au-centers could have a beneficial effect on the reaction conditions. However, no formation of the hydroxyphenoxylation product was evidenced when complex 4 or 2 were employed as catalyst, even after prolonged reaction times.\(^{[23]} \) Possibly, steric congestion could be thwarting the reaction. Alternatively, phosphine donor ligands may be less suitable for this transformation than N-heterocyclic carbenes. Furthermore, the NTf\(_2\) counterion has been shown to reduce reactivity in this reaction.\(^{[22]} \) We also consider the possibility that \( \sigma \)-activation of phenol leads to a \( \mu \)-OPh binding motif that blocks a coordination site for diphenylacetylene and pushes the catalyst into a thermodynamic well.
4.4 Conclusions

In conclusion, we have demonstrated that the redox-active PNHPiPr ligand is a suitable platform to preorganize two gold centers, which can be used as catalyst for selective $\sigma,\pi$-activation of functionalized alkynes. Halide abstraction from mixed-valent Au(I)-Au(III) complex 3 using AgNTf$_2$ results in highly unusual ligand-to-gold redox-reactivity involving two-electron ligand oxidation to generate chlorido-bridged Au(I)-Au(I) species 4 bearing a highly rigidified carbazolyl backbone. Reaction with phenylacetylene enabled the first crystallographically characterized intramolecular dual-gold $\sigma,\pi$-acetylide complex (5) supported by a single diphosphine ligand. The well-defined dinuclear Au$^+$ complexes do not seem to be potent candidates for $\sigma^+\pi$-activation reactions, but are good precatalysts for dual-gold catalysis involving selective $\sigma,\pi$-activation, inducing high regioselectivity in the gold-catalyzed heterocyclization of urea 11, without the need to add base or Ag-salts. Dilution experiments show that dinuclear catalyst 4 retains high selectivity at decreased catalyst loadings, unlike mononuclear Au(I) catalysts typically employed for this reaction. These results illustrate the benefits of preorganization of gold centers to invoke selective substrate activation in dual-gold catalysis.

4.5 Acknowledgements

Maxime A. Siegler is acknowledged for part of the X-ray diffraction studies. Daniël L. J. Broere contributed to initial work on complex 1 and is much thanked for inspiration and discussions. Anne C.H. Jans is kindly thanked for donation of substrate 11 and discussions on the dinuclear gold catalysis. Marianne Lankelma contributed to work on the (Au)$_2$(POP) analogues of the herein presented catalysts and is much thanked for discussions, enthusiasm and substrate synthesis. Ed Zuidinga is thanked for mass spectrometry measurements. Marc Devillard is thanked for fruitful discussions.
4.6 Experimental section

General methods

With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. Ligand \( L^H (\text{PN}^H\text{P}^{\text{ipr}}); \) bis(2-diisopropylphosphine-4-methylphenyl)amine\)\(^{[24]}\) and PhICl\(^2\)\(^{[25]}\) were synthesized according to literature procedures. Toluene, tetrahydrofuran and pentane were distilled from sodium benzophenone ketyl. CH\(_2\)Cl\(_2\) was distilled from CaH\(_2\). NMR spectra (\(^1\)H, \(^1\)H\{\(^{31}\)P\}, \(^{13}\)C\{\(^1\)H\}, \(^{31}\)P\{\(^1\)H\}) were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer at room temperature, unless noted otherwise. High resolution mass spectra were recorded on a JEOL AccuTOF LC, JMS-T100LP Mass spectrometer using cold spray ionization (CSI) or electron spray ionization (ESI) or on a JEOL AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer using field desorption (FD). UV-visible spectra were recorded on a Hewlett-Packard 8453 Spectrophotometer.

Synthesis and characterization of new compounds

\textit{Synthesis of complex 1}

\[
\begin{align*}
\text{Bis(2-diisopropylphosphine-4-methylphenyl)amine} & \quad (\text{PN}^H\text{P}^{\text{ipr}}, 343 \text{ mg, 0.80 mmol}) \text{ was dissolved in 8 mL dichloromethane} \\
& \text{under argon atmosphere. To the colorless solution, AuCl(SMe}\_2) & \quad (470 \text{ mg, 1.60 mmol}) \text{ was added and the mixture was stirred for} \\
& \text{2h before being concentrated to 2 mL. Then, 30 mL pentane was} & \text{added, leading to a white precipitate. The suspension was stirred} \\
& \text{for 5 minutes, the solids were allowed to settle and the supernatant was removed. Further} & \text{drying led to the isolation of complex 1 as a white solid (715 mg, 99\%). Single crystals} \\
& \text{suitable for X-ray diffraction were grown by slow diffusion of pentane into a THF} & \text{solution (white crystals).}
\end{align*}
\]

\(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\), ppm): \(\delta\) 7.42 (s, 1H), 7.27 (d, \(J = 10.5\) Hz, 2H), 7.22 (d, \(J = 8.7\) Hz, 2H), 6.88 (dd, \(J = 8.1, 5.1\) Hz, 2H), 2.72-2.54 (m, 4H), 2.34 (s, 6H), 1.45-1.04 (m, 24H); \(^{31}\)P\{\(^1\)H\} NMR (121 MHz, CD\(_2\)Cl\(_2\), ppm): 40.9 (br. s); \(^{13}\)C\{\(^1\)H\} NMR (126 MHz, CD\(_2\)Cl\(_2\), ppm): \(\delta\) 146.4 (d), 134.3 (br. s), 134.0 (d, \(J = 2.5\) Hz), 132.8 (d, \(J = 7.6\) Hz), 123.4 (br. s), 115.9 (br. d, \(J = 49.4\) Hz), 26.7 (d, \(J = 34.0\) Hz), 26.5 (d, \(J = 35.3\) Hz), 21.0 (s), 20.4 (d, \(J = 27.7\) Hz), 20.4 (d, \(J = 27.7\) Hz), 19.6 (d, \(J = 31.5\) Hz); HR-MS (CSI) calcd for [M-Cl]\(^+\) C\(_{26}\)H\(_{41}\)Au\(_2\)ClNP\(_2\) m/z: 858.1734, found 858.1720.
Synthesis of complex 2

A vial was loaded with 1 (46.1 mg, 0.05 mmol) and AgNTf₂ (20 mg, 0.05 mmol). To the vial was added 2 mL CH₂Cl₂ leading to a blue-ish mixture. After stirring for 2.5 hours the mixture was filtered over Celite and subsequently the volatiles were removed, yielding 2 as a slightly off-white crystalline solid (40 mg, 70%). Crystals suitable for X-ray diffraction were obtained from a CH₂Cl₂-pentane mixture.

\[ \text{[NTf}^2]^- \]

\[ \begin{array}{c}
\text{Au} \quad \text{Cl} \\
\text{P}[(iPr)_2] \quad \text{Au} \\
\text{Cl} \quad \text{P}[(iPr)_2] \\
\text{HN} \quad \text{NH}
\end{array} \]

\[ C_{26}H_{41}Au_2ClNP_2 \]

\[ m/z: 858.1734, \text{found 858.1763}. \]

\[ \text{Synthesis of complex 3} \]

Under an argon atmosphere, 1 (641 mg, 0.717 mmol) was dissolved in 30 mL dichloromethane. To this colorless solution, PhICl₂ (197 mg, 0.717 mmol) was added as a solid, leading to an immediate color change to purple. The mixture was stirred for 1.5 h, after which it was concentrated to ~4 mL. Addition of 40 mL pentane led to formation of purple precipitate. This mixture was stirred for 5 minutes, then the solids were allowed to settle. The liquid phase was removed by syringe. The solid residue was dissolved in dichloromethane and filtered through Celite. The volatiles were removed in vacuo. The solid was recrystallized from a DCM-pentane mixture leading to a purple crystalline solid as the desired product (645 mg, 97%). Crystals of 3 suitable for X-ray diffraction were grown by layering a DCM solution with pentane.

\[ \text{[NTf}^2]^- \]

\[ \begin{array}{c}
\text{Au} \quad \text{Cl} \\
\text{P}[(iPr)_2] \quad \text{Au} \\
\text{Cl} \quad \text{P}[(iPr)_2] \\
\text{N}
\end{array} \]

\[ C_{26}H_{41}Au_2ClNP_2 \]

\[ m/z: 858.1734, \text{found 858.1763}. \]
54.5 Hz), 116.9 (d, J = 19.8 Hz), 25.1 (d, J = 4.6 Hz), 20.7 (d, J = 3.6 Hz), 20.2 (s), 19.4 (d, J = 3.3 Hz), 18.8 (d, J = 1.2 Hz), 18.7 (d, J = 1.8 Hz), 18.2 (d, J = 19.9 Hz), 17.7 (d, J = 3.7 Hz); HR-MS (FD) calcd for [M]\(^+\)C\(_{26}\)H\(_{40}\)Au\(_2\)Cl\(_3\)NP\(_2\) m/z: 927.10326, found 927.10272.

**Synthesis of complex 4**

To a vial loaded with complex 3 (116 mg, 0.125 mmol) and AgNTf\(_2\) (97 mg, 0.250 mmol) was added CH\(_2\)Cl\(_2\) (4 mL). The mixture colored blue immediately and became turbid. The mixture was stirred for 17 h, before being filtered through a pad of Celite. The purple solution was evaporated to dryness. From a mixture of CH\(_2\)Cl\(_2\), EtOAc and pentane colorless crystals could be obtained (96 mg, 68%). Single crystals suitable for X-ray diffraction could be grown from DCM/pentane.

\(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\), ppm): \(\delta\) 10.53 (s, 1H), 8.18 (s, 2H), 7.35 (d, J = 10 Hz, 2H), 2.88-2.77 (m, 4H), 2.61 (s, 6H), 1.35 (dd, J = 20.4, 6.9 Hz, 12H), 1.20 (dd, J = 18.2, 6.9 Hz, 12H); \(^{31}\)P\(\{^1\)H\} NMR (202 MHz, CD\(_2\)Cl\(_2\), ppm): \(\delta\) 40.4 (s); \(^{13}\)C\(\{^1\)H\} NMR (126 MHz, CD\(_2\)Cl\(_2\), ppm): \(\delta\) 141.6 (d, J = 6.5 Hz), 131.4 (d, J = 2.2 Hz), 131.2 (d, J = 8.3 Hz), 125.9 (d, J = 2.7 Hz), 124.8 (dd, J = 7.3, 1.7 Hz), 120.4 (q, J = 321.5 Hz), 103.0 (d, J = 55.5 Hz), 25.9 (d, J = 36.6 Hz), 21.6 (s), 20.2 (d, J = 3.7 Hz), 18.3 (s); HR-MS (CSI) calcd for [M-NTf\(_2\)]\(^+\)C\(_{26}\)H\(_{39}\)Au\(_2\)ClNP\(_2\) m/z: 856.1577, found 856.1567.

**Synthesis of complex 5**

Phenylacetylene (5.5 µL, 0.05 mmol) was added to a solution of 4 (11.4 mg, 0.01 mmol) in 0.5 mL CH\(_2\)Cl\(_2\). Subsequently, the mixture was added to a vial loaded with K\(_2\)CO\(_3\) (1.4 mg, 0.01 mmol). The resulting suspension was stirred for 16.5 h before being filtered and then concentrated to ~0.2 mL. Pentane (15 mL) was added, resulting in the formation of a precipitate, which was allowed to settle. After removal of the supernatant, the solid was dried in vacuo resulting in a yellow powder as the desired product (12.4 mg, 99%). Crystals suitable for X-ray analysis were grown from DCM/pentane.

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\), ppm): \(\delta\) 10.57 (s, 1H), 8.15 (s, 2H), 7.71 – 7.65 (m, 1H), 7.58 – 7.44 (m, 2H), 7.35 (d, J = 9.6 Hz, 2H), 2.84 (d, J = 7.1 Hz, 4H), 2.61 (s, 6H), 1.33 (dd, J = 20.0, 6.9 Hz, 12H), 1.19 (dd, J = 17.5, 6.9 Hz, 12H); \(^{31}\)P\(\{^1\)H\} NMR (162 MHz, CD\(_2\)Cl\(_2\), ppm): \(\delta\) 43.3 (s); \(^{13}\)C\(\{^1\)H\} NMR (126 MHz, CD\(_2\)Cl\(_2\), ppm): \(\delta\) 141.8 (d, J = 7.8 Hz), 133.3 (s) , 131.9 (s), 131.7 (s), 131.0 (d, J = 7.8 Hz), 129.4 (s), 125.4 (s) , 124.8 (d,
J = 7.1 Hz), 120.4 (q, J = 321.7 Hz), 119.6 (s), 104.7 (s), 104.3 (s), 25.8 (d, J = 34.7 Hz), 21.6 (s), 20.2 (d, J = 5.0 Hz), 18.4 (s); HR-MS (CSI) calcd for [M-NTf₂]+ C₃₄H₄₄Au₂NP₂ m/z: 922.2280, found 922.2261.

Synthesis of complex 5′

A solution of 2 (34.2 mg, 0.015 mmol) in DCM (1.5 mL) was prepared to which phenylacetylene (16.5 μL, 0.15 mmol) was added. The mixture was stirred for 15 minutes and subsequently added to a vial charged with AgNTf₂ (11.3 mg, 0.03 mmol). The resulting suspension was stirred for 1.5 hour before it was filtered over Celite. The light yellow filtrate was concentrated to ~0.5 mL, then 15 mL pentane was added resulting in the formation of a precipitate. After allowing the solids to settle, the supernatant was removed and the light yellow solid was dried in vacuo (35 mg, 97%).

1H NMR (400 MHz, CD₂Cl₂, ppm): δ 7.63 (s, 1H), 7.61 (s, 2H), 7.53 – 7.42 (m, 3H), 7.24 (d, J = 8.4 Hz, 2H), 7.17 (dd, J = 9.7, 2.0 Hz, 2H), 6.97 (dd, J = 8.4, 5.3 Hz, 2H), 2.95 (ddp, J = 11.1, 6.7 Hz, 2H), 2.44 (pd, J = 7.2, 5.4 Hz, 2H), 2.36 (s, 6H), 1.43 (dd, J = 19.4, 6.7 Hz, 6H), 1.36 – 1.15 (m, 18H); 31P{1H} NMR (162 MHz, CD₂Cl₂, ppm): δ 44.1 (s); 13C{1H} NMR (75 MHz, CD₂Cl₂, ppm): δ 146.5 (d, J = 6.7 Hz), 134.4 (s), 133.6 (s), 133.3 (d, J = 7.9 Hz), 131.8 (s), 129.3 (s), 123.6 (d, J = 6.8 Hz), 120.3 (q, J = 319.5 Hz), 119.2 (s), 117.2 (s), 115.1 (s), 114.4 (s), 27.7 (d, J = 32.4 Hz), 23.1 (d, J = 35.5 Hz), 20.9 (s), 20.9 (s), 20.4 (d, J = 7.0 Hz), 19.7 (s), 17.91 (d, J = 1.5 Hz); HR-MS (CSI) calcd for [M-NTf₂]+ C₃₄H₄₄Au₂NP₂ m/z: 924.24365, found 924.24262.

Synthesis of substrate 14

Under N₂ atmosphere a DCM (2 mL) solution of 2-ethynylaniline (142 μL, 1.25 mmol) was prepared. While stirring, phenylisothiocyanate (150 μL, 1.25 mmol) was added and the resulting mixture was heated to reflux for 4 hours. Then, the solvent was removed under reduced pressure, yielding a light orange solid as the crude product. Column chromatography (hexanes : ethylacetate, 3:1, Rf = 0.38) yielded desired product 14 as an off-white solid (202 mg, 67%).

1H NMR (500 MHz, acetone-d₆, ppm): δ 9.36 (s, 1H), 8.71 (s, 1H), 8.30 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 7.8 Hz, 2H), 7.48 (d, J = 7.6 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.26 (t, J = 7.5 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 3.89 (s, 1H); 13C{1H} NMR (126 MHz, acetone-d₆, ppm): 180.8, 141.8, 139.2, 133.3, 130.0, 129.8, 126.9, 126.0, 125.8, 125.7, 125.6, 116.9, 85.7, 80.2. HR-MS (FD) calcd for C₁₅H₁₂N₂S m/z: 252.07212, found 252.07176.
**Catalytic studies on heterocyclization of 1-(o-ethynylphenyl)urea**

An oven-dried 4 mL vial was loaded with 50 µmol 1-(o-ethynylphenyl)urea (11),\textsuperscript{[5a]} the Au-catalyst and the respective additive. Subsequently, anhydrous DMF (0.5 mL) was added and the resulting mixture was heated to 60 °C and stirred for 5 hours. Then the mixture was diluted with CH₂Cl₂ and subsequently evaporated to dryness. The ratio between the ring-closing products N-phenyl-1H-indole-1-carboxamide (12) and 4-methylene-3,4-dihydroquinazolin-2-one (13) was determined by \textsuperscript{1}H NMR spectroscopy and confirmed at least in duplo. NMR spectra of both products have been reported in literature.\textsuperscript{[5a]} Full conversion of the starting material was observed, except for entries 1, 4 and 6 which proved to be catalytically virtually inactive and the ratio 12/13 could therefore not be determined.

**Dilution studies**

*Au-catalyst: (P'Bu₃)AuCl*

An oven-dried 4 mL vial was loaded with (P'Bu₃)AuCl. A DMF-solution containing 100 µmol 1-(o-ethynylphenyl)urea (11) was added. Then a solution containing an equimolar amount AgSbf₆ (with respect to the Au-catalyst) was added. The resulting mixture was heated to 60 °C and stirred for 20 hours. Subsequently, the mixture was diluted with 4 mL dichloromethane and filtered over activated aluminum oxide. The filtrate was evaporated to dryness and the ratio between the ring-closing products N-phenyl-1H-indole-1-carboxamide (12) and 4-methylene-3,4-dihydroquinazolin-2-one (13) was determined by \textsuperscript{1}H NMR spectroscopy.

Catalyst loadings (mol%): 5.0; 2.5; 1.25; 0.83; 0.625; 0.5

*Au-catalyst: Complex 4*

An oven-dried 4 mL vial was loaded with complex 4. A DMF-solution containing 100 µmol 1-(o-ethynylphenyl)urea (11) was added. The resulting mixture was heated to 60 °C and stirred for 20 hours. Subsequently, the mixture was diluted with 4 mL dichloromethane and filtered over activated aluminum oxide. The filtrate was evaporated to dryness and the ratio between the ring-closing products indole carboxamide (12) and 4-methylene-3,4-dihydroquinazolin-2-one (13) was determined by \textsuperscript{1}H NMR spectroscopy.

Catalyst loadings (mol% Au-centers): 5.0; 2.5; 1.25; 0.83; 0.625
X-ray Crystal Structure Determination of complexes 1, 4 and 5: All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with either Mo Kα radiation (λ = 0.71073 Å) for 1 and 5 or with Cu Kα radiation (λ = 1.54178 Å) for 4 under the program CrysAlisPro (Versions 1.171.36.32 or 1.171.37.35 Agilent Technologies, 2013-2014). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2013 or SHELXS-2014/7 and was refined on $F^2$ with SHELXL-2013 or SHELXL-2014/7.\[26]\] Absorption correction (analytical or numerical based on gaussian integration) over a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 13, AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 $U_{eq}$ of the attached C atoms. For 1, 4 and 5, the H atom attached to N1 was found from difference Fourier maps, and its coordinates were refined freely.

X-ray Crystal Structure Determination of complexes 2 and 3: X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.\[27]\] Absorption correction and scaling was performed with SADABS.\[28]\] The structures were solved using intrinsic phasing with the program SHELXT.\[27]\] Least-squares refinement was performed with SHELXL-2013 against $F^2$ of all reflections.\[29]\] Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times $U_{eq}$ of the attached C atoms.
4.7 References


However, hydrophenoxylation of diphenylacetylene. (successfully prepared to avoid possible interference of KOH or a Grignard reagent. We investigated the possibility to substitute the µ-

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Chem. Int. Ed.


We investigated the possibility to substitute the µ-Cl ligand for a hydroxide or propynilide using KOH or a Grignard reagent aiming to increase basicity of the bridging moiety. We decided to use oxygen analogues DBFPhos and DPEPhos instead of the diarylamino phosphino ligands, in order to avoid possible interference of the N-H with the basic reagents. The digold propynilide species were successfully prepared with both DBFPhos (4,6-bis(diphenylphosphino)dibenzofuran) and DPEPhos (1,2-bis(diphenylphosphino)diphenylether). These systems were employed in the hydrophenoxylation of diphenylacetylene. Different counterions were tested (SbF₆ and PF₆). However, no appreciable reactivity to form the desired product was found.


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Chapter 5

Ligand Reactivity in a Dinuclear Mixed-Valent Au(I)-Au(III) Complex bearing a Bridging PNP Ligand – a Mechanistic Investigation
5.1 Introduction

Redox non-innocent ligands have been the subject of interest in the recent years. Essentially, these ligands are involved in redox processes allowing them to accept and donate electrons. This means that for complexes bearing redox non-innocent ligands, ambiguity over the oxidation state of metal and ligand can exist (oxidation/reduction at ligand vs. metal center).\[1-3\] The ligands are commonly utilized following two main approaches: i) the ligand serves as an electron-reservoir (passive role), or ii) the ligand participates in reactions by invoking redox-induced radical character (active role).\[2,3\] The application of redox non-innocent ligands in catalysis requires a thorough understanding of their behavior upon oxidation or reduction, including (unwanted) reactivity at the ligand.

Various nitrogen-based ligands (and substrates) have been described to be redox non-innocent.\[4\] For example, tridentate diarylaminophosphino (PNP) ligands have been shown to engage in reversible one-electron oxidation processes upon deprotonation and coordination of the central amido functionality to a (transition) metal. This is explained by the dominance of the amido $p$-orbital in the HOMO of these complexes, leading to a large contribution of this orbital in the SOMO of the oxidized complex. Additionally, there is substantial delocalization of the spin density over the phenyl rings of the ligand backbone.\[4\] As a result, the aromatic rings are susceptible toward radical reactivity at the ortho and para position with respect to the amido functionality, which itself also bears substantial radical character (Figure 1).

![Figure 1. Oxidation of the PNP scaffold and resulting positions of reactivity](image)

There are several reports of transition metal complexes wherein the PNP ligand has shown redox non-innocent behavior. For example, one-electron oxidation of a (PNP)NiCl complex was found to be a reversible process. Using a wide range of spectroscopic techniques and DFT calculations, Mindiola et al. showed that the spin density in the oxidized species predominantly resides at the ligand (31% at N, 38% at C residues).\[5\] We have shown by DFT calculations that the PNP ligand behaves similarly in the oxidation of a (PNP)NiN$_3$ complex (see Chapter 2).\[6\] The PNP ligand further contributes strongly in the redox-chemistry of \{(PNP)Cu\}_2 complexes. Two-electron oxidation of these dinuclear complexes (one electron per monomer) with “naked” aryl groups led to
reactivity *para* relative to the amido functionality (Figure 2). This could be prevented by introduction of steric bulk at this position.[7] Redox non-innocence of the PNP ligand has also been reported for complexes with Group 7 metals (Mn and Re). This was exemplified by chemical reactivity on the ligand of the oxidized species. Again, the reactivity selectively occurred *para* to the amido substituent (Figure 2).[8]

**Figure 2.** Ligand reactivity upon oxidation occurring *para* to the amido donor

In Chapter 4 we demonstrated that the PNP ligand can serve as a suitable scaffold to generate mixed-valent Au\(^{+}\)Au\(^{III}\) complex 1 (Figure 3). This complex is characterized by two distinctly different signals in the \(^{31}\)P NMR spectrum (105.3 ppm for P(Au\(^{III}\)) and 44.3 ppm for P(Au\(^{+}\))). Studying the effect of chloride abstraction, we observed sole formation of the well-characterized product 2 upon addition of two equivalents of AgNTf\(_2\) (or two equivalents of the Lewis acid GaCl\(_3\)) to a solution of 1 (Figure 3). The backbone of the PNP ligand undergoes a two-electron oxidation resulting in the formation of a carbazole moiety. This implies redox reactivity at the two aryl positions *ortho* to the amido substituent, which is in contrast to all previously reported cases of *para*-regioselective oxidative radical reactivity. The overall reaction also involves two-electron reduction of the Au\(^{III}\) center and is therefore redox neutral. A notable attribute of complex 2 is the µ-Cl ligand bridging the two Au-centers.

**Figure 3.** *Ortho* reactivity in the PNP ligand backbone by means of oxidative C-C coupling: \(\text{Au} = \text{Au(I)}; \ \text{Au} = \text{Au(III)}\).

The unexpected outcome of the described reaction, together with the new position of redox-reactivity displayed by the ligand caught our attention. In this Chapter, we will
therefore address the question as to what the mechanism behind this reaction is. We describe a systematic investigation of the transformation in order to obtain more insight into the novel redox chemistry displayed by the PNP ligand, to understand the role of Ag\(^+\) in this reaction sequence, to isolate and characterize intermediates of the reaction and to propose a mechanism of this interesting conversion.

5.2 Results and discussion

5.2.1 Division in stoichiometric reactions

Our studies showed that the reaction in question can be divided in a set of stoichiometric steps (Figure 4). In the following sections we will describe each step separately. Combining these reactions will culminate in a final proposal for the mechanism of the formation of 2.
Figure 4. Set of stoichiometric reactions that lead to transformation of Au\(^{1}\)Au\(^{\text{III}}\) complex 1 into Au\(^{1}\)Au\(^{1}\) complex 2. \textbf{Au} = \text{Au(I)}; \textbf{Au} = \text{Au(III)}.
5.2.2 Formation of tetragold assemblies

We propose that tetragold monosilver assembly 3 is the first intermediate in the investigated mechanism (Figure 5). Its formation was observed in a reaction involving the addition of 0.5 molar equivalent AgNTf₂ (instead of 2 eq., as used in the overall reaction) to a solution of complex 1. This rapidly resulted in a color change from purple to dark blue. The mass spectrum of the crude mixture contained a signal with the mass and matching isotope pattern of two complexes 1 and Ag⁺ (m/z: found 1965.1010, calculated 1965.1082). The mixture was furthermore analyzed by NMR spectroscopy. Full conversion of the starting material was observed in the ³¹P NMR spectrum (Figure 6). The P(Au¹) signal remained unaffected, whereas the P(Au³⁺) signal shifted downfield (111.0 ppm). The broadening of the latter peak suggests that more dynamic processes are present in this complex. Similar broadening was also observed in the ¹H NMR spectrum.

The combined NMR and mass spectrometry data indicate the formation of an assembly in which Ag⁺ is interacting with two molecules of 1 to form dimeric structure 3. Incorporation of Ag⁺ in gold complexes via non-covalent interactions is not unprecedented and has been reported by the group of Yip and more recently by Jones and coworkers.⁹,¹⁰ The group of Shi reported on the influence that silver can have on gold catalysis.¹¹

**Figure 5.** Reaction of starting compound 1 with 0.5 molar equivalent of AgNTf₂ leads to formation of tetragold assembly 3. Au = Au(I); Au = Au(III).
Figure 6. Top: reaction of 1 with AgNTf₂ in a 2:1 ratio, proposed formation of dimeric species 4; Au = Au(I); Au = Au(III). Bottom: ³¹P NMR spectra of 1 (bottom), 4 (middle) and 3 (top);

Unfortunately, attempts to cleanly isolate complex 3 were unsuccessful. However, addition of 0.5 equivalent TlPF₆ to a solution of 1 resulted in clean conversion to complex 4 (Figure 7). The ³¹P NMR spectrum of 4 shows a signal at 110.1 ppm, indicating that the P atom coordinated to a Au₃⁺ center is only subtly affected by the reaction (Figure 6). As for 3, the signal at 44 ppm has not shifted compared to the starting material. The ¹H NMR spectrum of product 4 displays minor shifts compared to 1. Similar to the spectrum of the starting material, a very upfield shifted aromatic signal (δ 5.83 ppm) is observed, which is attributed to shielding effects by the adjacent phenyl ring (see Chapter 4). These findings indicate that the structural integrity of the starting material is preserved upon reaction with Tl⁺.

ESI-MS data of product 4 (m/z: 2061.1802) are in line with the incorporation of thallium into complex 1 in a 1:2 ratio (TlPF₆ : 1). The generation of 4 is also accompanied by a
color change from purple to dark blue. UV-vis spectroscopy shows a small red-shift of the absorption bands compared to the starting material 1 (593, 354 and 278 nm for 4 vs 573, 347 and 276 nm for 1) and roughly doubling of the extinction coefficients. The preparation and the respective NMR and mass spectra of 3 and 4 are quite similar. We therefore propose that the structure of 3 should resemble the structure of 4.

![Schematic representation of Tl⁺ scavenging by 1. Au = Au(I); Au = Au(III). Bottom: ORTEP plots (50% probability level) for 4. Hydrogen atoms and PF₆ counterion are omitted for clarity, selected bond lengths (Å) and angles (°): Au1---Au2 3.185(1); P1-Au1 2.246(4); Au1-C11 2.313(4); P2-Au2 2.265(4); N1-Au2 2.02(1); Au2-C12 2.313(4); Au2-C13 2.376(4); P1-Au1-C11 178.2(1); N1-Au2-C12 172.2(4); P2-Au2-C13 173.0(1); C11-Tl1 3.267; Cl2-Tl1 3.100; C13-Tl1 3.108; C6-C1-C7-C8 77(1).](image)

Figure 7. Top: Schematic representation of Tl⁺ scavenging by 1. Au = Au(I); Au = Au(III). Bottom: ORTEP plots (50% probability level) for 4. Hydrogen atoms and PF₆ counterion are omitted for clarity, selected bond lengths (Å) and angles (°): Au1---Au2 3.185(1); P1-Au1 2.246(4); Au1-C11 2.313(4); P2-Au2 2.265(4); N1-Au2 2.02(1); Au2-C12 2.313(4); Au2-C13 2.376(4); P1-Au1-C11 178.2(1); N1-Au2-C12 172.2(4); P2-Au2-C13 173.0(1); C11-Tl1 3.267; Cl2-Tl1 3.100; C13-Tl1 3.108; C6-C1-C7-C8 77(1).

X-ray analysis of single crystals grown from a CH₂Cl₂/pentane solution allowed for further elucidation of the nature of complex 4. The crystal structure displays a dimeric complex in which a thallium(I) core is incorporated in-between the chlorido ligands of two digold complexes 1 (Figure 7). The distances between the Tl⁺ core and the chloride atoms coordinated to the Au₃⁺ center were found to be around 3.100 Å and 3.108 Å, indicating non-covalent interactions that likely cause the downfield shift of the P(Au₃⁺) peak in the ³¹P NMR spectrum. The distance between the Cl1 and the thallium core was...
found to be slightly longer, around 3.267 Å, which may still allow for a weak interaction. It is, however, possible that this interaction is only present in the solid state, given that no shift was observed for the P(AuI) donor in the 31P NMR spectrum. Complex 1 possesses axial chirality which is transferred to complex 4. Both (S,S) and (R,R) enantiomers were found in the crystal, indicating a 1:1 ratio.

Compared to the X-ray structure of 1 (see Chapter 4), a major difference is the orientation of the AuI center. In the structure of 4 this orientation allows for a AuI—AuIII distance of only 3.185(1) Å. This is significantly shorter than the sum of their van der Waals radii, allowing for a d8-d10 interaction to occur, a feature that was not found for 1.

5.2.3 Acid-induced disproportionation of 3

Exposing in situ generated complex 3 to an equimolar amount of HBF4 resulted in the formation of a mixture of equal amounts of complexes 5 and 6 (Figure 8). Treatment of the thallium congener, 4, with HBF4 resulted in a comparable mixture, albeit less cleanly. These results indicate that these tetrangold assemblies are sensitive toward disproportionation by Brønsted acids.

Addition of an equimolar amount of AgNTf2 to a solution of 1 also generated products 5 and 6 in a 1:1 molar mixture (Figure 8). Moreover, formation of final product 2 was observed by 1H NMR (Figure 9). Analysis of the 31P NMR spectrum shows the presence of peaks at 40.3 ppm (for 2), 40.5 ppm (for 5) and 102.1 ppm (for 6). As described in the
introduction, the formation of 2 is accompanied by the release of one equivalent of HNTf₂. This explains why no trace of the proposed first intermediate 3 was found.
with respect to starting compound 1. The overall reaction is redox-neutral given the two-electron reduction required to co-generate 5 (Figure 9).

Figure 10. ORTEP plot (50% probability level) for 6. Hydrogen atoms and NTf$_2$ counterion are omitted for clarity, selected bond lengths (Å) and angles (°): C7-N1-C6 112(1); C7-N1-Au2 113.0(8); Au1-N1-C6 112.8(8); Au1-N1-Au2 100.0(4); Au1---Au2 3.2487(7); N1-Au1 2.14(1); Au1-C11 2.280(4); Au1-C12 2.341(3); P1-Au1 2.285(3); N1-Au2 2.10(1); Au2-C13 2.336(3); Au2-C14 2.275(3); P2-Au2 2.290(3); N1-Au1-C11 178.8(3); P1-Au1-C12 177.6(1); N1-Au2-C14 178.7(3); P2-Au2-C13 177.8(1); C5-C6-C7-C8 93(1).

The oxidation states of the gold centers in the series 5 - 1 - 6 increase in steps of two from Au$^1$Au$^1$ to Au$^1$Au$^{III}$ and Au$^{III}$Au$^{III}$, respectively, stabilized by the PNP ligand as either a neutral or monoanionic ligand. A reaction of 5 with one equivalent of the two-electron oxidant dichloro-λ$^3$-(iodanyl)benzene (PhICl$_2$) did however not lead to formation of 1 (Figure 11). Instead a 1:1 mixture of the starting material and 6 formed, suggesting the intermediacy of a compound with either a lower oxidation potential than the starting material or with the tendency to disproportionate into 5 and 6. Reaction of two equivalents of PhICl$_2$ with 5 led to full conversion into Au$^{III}$Au$^{III}$ species 6. The reaction of 1 with PhICl$_2$ resulted in a mixture of products, in which 6 was present only as a minor species (<10%, determined by $^{31}$P NMR spectroscopy).
Figure 11. Reactivity of complexes 5 and 1 with PhICl$_2$. \(\text{Au} = \text{Au(I)}\); \(\text{Au} = \text{Au(III)}\).

5.2.4 Halide abstraction from 5 and further reactivity

Figure 12. Full consumption of 5 and 6 to generate carbazole product 2. \(\text{Au} = \text{Au(I)}\); \(\text{Au} = \text{Au(III)}\).

Full conversion to complex 2 was observed upon addition of three equivalents AgNTf$_2$ to a 1:1 mixture of 5 and 6 (Figure 12), confirming the role of these two complexes as intermediates in the formation of 2. Without addition of AgNTf$_2$, these two compounds are stable and do not react together. Treating complex 6 separately with AgNTf$_2$ did not result in appreciable conversion to 2 (< 5%), although NMR spectra did indicate interaction of the silver salt with the complex. Reaction of compound 5 with AgNTf$_2$ resulted in the formation of ‘dicationic’ complex 7 (Figure 13). Weak coordination of the NTf$_2$ anions to the gold centers is manifested by a small shift in the $^{19}$F NMR spectrum compared to 5 (-75.9 ppm for 7 vs -79.5 ppm for 5). Compound 7 was also prepared by treatment of the parent (PNP)Au$_2$Cl$_2$ complex with two equivalents of AgNTf$_2$. Reactivity studies showed that addition of an equimolar amount of HCl (0.1 M solution in water) to
7 regenerates the μ-Cl complex 5 (Figure 13). Reaction of 7 with two equivalents PhICl\textsubscript{2} led to quantitative formation of 6.

**Figure 13.** Interconversion between species 5 and 7 by reaction with halide abstracting agent or hydrochloric acid. Preparation of species 6 from 7 by two-electron oxidation. \( \text{Au} = \text{Au(I)}; \ \text{Au} = \text{Au(III)}. \)

### 5.2.5 Formation of final product 2

Complex 6 is believed to be the precursor to the final carbazole product 2, as its high oxidation state and potentially strongly oxidizing character may invoke two-electron oxidation of the ligand backbone. This conversion is accompanied by formal release of HCl and two-electron reduction of the complex. It should therefore be triggered by the addition of a suitable two-electron reductant to complex 6. A reaction of 6 with Pd\textsuperscript{0}(dba)\textsubscript{2} in this role indeed resulted in quantitative conversion (Figure 14), as indicated by NMR spectra and the mass spectrum of the reaction mixture. The reaction did not proceed without the addition of AgNTf\textsubscript{2}. These findings are in agreement with complex 6 being the final isolable precursor of 2. A reaction with ferrocene as a (one-electron) reductant did not result in formation of 2.

**Figure 14.** Reaction of complex 6 with Pd\textsuperscript{0}(dba)\textsubscript{2} as sacrificial two-electron reducing agent forming 2, in the presence of AgNTf\textsubscript{2}. Products in frame were not detected. \( \text{Au} = \text{Au(I)}; \ \text{Au} = \text{Au(III)}. \)

The reactivity of 6 with 7 was investigated by preparation of a 1:1 mixture of these compounds in dichloromethane. Analysis of the reaction mixture by NMR spectroscopy revealed the presence of the carbazole product 2 and complexes 5 and 6 in equal amounts,
whereas species 7 was found to be fully consumed. The observed product ratio is in line with the expected values (Figure 15). Complex 7 serves both as a two-electron reductant to form 6 and as a HCl scavenger to produce 5. This implies that only two-thirds of 6 can react to product 2 before 7 is completely converted and the reaction comes to a halt. This experiment shows that halide abstracting agents are not necessary for formation of 2, but rather facilitate the formation of compounds able to react with precursor 6.

Figure 15. Schematic representation of reaction of complexes 6 with 7 and a proposal for the observed ratio of products. \( \text{Au} = \text{Au(I)}; \) \( \text{Au} = \text{Au(III)} \).

5.2.6 Proposal for a mechanism

The combined findings described in the previous subsections lead to the following mechanistic proposal for the investigated reaction (Figure 16). Initial Ag\(^+\) scavenging by two Au\(^{1}\)Au\(^{III}\) complexes 1 leads to the formation of complex 3. This intermediate undergoes an acid-induced disproportionation reaction, as supported by stoichiometric reaction with HBF\(_4\). No external Brønsted acid is added to the reaction, so we propose that disproportionation in the original sequence is initially induced by trace amounts present in the solvent. This disproportionation produces Au\(^{1}\)Au\(^{1}\) complex 5 and Au\(^{III}\)Au\(^{III}\) complex 6. The former reacts with AgNTf\(_2\) to form 7 via salt metathesis. Stoichiometric reaction of 7 with 6 converts the latter to the final product 2 with concomitant oxidative
C-C bond formation. \[^{[12]}\] The HCl and two-electron oxidation equivalents (Cl\(_2\)) released in this process react with 7 to regenerate complexes 5 and 6 in a 2:1 ratio with concomitant generation of HNTf\(_2\). This acid can drive the disproportionation reaction to completion. A total of two equivalents of AgNTf\(_2\) is required to drive the overall reaction to full conversion.

**Figure 16.** Postulated mechanism for the formation of 2 from reaction of 1 with AgNTf\(_2\). \(\text{Au} = \text{Au(I)}\); \(\text{Au} = \text{Au(III)}\).

Cross-over experiments were conducted to further prove the proposed pathway. For this purpose (\(^{10}\text{PhPNp}^{10}\))Au\(_2\)(NTf\(_2\))\(_2\) was prepared (complex 7-Ph, see Appendix 5.A3 for crystal structure) via the same route as used for the bis(isopropyl)phosphine congener. Mixing this complex with 6 initially led to exclusive (but incomplete) conversion of the latter to product 2, while the expected formation of 5-Ph, 6-Ph and 2-Ph was also observed in the NMR spectra (Figure 17). After prolonged reaction time, however, almost full consumption of 6 was observed in NMR spectra, accompanied by generation of 6-Ph and 5. These results show the reactivity between 6 and 5-Ph to generate 5 and 6-Ph. The effect of additives on the transformation from 1 to 2 was also studied; these results are described in Appendix 5.A1. In Appendix 5.A2 we describe the redox chemistry of 1, excluding the possibility for AgNTf\(_2\) to act as an oxidant for 1.
Figure 17. $^{31}$P NMR spectrum of product mixture after reacting 6 and 7-Ph for 1 hour (SM = starting material). * is putatively assigned to 2-Ph.

5.3 Conclusion

In conclusion, this Chapter describes a mechanistic investigation of the reaction of Au$^I$Au$^{III}$ complex 1 with AgNTf$_2$ that results in Au$^I$Au$^I$ complex 2. The isolation and characterization of dinuclear gold intermediate complexes leads to the formulation of a plausible reaction mechanism. Initial scavenging of Ag$^+$ by two complexes 1 is followed by an acid-induced disproportionation reaction, resulting in Au$^I$Au$^I$ compound 5 and Au$^{III}$Au$^{III}$ compound 6. Chloride abstraction from 5 leads to ‘dicationic’ species 7. This complex can react with 6, which then converts to final product 2. The conversion requires a two-electron reductant and is accompanied by release of HCl. Complex 7 functions both as the acceptor of the acid and as the two-electron reductant. Cross-over experiments and the use of Pd(dba)$_2$ as alternative reductant (or Cl$_2$ acceptor) confirm that 6 should be regarded as the precursor to 2. We speculate that the exhibited ortho-reactivity of the ligand backbone arises from a combination of steric preorganization and stepwise oxidation of the ligand by the gold centers.

The range of oxidation states of the isolated structures, from Au$^I$Au$^I$ to Au$^{III}$Au$^{III}$, highlights the versatility of the PNP ligand. The central amine functionality of the PNP ligand seems to be essential for the stabilization of the complexes in higher oxidation states, while it also allows for Au$^I$Au$^I$ structures. The isolation of Tl-adduct 4 and the proposed intermediacy of Ag-congener 3 show that halide abstracting agents are not innocent per se and that their incorporation into quasi-stable complexes should be considered for future gold chemistry.
5.4 Acknowledgements

Maxime Siegler is thanked for X-ray diffraction studies on complex 6. Ed Zuidinga is acknowledged for mass spectrometry measurements.

5.5 Appendix

5.A1 Effect of additives on reaction A

In the proposed mechanism for the investigated reaction, Au^I Au^III complex 1 remains a precursor for the Au^I Au^I complex 2 without much further relevance. We therefore decided to investigate ways to intervene in the reaction and prevent the conversion to 2. Abstraction of chloride ligands remains a prerequisite for Au-catalysis. Hence, the effect of additives on the reaction was studied. For this purpose, tetrahydrothiophene (THT) and phenylacetylene were used. THT was selected for its well-known ability to stabilize cationic gold centers, while phenylacetylene could function as a π-donor to a Au-center and as a potential substrate in follow-up reactions. The reaction was carried out in the presence of the additives and the product mixtures were analyzed for the presence of Au^I Au^III species.

Pre-mixing a purple DCM solution of complex 1 with THT in a 1:10 ratio and subsequent addition of the mixture to AgNTf₂ resulted in a dark blue suspension. NMR analysis revealed the presence of multiple unidentifiable species in the mixture, whereas complex 2 was not detected. Major signals in the region of 35 – 50 ppm of the 31P NMR spectrum suggest that the main products contain solely Au^I centers. Mass spectrometry of the product mixture shows the presence of a Au₂Cl(PN₂P) species. No indications for a Au^I Au^III species present in the mixture were found, but the reaction shows that formation of 2 can be avoided by the addition of a proper additive.

In a different reaction, a purple acetone solution of complex 1 was mixed with phenylacetylene. Next, the solution was added to AgOTf. In this case, the color of the suspension ultimately turned red. After stirring overnight and filtering the suspension over Celite a red solution was obtained. NMR analysis again indicated that a mixture of products had formed, none of which seemed to be a Au^I Au^III species. Single crystals of the major product (as determined by integration of signals in the 31P NMR spectrum) could be obtained. X-ray diffraction of the crystals gave insight in newly formed compound 8 (Figure 18). Interestingly, the obtained crystal structure displays a square planar mononuclear Au^III complex. The PNP ligand is deprotonated and functions as a tridentate ligand. The fourth coordination site is occupied by phenylacetylide and OTf⁻ is present as counterion.
Square planar Au\textsuperscript{III} complexes have emerged as a curious class of compounds over the last few years. Generation of these structures from Au\textsuperscript{I} compounds by means of oxidative addition reactions is known to be exceedingly difficult. Specifically designed ligands and strategies or the use of strongly oxidizing agents (e.g. PhI\textsubscript{2} compounds) are in general necessary for this elementary reaction.\textsuperscript{[13]} Au\textsuperscript{III} complexes bearing tridentate ligands have been used in coordination chemistry,\textsuperscript{[14–17]} photoluminescence,\textsuperscript{[18–20]} medicinal studies\textsuperscript{[21,22]} and in few examples of catalysis.\textsuperscript{[21,24]} In this context, further study of structure 8 would be of interest. We therefore attempted to isolate this complex on a larger scale. Unfortunately, preliminary attempts of purification through bulk crystallization and column chromatography were unsuccessful.

The exact mechanism for formation of 8 remains a matter of speculation. To assess whether dinuclear Au\textsuperscript{III}/Au\textsuperscript{III} complex 6 plays a role in the process, a reaction of 6 with AgNTf\textsubscript{2} in the presence of phenylacetylene was conducted. This did not deliver 8 and it therefore seems likely the complex is formed in an earlier stage. In view of the purification issues, of the waste generated in the synthesis of complex 8 and of the scope of this Chapter, further exploration of the structure was abandoned and reconsideration of a targeted synthetic protocol is deemed essential to uncover the chemistry of this mononuclear Au(III) pincer. However, it is clear that (neutral) additives may substantially suppress the reaction scrutinized in this Chapter.
5.A2 Redox chemistry of complex 1

We also considered the possible role of AgNTf₂ as an oxidant in the studied reaction (see introduction 5.1, Figure 3), given the relatively strong oxidation potential of Ag⁺ in CH₂Cl₂ is 0.64 V (vs. Fc).[25] Although the overall reaction is redox-neutral, we speculated that oxidation could be an initial step in the reaction. Because the PNP ligand coordinates in a monoanionic form with an amido-fragment bound to one of the metal centers in complex 1, which bears similarity with the coordination found in the aforementioned Cu, Ni, Mn and Re complexes, oxidation of 1 would be expected to be ligand-based and as such potentially the initial step in the reaction.

Cyclic voltammetry experiments with complex 1 showed an irreversible oxidation event at 0.79 V vs. Fc⁰⁺ (Figure 19), which is well above the oxidation potential of Ag⁺. Additionally, the CV shows an irreversible reduction event at -1.22 V, most likely attributable to reduction of the AuIII center. We subsequently decided to perform the reaction under investigation in acetone, as the oxidation potential of Ag⁺ is much milder in this solvent (0.18 V vs. Fc).[25] This reaction proceeded equally selectively and smoothly, establishing that AgNTf₂ does not act as an oxidant.

![Figure 19. Cyclic voltammogram of 1 in CH₂Cl₂ (scan speed 0.1 V/s)](image)

DFT studies were performed in an attempt to rationalize the irreversible nature of the electrochemical oxidation process. The HOMO of complex 1 is primarily located at the PNP ligand, more specifically at the part chelating the AuIII center (Figure 20). Optimization of the corresponding one-electron oxidized structure of 1 showed localization of the spin density at the N (34%) and at the chelating phenyl ring (58%)
The lack of delocalization of the spin density over both phenyl rings likely leads to ligand-based reactivity and therefore to the irreversible oxidation of 1. In addition, opposed to the bidentate coordination in 1, all reported examples of reversible oxidation of PNP-complexes involve the framework engaged in coordination to a single metal as a tridentate ligand, providing extra stabilization of the metal center in oxidized species.

**Figure 20.** HOMO of 1 (left) and spin density plot of 1⁺ (right) (b3-lyp, def2-TZVP, disp3)

**5. A3 X-ray structure determination of 7-Ph**

![ORTEP plot for 7-Ph](image)

**Figure 21.** ORTEP plot (50% probability level) for 7-Ph. Hydrogen atoms and NTf₂ counterion are omitted for clarity, selected bond lengths (Å) and angles (°): P1-Au1 2.222(3), Au1-N2 2.117(9), P2-Au2 2.234(2), Au2-N3 2.106(9), N2-Au1-P1 177.8(3), N3-Au2-P2 175.8(3), C1-C2-C9-C8 127(2).
5.6 Experimental

General methods

With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. PN\textsubscript{H}P\textsubscript{iPr} (bis(2-diisopropylphosphino-4-methylphenyl)amine\textsuperscript{[26]}, PN\textsubscript{H}P\textsubscript{Ph} (bis(2-diphenylphosphine-4-methylphenyl)amine\textsuperscript{[27]} and PhICl\textsubscript{2}\textsuperscript{[28]} were synthesized according to literature procedures. Compounds 1, 5 and (PN\textsubscript{H}P\textsubscript{iPr})Au\textsubscript{2}Cl\textsubscript{2} were prepared as described in Chapter 4. Toluene, tetrahydrofuran, diethylether and pentane were distilled from sodium benzophenone ketyl. CH\textsubscript{2}Cl\textsubscript{2} was distilled from CaH\textsubscript{2}. NMR spectra (\textsuperscript{1}H, \textsuperscript{1}H\textsubscript{\{}\textsuperscript{31}P\textsuperscript{\}}, \textsuperscript{13}C\textsuperscript{\{}\textsuperscript{1}H\textsuperscript{\}}, \textsuperscript{31}P\textsuperscript{\{}\textsuperscript{1}H\textsuperscript{\}}) were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer at room temperature, unless noted otherwise. High resolution mass spectra were recorded on a JEOL AccuTOF LC, JMS-T100LP Mass spectrometer using cold-spray ionization (CSI) and electron-spray ionization (ESI) and on a JEOL AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer using field desorption (FD). UV-visible spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. Cyclic voltammetry measurements were performed in THF containing N(n-Bu\textsubscript{4})PF\textsubscript{6} (0.1 M) at room temperature under a nitrogen atmosphere using a platinum disk working electrode, a platinum coil counter electrode and a silver coil reference electrode. All redox potentials are referenced to Fc/Fc\textsuperscript{+}.

Computational details

Geometry optimizations were carried out with the Turbomole program package\textsuperscript{[29]} coupled to the PQS Baker optimizer\textsuperscript{[29]} via the BOpt package\textsuperscript{[29]} at the DFT/b3-lyp\textsuperscript{[29]} level. We used the def2-TZVP basis set.\textsuperscript{[29]} Dispersion corrections were applied.\textsuperscript{[30]} All minima (no imaginary frequencies) were characterized by calculating the Hessian matrix.
Synthesis and characterization of new compounds

**Synthesis of complex 4**

A flame-dried Schlenk under argon atmosphere was loaded with 1 (33 mg, 0.0355 mmol) and TlPF₆ (6.2 mg, 0.0177 mmol) before addition of DCM (1.5 mL), which instantaneously led to a dark blue solution. After stirring for 3h, the solution was filtered and then concentrated to ~0.5 mL. Subsequent addition of pentane led to precipitation of a dark blue solid. The supernatant was removed and the residue was dried to yield product 4 (36 mg, 92%). Single crystals suitable for X-ray diffraction were grown from DCM-pentane.

**¹H NMR** (400 MHz, CD₂Cl₂, ppm): δ 7.46 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.7 Hz, 1H), 7.11 (dd, J = 8.1, 4.7 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 6.95 (d, J = 10.8 Hz, 1H), 5.83 (dd, J = 8.7, 4.8 Hz, 1H), 3.37 – 3.23 (m, 1H), 3.12 – 3.00 (m, 1H), 2.86 – 2.71 (m, 1H), 2.47 (s, 3H), 2.25 (s, 3H), 2.09 – 1.95 (m, 1H), 1.71 (dd, J = 19.4, 7.0 Hz, 3H), 1.60 (dd, J = 20.4, 7.0 Hz, 3H), 1.52 – 1.25 (m, 12H), 1.14 (dd, J = 18.5, 7.3 Hz, 3H), 1.02 (dd, J = 16.3, 7.2 Hz, 3H); **³¹P{¹H} NMR** (162 MHz, CD₂Cl₂, ppm): δ 110.1 (s), 44.3 (s), -144.5 (hept, J = 711.1 Hz); **¹³C{¹H} NMR** (126 MHz, CD₂Cl₂, ppm): δ 165.2 (d, J = 11.0 Hz), 152.7 (d, J = 6.0 Hz), 138.0 (d, J = 7.6 Hz), 136.7 (d, J = 2.9 Hz), 134.5 (d, J = 2.0 Hz), 133.4 (d, J = 6.0 Hz), 132.5 (d, J = 2.9 Hz), 131.7 (d, J = 2.3 Hz), 131.6 (d, J = 9.7 Hz), 126.6 (d, J = 55.3 Hz), 116.8 (d, J = 13.2 Hz), 104.3 (d, J = 58.3 Hz), 29.3 (d, J = 28.1 Hz), 29.1 (d, J = 34.0 Hz), 26.5 (d, J = 33.2 Hz), 23.8 (d, J = 33.0 Hz), 21.6 (s), 21.4 (d, J = 4.2 Hz), 20.8 (d, J = 3.6 Hz), 20.2 (s), 19.5 (d, J = 4.1 Hz), 18.5 (d, J = 56.7 Hz), 18.0 (d, J = 70.6 Hz), 17.6 (d, J = 3.7 Hz); **HR-MS** (ESI) calcd for [M - PF₆]⁺ C₅₂H₈₀Au₄Cl₆N₂P₄Tl m/z: 2061.1776, found 2061.1802.
UV-vis spectrum of 4 in DCM:

Synthesis of complex 6

A solution of 5 (55 mg, 0.05 mmol) in 2 mL DCM was prepared in a vial. To the colorless mixture was added PhICl2 (27 mg, 0.10 mmol) as a solid, causing an immediate color change to yellow. The resulting mixture was stirred for 45 minutes. Then, pentane was added resulting in the precipitation of a yellow solid. The supernatant was removed and the yellow product was dried. The crude product could be recrystallized from DCM-pentane resulting in yellow/orange crystals (58 mg, 96%). Crystals suitable for X-ray analysis were grown from DCM-toluene.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.56 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 9.6$ Hz, 2H), 7.04 (dd, $J = 8.7$, 4.5 Hz, 2H), 3.94 (hept, $J = 7.4$ Hz, 2H), 3.56 – 3.41 (m, 2H), 2.54 (s, 6H), 1.87 (dd, $J = 20.3$, 7.2 Hz, 6H), 1.74 – 1.54 (m, 18H); $^{31}$P{${^1}$H} NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 102.1 (s); $^{13}$C{${^1}$H} NMR (101 MHz, CD$_2$Cl$_2$, ppm): δ 158.4 (d, $J = 8.0$ Hz), 142.3 (d, $J = 8.2$ Hz), 138.0 (d, $J = 2.7$ Hz), 133.6 (d, $J = 1.6$ Hz), 128.5 (d, $J = 10.7$ Hz), 121.1 (d, $J = 51.0$ Hz), 119.8 (q, $J = 321.4$ Hz), 35.9 (d, $J = 25.1$ Hz), 29.8 (d, $J = 28.0$ Hz), 21.2 (d, $J = 5.6$ Hz), 20.5 (s), 19.9 (s), 18.9 (d, $J = 2.1$ Hz), 18.6 (d, $J = 4.6$ Hz); HR-MS (ESI) calcd for [M – NTf$_2$]$^+$ C$_{26}$H$_{40}$Au$_2$Cl$_4$NP$_2$ m/z: 964.0695, found 964.0676.
UV-vis spectrum of 6 in DCM:

Synthesis of complex 7

A vial was loaded with \((\text{PN}^{\text{HPr}}\text{P})\text{Au}_2\text{Cl}_2\) (89 mg, 0.1 mmol) and AgNTf$_2$ (78 mg, 0.2 mmol), then 5 mL DCM was added. The resulting mixture was stirred for 1.5 hours. Subsequently, it was filtered over Celite and the volatiles were removed under reduced pressure. The slightly purple crude product (113 mg, 82%) was recrystallized from a DCM-pentane mixture, leading to colorless crystals (78 mg, 56%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 7.32 – 7.25 (m, 4H), 6.83 (dd, $J$ = 8.2, 5.2 Hz, 2H), 6.39 (s, 1H), 2.78 (dp, $J$ = 10.2, 6.8 Hz, 2H), 2.45 (h, $J$ = 7.2 Hz, 2H), 2.36 (s, 6H), 1.41 (dd, $J$ = 19.5, 6.7 Hz, 6H), 1.32 – 1.17 (m, 18H); $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 42.9 (s); $^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 147.4 (d, $J$ = 5.7 Hz), 135.0 (d, $J$ = 2.3 Hz), 134.5 (d, $J$ = 9.2 Hz), 134.1 (s), 126.2 (s), 119.6 (q, $J$ = 323.1 Hz), 115.7 (d, $J$ = 56.7 Hz), 28.5 (d, $J$ = 35.9 Hz), 24.3 (d, $J$ = 37.7 Hz), 21.0 (s), 20.6 (d, $J$ = 2.5 Hz), 20.3 (d, $J$ = 5.6 Hz), 19.3 (s), 18.88 (s); $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$, ppm): $\delta$ -75.9 (s);

HR-MS (ESI) calcd for [M-NTf$_2$]$^+$ C$_{28}$H$_{41}$Au$_2$F$_6$N$_2$O$_4$P$_2$S$_2$ $m/z$: 1103.1218, found 1103.1210.
Synthesis of complex $PN^HP^PhAu_2Cl_2$

A flame-dried Schlenk under N$_2$-atmosphere was charged with a DCM solution (5 mL) of $PN^HP^Ph$ (139 mg, 0.25 mmol). To this colorless solution AuCl(SMe$_2$) (147 mg, 0.50 mmol) was added, leading to the formation of a white solid. The suspension was stirred overnight before 10 mL pentane was added. The solid was allowed to settle and the supernatant was removed. The product ($PN^HP^PhAu_2Cl_2$) was dried in vacuo yielding a white powder (194 mg, 75% yield). The product proved to be barely soluble in common NMR solvents, hindering complete spectroscopic characterization.

$^1H$ NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.59-7.36 (m, 17H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.25-7.16 (m, 3H), 7.15-7.08 (m, 2H), 6.42 (d, $J = 12.7$ Hz, 2H), 5.82 (s, 1H), 2.14 (s, 6H);
$^{31}P{^1H}$ NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 19.6 (s); HR-MS (ESI) calcd for [M-Cl]$^+$ C$_{38}$H$_{33}$Au$_2$ClNP$_2$ m/z: 994.1108, found 994.1135.

Synthesis of complex 5-Ph

A vial was charged with $PN^HP^PhAu_2Cl_2$ (50.2 mg, 0.05 mmol) and AgNTf$_2$ (19.4 mg, 0.05 mmol). Then, 5 mL DCM was added and the resulting suspension was stirred for 45 minutes during which it slightly colored purple. The mixture was then filtered over Celite. The colorless filtrate was then dried under removed pressure, yielding the product (5-Ph) as an off-white solid (52 mg, 82%).

$^1H$ NMR (300 MHz, CD$_2$Cl$_2$, ppm): δ 7.74 – 7.39 (m, 20H), 7.10 (d, $J = 8.5$ Hz, 2H), 7.05 (s, 1H), 6.59 – 6.42 (m, 4H), 2.12 (s, 6H); $^{31}P{^1H}$ NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 18.5 (s); $^{13}C{^1H}$ NMR (126 MHz, CD$_2$Cl$_2$, ppm): δ 144.1 (d, $J = 7.6$ Hz), 135.2 (d, $J = 2.4$ Hz), 134.8 (t, $J = 13.7$ Hz), 134.2 (s), 134.2 (s), 134.1 (s), 133.8 (s), 133.4 (s), 126.3 (s), 125.8 (s), 125.3 (s), 122.4 (d, $J = 6.7$ Hz), 120.3 (q, $J = 321.7$ Hz), 118.0 (s), 117.5 (s), 20.8 (s); $^{19}F$ NMR (282 MHz, CD$_2$Cl$_2$, ppm): δ -79.5 (s); HR-MS (ESI) calcd for [M-NTf$_2$]$^+$ C$_{38}$H$_{33}$Au$_2$ClNP$_2$ m/z: 994.1108, found 994.1120.
Synthesis of complex 7-Ph

A vial was charged with \( \text{PN}^{\text{H}}\text{P}^\text{Ph}^\text{Au}_{\text{Cl}} \) (50.2 mg, 0.05 mmol) and \( \text{AgNTf}_2 \) (38.8 mg, 0.10 mmol). Then, 5 mL DCM was added and the resulting suspension was stirred for 1h45min during which it colored purple. The mixture was filtered over Celite and the colorless filtrate was concentrated under reduced pressure, leaving 7-Ph as an off-white solid in high yield (66 mg, 87%). Single crystals were grown by slow diffusion of pentane into a DCM solution of the compound.

\(^1\text{H NMR}\) (400 MHz, CD\(_2\)Cl\(_2\), ppm): \( \delta \) 7.60 (dd, \( J = 8.5, 6.2 \) Hz, 2H), 7.50 (td, \( J = 7.8, 2.8 \) Hz, 4H), 7.44 – 7.16 (m, 16H), 7.13 (dd, \( J = 13.4, 1.9 \) Hz, 2H), 4.95 (s, 1H), 2.16 (s, 6H); \(^{31}\text{P}\{^1\text{H}\} \text{NMR}\) (162 MHz, CD\(_2\)Cl\(_2\), ppm): \( \delta \) 17.6 (s); \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (101 MHz, CD\(_2\)Cl\(_2\), ppm): \( \delta \) 145.4 (d, \( J = 8.2 \) Hz), 135.5 (d, \( J = 2.4 \) Hz), 135.4 (d, \( J = 14.4 \) Hz), 134.9 (d, \( J = 10.1 \) Hz), 134.1 (d, \( J = 7.2 \) Hz), 133.2 (s), 133.1 (d, \( J = 8.5 \) Hz), 130.4 (d, \( J = 12.4 \) Hz), 129.9 (d, \( J = 12.6 \) Hz), 127.2 (d, \( J = 68.4 \) Hz), 126.1 (d, \( J = 67.0 \) Hz), 125.1 (d, \( J = 6.8 \) Hz), 119.7 (q, \( J = 323.4 \) Hz), 117.7 (s), 117.1 (s), 20.9 (s); \(^{19}\text{F NMR}\) (282 MHz, CD\(_2\)Cl\(_2\), ppm): \( \delta \) -75.4 (s); \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (101 MHz, CD\(_2\)Cl\(_2\), ppm) calcd for [M-NTf\(_2\)]\(^+\) C\(_40\)H\(_{33}\)Au\(_2\)F\(_6\)N\(_2\)O\(_4\)P\(_2\)S\(_2\) m/z: 1239.0592, found 1239.0624.

Synthesis of complex 6-Ph

A vial was charged with 5-Ph (25.5 mg, 0.02 mmol) dissolved in 1 mL DCM. While stirring the colorless solution, PhICl\(_2\) (11.0 mg, 0.04 mmol) was added as a solid. The resulting yellow mixture was stirred for 45 minutes. Then pentane was added with resulted in the precipitation of a solid. The supernatant was removed and the product was evaporated to dryness, yielding a yellow solid (25 mg, 90%).

\(^1\text{H NMR}\) (400 MHz, CD\(_2\)Cl\(_2\), ppm): \( \delta \) 8.06 (dd, \( J = 15.0, 7.8 \) Hz, 4H), 7.98-7.85 (m, 8H), 7.82-7.75 (m, 4H), 7.73-7.65 (m, 4H), 7.44 (d, \( J = 12.3 \) Hz, 2H), 7.39 (d, \( J = 8.9 \) Hz, 2H), 6.71 (dd, \( J = 8.5, 5.2 \) Hz, 2H), 2.45 (s, 6H); \(^{31}\text{P}\{^1\text{H}\} \text{NMR}\) (162 MHz, CD\(_2\)Cl\(_2\), ppm): \( \delta \) 63.3 (s); \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (101 MHz, CD\(_2\)Cl\(_2\), ppm) calcd for [M-NTf\(_2\)]\(^+\) C\(_38\)H\(_{32}\)Au\(_2\)Cl\(_4\)NP\(_2\) m/z: 1098.0095, found 1098.0113.
Synthesis of complex 8

Complex 1 (36.9 mg, 0.04 mmol) was dissolved in 3 mL acetone. To the purple solution was added phenylacetylene (8.7 µL, 0.08 mmol). Subsequently, AgOTf (20.4 mg, 0.08 mmol) dissolved in 0.7 mL acetone was added. After stirring for 1 hour the mixture turned red and turbid. The solids were filtered off and the volatiles were removed in vacuo to yield 8.

\[ \text{Complex 8} \]

\[^{1}H\text{ NMR}\ (400 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm):} \delta 7.57\ (\text{dt, } J = 8.8, 2.6 \text{ Hz, 2H}), 7.43 - 7.34\ (\text{m, 5H}), 7.22\ (\text{d, } J = 8.7 \text{ Hz, 2H}), 7.09\ (\text{t, } J = 5.1 \text{ Hz, 2H}), 3.14\ (\text{pd, } J = 7.2, 2.6 \text{ Hz, 4H}), 2.34\ (\text{s, 6H}), 1.58 - 1.48\ (\text{m, 12H}), 1.41 - 1.30\ (\text{m, 12H}); \]^{}\[^{31}P\{^{1}H\}\text{ NMR}\ (162 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm):} \delta 77.5\ (\text{s}); \]^{}\[^{13}C\{^{1}H\}\text{ NMR}\ (126 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm):} \delta 159.7\ (\text{t, } J = 6.9 \text{ Hz}), 135.8\ (\text{s}), 133.6\ (\text{t, } J = 2.3 \text{ Hz}), 132.0\ (\text{t, } J = 4.7 \text{ Hz}), 131.6\ (\text{s}), 129.0\ (\text{s}), 128.9\ (\text{s}), 124.4\ (\text{s}), 117.4\ (\text{t, } J = 5.7 \text{ Hz}), 114.3\ (\text{s}), 112.8\ (\text{t, } J = 25.7 \text{ Hz}), 27.2\ (\text{t, } J = 15.2 \text{ Hz}), 20.3\ (\text{s}), 18.2\ (\text{s}), 18.1\ (\text{s}); \]^{}\[^{19}F\text{ NMR}\ (282 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm):} \delta -79.0\ (\text{s}); \]^{}\[^{HR-MS}\ (\text{CSI})\text{ calcd for }[\text{M-OTf}^+]^+\ C_{34}H_{45}AuNP_2 \text{ m/z: 726.2693, found 726.2662.} \]

X-ray Crystal Structure Determination of complexes 4 and 8: X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (\(\lambda = 0.71073\ \text{Å}\)) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.\(^{[31]}\) Absorption correction and scaling was performed with SADABS.\(^{[32]}\) The structures were solved using intrinsic phasing with the program SHELXT.\(^{[31]}\) Least-squares refinement was performed with SHELXL-2013\(^{[33]}\) against \(F^2\) of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times \(U_{eq}\) of the attached C atoms.
The postulated mechanism explains the observed intermediates and the required amount of AgNTf$_2$; for the overall reaction, the driving force behind the oxidative C-C bond formation remains speculative. Possibly, initial two-electron reduction of 6 leads to a transient Au$^0$/Au$^+$ species. One-electron oxidation of the PNP ligand leads to a transient Au$^+$/Au$^{ii}$ species. One-electron oxidation of the PNP ligand by a Au$^{ii}$ center may subsequently occur. Steric preorganization by the severe twisting of the backbone observed in 6 could then facilitate orbital overlap of the ortho C-positions and generation of a C-C bond. A second one-electron oxidation step would ultimately lead to release of two protons and render a neutral ligand. Other pathways can not be ruled out at this point.

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5.7 References

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134–141.


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 N₂-splitting or N-transfer reactions. A new Ni(PNP)N₃ complex is used as the starting point for this study. Azido groups (N₃⁻) are widely recognized as entry to nitrido species, as activation leads to expulsion of N₂. The synthesis of the complex is described and a full spectroscopic characterization is given. We show that the Ni(PNP)N₃ 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 N₂ 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$_2$N$_2$ 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(PNPNC1) species upon reaction of the dimer with HCl.
In **Chapter 4** we use the PNP ligand to prepare a dinuclear (PNP)Au$_2$Cl$_2$ complex. Selective two-electron oxidation leads to a (PNP)Au$^{I}$Au$^{III}$-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$^I$-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.

The mechanism behind the reaction we describe in Chapter 4 involving the Ag$^+$-induced conversion of a mixed-valent (PNP)Au$^{I}$Au$^{III}$ 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 tetrargold complex with the scavenging element sequestered between two Au$_2$ units. A Brønsted acid induced disproportionation reaction results in a Au$^1$Au$^1$ 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](image-url) 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 $\sigma,\pi$-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 $\sigma,\pi$-activation compared to $\pi$-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.
Samenvatting

PNP Pincer Liganden in Late Overgangsmetaal
Nitrido Chemie en Goud Katalyse

Het belang van katalysatoren voor de samenleving van de eenentwintigste eeuw is groot. Zo zijn deze verbindingen essentieel voor de productie van vele waardevolle en onvervangbare materialen en stoffen zoals medicijnen, petrochemicaliën, landbouwchemicaliën en polymeren (plastics). Katalysatoren kunnen de snelheid van een chemische reactie verhogen en de voor deze reactie benodigde energie verlagen. Daarnaast kunnen katalysatoren voor een hogere selectiviteit zorgen, wat betekent dat per massa-eenheid uitgangsmateriaal netto meer product kan worden verkregen, waarmee de productie van onnodig chemisch afval wordt verlaagd. Door deze eigenschappen kunnen katalysatoren bijdragen aan duurzame en milieuvriendelijke chemische processen. Een belangrijk type homogene katalysatoren zijn de coördinatiecomplexen. Deze bestaan uit een (overgangs)metaalcentrum met daaraan coördinerende liganden. Het is daarom interessant om deze complexen te gebruiken voor onderzoek naar fundamentele coördinatiechemie en toepassingen in katalyse.

Pincer (tang) liganden onderscheiden zich door een drietalige coördinatiemodus en een voorkeur voor een meridionale configuratie. Deze coördinatiemodus leidt normaal gesproken tot stabiele metaal-pincer complexen. Dat maakt deze complexen geschikt om toegepast te worden als katalysator voor hoog-endotherme reacties en om gebruikt te worden voor fundamentele reactiviteitstudies. In Hoofdstuk 1 wordt de ontwikkeling van monoanionische diarylamine phosphine (PNP) pincer liganden en hun toepassing in late overgangsmetaalcomplexen beschreven. Voorbeelden van zowel de coördinatiechemie van deze structuren als van toepassingen in katalytische reacties worden behandeld. Daarnaast wordt het doel van dit proefschrift beschreven en wordt een kort overzicht van de inhoud van de overige hoofdstukken gegeven. Het PNP ligand is relevant in alle overige hoofdstukken van dit proefschrift.

In Hoofdstuk 2 beschrijven we een studie naar de mogelijkheid om een nikkel-nitrido complex te vormen. Goed gekarakteriseerde Groep 10 nitrido complexen ontbreken nog in de wetenschappelijke literatuur. Deze structuren kunnen model staan voor intermediairen in belangrijke stikstofsplitsings- en stikstof-atoomoverdrachtsreacties. Een nieuw Ni(PNP)N₃ complex is als startmateriaal gebruikt voor de studie. Azide (N₃⁻) groepen worden veel gebruikt voor de formatie van nitrido-complexen, omdat activatie van zo’n eenheid kan leiden tot de gewenste functionele groep met uitstoot van N₂ als bijproduct. De synthese van het complex wordt beschreven en een volledige spectroscopische karakterisering wordt gegeven. We laten zien dat het Ni(PNP)N₃
complex onder (elektro)chemische oxidatie en bij hoge temperatuur stabiel is. Bestraling van een benzeenoplossing van het complex resulteert echter in een reactie waarin een stikstofatoom zich in een Ni-P binding gevoegd heeft en C-H activatie van benzeen over de resulterende Ni-N binding heeft plaatsgevonden (Figuur 1). We beschrijven een DFT studie die tot een voorstel van een reactiemechanisme leidt. Dit voorstel behelst de uitstoot van N₂ als gevolg van fotochemische activering van de azide-groep, resulterend in de vorming van een kortlevend nikkel-nitrido complex. Vervolgens migreert het stikstofatoom naar de Ni-P binding, wat resulteert in een onverzadigd Ni²⁺-complex dat in staat is om een C-H binding van benzeen te activeren. Deze laatste stap kan zowel thermisch als fotochemisch geïnitieerd zijn. Deze resultaten laten zien dat het maken van een nikkel-nitrido complex mogelijk is, hoewel pogingen om een intact Ni-N fragment te vangen niet gelukt zijn.

![Figuur 1](image-url) *Figuur 1*. Beschrijving van een Ni(PNP)N₃ complex leidt uiteindelijk tot N-insertie en C-H activering van benzeen.

In Hoofdstuk 3 is de activering van een Co(PNP)N₃ complex onderzocht. We vergelijken de resultaten van onze studie met eerdere publicaties over de activering van Groep 9 metaal-azide complexen. Daarin staat beschreven dat activering van deze azide complexen kan leiden tot intra- of intermoleculaire reactiviteit van resulterende (vergankelijke) kobalt-nitrido fragmenten. We onderzoeken ook of het mogelijk is om een kobalt-nitrido complex met EPR spectroscopie te detecteren door bestralingsexperimenten bij lage temperatuur uit te voeren. Thermische en fotochemische decompositie van de azidegroep leiden tot hetzelfde nieuwe product. De structuur van dit product kon worden bepaald door middel van kristalstructuuranalyse met behulp van Röntgenstralen. Daarmee is vastgesteld dat azide-N insertie in een Co-P binding heeft plaatsgevonden, wat duidt op intramoleculaire reactiviteit. Anders dan bij het corresponderende nikkel complex zijn twee Co-fragmenten samengekomen waarbij een Co₂N₂ kern is ontstaan (Figuur 2). Een ander verschil is het ontbreken van reactie met het oplosmiddel onder fotolytische condities. Het bestuderen van de fotolyse bij lage temperatuur met EPR spectroscopie heeft niet geleid tot definitief bewijs voor het bestaan van een vergankelijk kobalt-nitrido deeltje. DFT berekeningen laten echter zien dat dit

Figuur 2. Azide-activering door middel van thermolyse of fotolyse, resulterend in een dimerisatieproduct.

In Hoofdstuk 4 wordt het PNP ligand gebruikt voor de synthese van een dinucleair (PNP)Au₂Cl₂ complex. Selectieve twee-elektron oxidatie leidt tot een (PNP)Au¹ Au³-verbinding (Figuur 3). We beschrijven in dit Hoofdstuk dat dit gemengde-valentie deeltje een opmerkelijke reactie ondergaat bij blootstelling aan zilverzouten of GaCl₃. Het product van deze reactie is een nieuw bisgoud(I) carbazool complex. We gebruiken de nieuwe (PNP)Au¹₂-verbindingen om een concept te onderzoeken waarbij het PNP ligand wordt gebruikt om twee goud-centra zo te organiseren dat σ,π-activatie van alkyn-verbindingen wordt geforceerd. Eerdere studies door andere onderzoeksgroepen hebben laten zien dat deze vorm van duale activering tot een andere selectiviteit in goud katalyse kan leiden dan traditionele π-activering door mononucleaire [Au]⁺-katalysatoren. We gebruiken een heterocyclisatie reactie van een urea-alkyn om het concept te evalueren. We laten in dit Hoofdstuk zien dat een door het ligand geforceerde nabijheid van twee goud centra tot hoge selectiviteit leidt naar het product van σ,π- activering, zelfs bij lage katalysatorhoeveelheden. Verder laten we zien deze aanpak niet geschikt is voor andere vormen van duale activering.

Het mechanisme achter de in Hoofdstuk 4 beschreven reactie waarbij Ag\(^+\) de omzetting van een gemengd-valente (PNP)Au\(^{\text{I}}\)Au\(^{\text{III}}\) verbinding naar een carbazool (PNP)Au\(^{\text{I}}\)\(_2\) complex induceren (zie Figuur 3) is het onderwerp van nader onderzoek in Hoofdstuk 5. Deze reactie is interessant vanwege de nieuwe type ortho-redox reactiviteit die aan het PNP ligand plaatsvindt. We laten zien dat het mogelijk is om deze transformatie in een set stoichiometrische reacties op te delen. Toevoeging van een zilver(I) bron leidt in eerste instantie tot de formatie van een tetranuclear goud complex met het zilver-ion tussen de twee Au\(_2\) elementen. Een door een Brønsted-zuur geïnduceerde disproportioneeringsreactie resulteert vervolgens in een Au\(^{\text{I}}\)Au\(^{\text{I}}\)\(_2\) en een Au\(^{\text{III}}\)Au\(^{\text{III}}\) verbinding (Figuur 4). De laatstgenoemde vormt, als een geschikte twee-elektron reductor wordt toegevoegd, het eindproduct, terwijl de eerstgenoemde naar het Au\(^{\text{III}}\)Au\(^{\text{III}}\)\(_2\) complex wordt omgezet in een vier-elektron oxidatiereactie. De verzamelde resultaten van de stoichiometrische reacties leiden tot een voorstel voor een mechanisme van de onderzochte reactie.

Figuur 4. Deel van het reactiemechanisme dat omgeschreven wordt in Hoofdstuk 5.

Au(I)-katalyse door σ,π-activering kan worden gebruikt om een andere productselectiviteit te verkrijgen in vergelijking met π-activering door goud(I)-katalysatoren. In dit proefschrift hebben we een nieuw concept geïntroduceerd om de duale-activeringsmodus te forceren door gebruik te maken van ligand-preorganisatie van twee Au(I) centra. Het vinden van de exacte reden van de verschillende selectiviteit van σ,π-activatie vergeleken met π-activatie zou een goede basis voor vervolgstudies kunnen zijn. Die studies zouden dan geconcentreerd moeten worden op het uitbreiden van de bruikbare substraten en op het ontwikkelen van actievere katalysatoren.
List of Publications

Related to PhD studies:


1 Conceptual ideas
2 Experimental work
3 Data interpretation
4 Preparation of the manuscript
5 Computational studies
6 X-ray structure determination
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