PNP pincer ligands in late transition metal nitrido chemistry and gold catalysis

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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).\textsuperscript{[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).\textsuperscript{[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.\textsuperscript{[4]} For example, tridentate diarylamino phosphino (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.\textsuperscript{[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](image)

**Figure 1.** Oxidation of the PNP scaffold and resulting positions of reactivity

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 \textit{et al.} showed that the spin density in the oxidized species predominantly resides at the ligand (31\% at N, 38\% at C residues).\textsuperscript{[5]} We have shown by DFT calculations that the PNP ligand behaves similarly in the oxidation of a (PNP)NiN\textsubscript{3} complex (see Chapter 2).\textsuperscript{[6]} The PNP ligand further contributes strongly in the redox-chemistry of \{(PNP)Cu\}\textsubscript{2} complexes. Two-electron oxidation of these dinuclear complexes (one electron per monomer) with “naked” aryl groups led to
reactivity \textit{para} relative to the amido functionality (Figure 2). This could be prevented by introduction of steric bulk at this position.\textsuperscript{[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 \textit{para} to the amido substituent (Figure 2).\textsuperscript{[8]}

\textbf{Figure 2.} Ligand reactivity upon oxidation occurring \textit{para} to the amido donor

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

\textbf{Figure 3.} \textit{Ortho} reactivity in the PNP ligand backbone by means of oxidative C-C coupling; \textbf{Au} = \text{Au(I)}; \textbf{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\textsuperscript{I}Au\textsuperscript{III} complex 1 into Au\textsuperscript{I}Au\textsuperscript{I} complex 2. Au = Au(I); Au = Au(III).
5.2.2 Formation of tetragold assemblies

![Chemical structure diagram]

**Figure 5.** Reaction of starting compound 1 with 0.5 molar equivalent of AgNTf₂ leads to formation of tetragold assembly 3. \( \text{Au} = \text{Au(I); Au} = \text{Au(III)} \).

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 \( ^{31} \text{P} \) NMR spectrum (Figure 6). The P(Au⁺) 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 \( ^1 \text{H} \) 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.\[^11\]

[^9]: Reference citation
[^10]: Reference citation
[^11]: Reference citation
Figure 6. Top: reaction of 1 with AgNTf$_2$ in a 2:1 ratio, proposed formation of dimeric species 4; Au = Au(I); Au = Au(III). Bottom: $^{31}$P 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 TIPF$_6$ to a solution of 1 resulted in clean conversion to complex 4 (Figure 7). The $^{31}$P NMR spectrum of 4 shows a signal at 110.1 ppm, indicating that the P atom coordinated to a Au$^{III}$ 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 $^1$H 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 (TIPF$_6$ : 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.

![Diagram](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-Cl1 2.313(4); P2-Au2 2.265(4); N1-Au2 2.02(1); Au2-Cl2 2.313(4); Au2-Cl3 2.376(4); P1-Au1-Cl1 178.2(1); N1-Au2-Cl2 172.2(4); P2-Au2-Cl3 173.0(1); Cl1-Tl1 3.267; Cl2-Tl1 3.100; Cl3-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 $^{31}$P 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 $d^8$-$d^{10}$ interaction to occur, a feature that was not found for 1.

5.2.3 Acid-induced disproportionation of 3

Figure 8. Reaction of assembly 3 with HBF$_4$, assignment of counterions BF$_4$ and NTf$_2$ is arbitrary (left). Reaction of complex 1 with one equivalent AgNTf$_2$ (half of required amount for full conversion) leading to compound 2, 5 and 6 (right). Au = Au(I); Au = Au(III).

Exposing *in situ* generated complex 3 to an equimolar amount of HBF$_4$ resulted in the formation of a mixture of equal amounts of complexes 5 and 6 (Figure 8). Treatment of the thallium congener, 4, with HBF$_4$ resulted in a comparable mixture, albeit less cleanly. These results indicate that these tetragold assemblies are sensitive toward disproportionation by Brønsted acids.

Addition of an equimolar amount of AgNTf$_2$ 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 $^1$H NMR (Figure 9). Analysis of the $^{31}$P 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.

Figure 9. ¹H NMR spectrum of product mixture of the reaction between AgNTf₂ and 1 (1:1 ratio in DCM-²). Assignment of peaks for 2 (◊), 5 (◊) and 6 (¤); red color for N-H.

The independent synthesis and full characterization of complex 5 has been described in Chapter 4. Its formation from 1 implies two-electron reduction of the Au³⁺ center as well as reprotonation of the central amide, whilst leaving the ligand backbone unaffected. The structure of 5 differs from final product 2 only by the absence of the C-C bond between the phenyl groups in the ligand. The identity of compound 6 was established by a combination of spectroscopic techniques. The ³¹P NMR spectrum consists of one singlet at 102.1 ppm, suggesting C₂ symmetry. The ¹H NMR spectrum confirmed this, displaying an unaffected ligand backbone with three signals for the six tolyl hydrogen atoms. UV-vis spectroscopy of the compound shows absorption peaks at 305 and 334 nm (ε = 9.7 × 10³ and 9.1 × 10³ mol L⁻¹ cm⁻¹) and a shoulder at 385 nm (ε = 5.2 × 10³ mol L⁻¹ cm⁻¹) accounting for the yellow-orange color of 6.

Single crystals of 6 suitable for X-ray diffraction were grown from a CH₂Cl₂/toluene mixture. Consistent with the NMR data, the obtained structure shows a symmetrical complex with two Au³⁺ centers in a square planar configuration (Figure 10). The crystals consist of a racemic mixture of (R)- and (S)-enantiomers of 6. The central amide functionality is ligated to both Au centers. A similar configuration of the nitrogen is seen in a dinuclear copper complex {([₄BuPNP]Cu)₂ reported by Peters et al.[7] Both gold centers are further coordinated by a P atom and two chloride ligands. The backbone of the ligand is severely twisted (dihedral angle C5-C6-C7-C8 = 93(1)°), leading to an almost orthogonal placement of the two phenyl rings. The nature of compound 6 was further confirmed by HR-MS and the downfield signal found in the ³¹P NMR spectrum is in line with the presence of two Au³⁺ centers. The structure of 6 implies a two-electron oxidation
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-$\lambda^3$-(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).
5.2.4 Halide abstraction from 5 and further reactivity

Full conversion to complex 2 was observed upon addition of three equivalents AgNTf₂ 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 AgNTf₂, these two compounds are stable and do not react together. Treating complex 6 separately with AgNTf₂ 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 AgNTf₂ resulted in the formation of ‘dicationic’ complex 7 (Figure 13). Weak coordination of the NTf₂ anions to the gold centers is manifested by a small shift in the ¹⁹F 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)Au₂Cl₂ complex with two equivalents of AgNTf₂. 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 PhICl₂ led to quantitative formation of 6.

![Figure 13](image)

**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. Au = Au(I); Au = 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 Pd⁰dba 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 AgNTf₂. 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](image)

**Figure 14.** Reaction of complex 6 with Pd⁰dba as sacrificial two-electron reducing agent forming 2, in the presence of AgNTf₂. Products in frame were not detected. Au = Au(I); Au = 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. Au = Au(I); Au = 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 Au¹Au³ complexes 1 leads to the formation of complex 3. This intermediate undergoes an acid-induced disproportionation reaction, as supported by stoichiometric reaction with HBF₄. 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 Au¹Au¹ complex 5 and Au³Au³ complex 6. The former reacts with AgNTf₂ 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. The HCl and two-electron oxidation equivalents (Cl₂) released in this process react with 7 to regenerate complexes 5 and 6 in a 2:1 ratio with concomitant generation of HNTf₂. This acid can drive the disproportionation reaction to completion. A total of two equivalents of AgNTf₂ is required to drive the overall reaction to full conversion.

Figure 16. Postulated mechanism for the formation of 2 from reaction of 1 with AgNTf₂. Au = Au(I); Au = Au(III).

Cross-over experiments were conducted to further prove the proposed pathway. For this purpose (PhPnPPh)Au₂(NTf₂)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 AgNTf₂ to act as an oxidant for 1.
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 \(\pi\)-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 AgNTf\(_2\) 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 \(^{31}\)P NMR spectrum suggest that the main products contain solely Au\(^{I}\) centers. Mass spectrometry of the product mixture shows the presence of a Au\(_2\)Cl(PN\(^{III}\)P) 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 \(^{31}\)P 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.
Figure 18. ORTEP plots (50% probability level) for 8. Hydrogen atoms are omitted for clarity, selected bond lengths (Å) and angles (°): N1-Au1-C1 175.8(3); P1-Au1-P2 166.77(8); Au1-C1-C2 172.1(8); C1-C2-C4 177(1); Au1-N1 2.024(9); P1-Au1 2.321(2); P2-Au1 2.329(2); Au1-C1 1.99(1); C1-C2 1.17(2); N1-Au2 2.10(1).

Square planar AuIII complexes have emerged as a curious class of compounds over the last few years. Generation of these structures from AuI 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. PhIX2 compounds) are in general necessary for this elementary reaction.13 AuIII complexes bearing tridentate ligands have been used in coordination chemistry,14–17 photoluminescence,18–20 medicinal studies21,22 and in few examples of catalysis.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 AuIIIAuIII complex 6 plays a role in the process, a reaction of 6 with AgNTf2 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 AgNTf$_2$ as an oxidant in the studied reaction (see introduction 5.1, Figure 3), given the relatively strong oxidation potential of Ag$^+$ in CH$_2$Cl$_2$ 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. Fc$^{0+/+}$ (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 Au$^{III}$ 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 AgNTf$_2$ does not act as an oxidant.

![Cyclic voltammogram of 1 in CH$_2$Cl$_2$ (scan speed 0.1 V/s)](image)

**Figure 19.** Cyclic voltammogram of 1 in CH$_2$Cl$_2$ (scan speed 0.1 V/s)

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 Au$^{III}$ 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](image)

**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

![Figure 21](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. \( \text{PN}^{\text{HPr}} \text{P} \text{PiPr} \) (bis(2-diisopropylphosphino-4-methylphenyl)amine)[26], \( \text{PN}^{\text{HPh}} \text{P} \text{Ph} \) (bis(2-diphenylphosphine-4-methylphenyl)amine)[27] and \( \text{PhICl}_2 \) were synthesized according to literature procedures. Compounds 1, 5 and \( (\text{PN}^{\text{HPr}})\text{Au}_2\text{Cl}_2 \) were prepared as described in Chapter 4. Toluene, tetrahydrofuran, diethylether and pentane were distilled from sodium benzophenone ketyl. CH\(_2\)Cl\(_2\) was distilled from CaH\(_2\). NMR spectra (\( ^1\text{H}, \ ^1\text{H}\{\ ^{31}\text{P}\}, \ ^{13}\text{C}\{\ ^1\text{H}\}, \ ^{31}\text{P}\{\ ^1\text{H}\}) \) 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) 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)\(_4\)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\(^+\).

Computational details

Geometry optimizations were carried out with the Turbomole program package[29] coupled to the PQS Baker optimizer[29] via the BOpt package[29] at the DFT/b3-lyp[29] level. We used the def2-TZVP basis set.[29] Dispersion corrections were applied.[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 TlPF$_6$ (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.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 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); $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 110.1 (s), 44.3 (s), -144.5 (hept, $J = 711.1$ Hz); $^{13}$C($^1$H) NMR (126 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 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 - PF$_6$]$^+$ C$_{52}$H$_{80}$Au$_4$Cl$_6$N$_2$P$_4$Tl $m/z$: 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.

\textbf{1}H NMR (400 MHz, CD₂Cl₂, 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);

\textbf{3}\textsuperscript{1}P\{\textsuperscript{1}H\} NMR (162 MHz, CD₂Cl₂, ppm): δ 102.1 (s);

\textbf{1}3\textsuperscript{1}C\{\textsuperscript{1}H\} NMR (101 MHz, CD₂Cl₂, 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);

\textbf{HR-MS} (ESI) calcd for [M – NTf₂]⁺ C₂₆H₄₀Au₂Cl₄NP₂ m/z: 964.0695, found 964.0676.
UV-vis spectrum of 6 in DCM:

![UV-vis spectrum of 6 in DCM](image)

**Synthesis of complex 7**

A vial was loaded with \((\text{PN}^{\text{H}}\text{P}^{\text{iPr}})\text{Au}_2\text{Cl}_2\) (89 mg, 0.1 mmol) and AgNTf₂ (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%).

**\(^1\text{H NMR}\)** (400 MHz, CD₂Cl₂, 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); **\(^{31}\text{P}\{^1\text{H}\}\text{NMR}\)** (162 MHz, CD₂Cl₂, ppm): \(\delta\) 42.9 (s); **\(^{13}\text{C}\{^1\text{H}\}\text{NMR}\)** (101 MHz, CD₂Cl₂, 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); **\(^{19}\text{F NMR}\)** (282 MHz, CD₂Cl₂, ppm): \(\delta\) -75.9 (s); **HR-MS** (ESI) calcd for [M-NTf₂]+ \(\text{C}_{28}\text{H}_{41}\text{Au}_2\text{F}_6\text{N}_2\text{O}_4\text{P}_2\text{S}_2\) \(m/z\): 1103.1218, found 1103.1210.
Synthesis of complex $\text{PN}^{\text{H}}\text{P}^{\text{Ph}}\text{Au}_2\text{Cl}_2$

A flame-dried Schlenk under N$_2$-atmosphere was charged with a DCM solution (5 mL) of $\text{PN}^{\text{H}}\text{P}^{\text{Ph}}\text{Au}_2\text{Cl}_2$ (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 ($\text{PN}^{\text{H}}\text{P}^{\text{Ph}}\text{Au}_2\text{Cl}_2$) 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.

$^1\text{H NMR}$ (400 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 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); $^{31}\text{P}^{(1}\text{H})$ NMR (162 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 19.6 (s); HR-MS (ESI) calcd for $[\text{M-Cl}]^+$ 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 $\text{PN}^{\text{H}}\text{P}^{\text{Ph}}\text{Au}_2\text{Cl}_2$ (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%).

$^1\text{H NMR}$ (300 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 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); $^{13}\text{C}^{(1}\text{H})$ NMR (126 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 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); $^{19}\text{F NMR}$ (282 MHz, CD$_2$Cl$_2$, ppm): $\delta$ -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 **PN**\(^{2+}\)\(\text{Ph}^+\)\(\text{AuCl}_2\) (50.2 mg, 0.05 mmol) and 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.

\(^{1}H\) NMR (400 MHz, CD\(_2\)Cl\(_2\), ppm): δ 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);

\(^{31}P\)\(^{1}H\) NMR (162 MHz, CD\(_2\)Cl\(_2\), ppm): δ 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);

\(^{19}F\) NMR (282 MHz, CD\(_2\)Cl\(_2\), ppm): δ -75.4 (s);

HR-MS (ESI) calcd for \([\text{M-NTf}_2]^+\) 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%).

\(^{1}H\) NMR (400 MHz, CD\(_2\)Cl\(_2\), ppm): δ 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);

\(^{31}P\)\(^{1}H\) NMR (162 MHz, CD\(_2\)Cl\(_2\), ppm): δ 63.3 (s);

\(^{13}C\)\(^{1}H\) NMR (101 MHz, CD\(_2\)Cl\(_2\), ppm): δ 156.1 (d, \(J = 12.2\) Hz), 143.8 (d, \(J = 9.2\) Hz), 139.6 (s), 136.6 (d, \(J = 3.3\) Hz), 136.4 (s), 136.3 (s), 134.7 (d, \(J = 11.1\) Hz), 134.1 (s), 131.3 (d, \(J = 13.2\) Hz), 130.3 (d, \(J = 14.4\) Hz), 128.3 (d, \(J = 12.1\) Hz), 123.1 (d, \(J = 5.2\) Hz), 122.4 (d, \(J = 2.0\) Hz), 121.3 (s), 120.5 (s), 120.3 (q, \(J = 323.2\) Hz), 20.81 (s); HR-MS (ESI) 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.

\[ ^1H \text{NMR} \ (400 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm}): \delta \ 7.57 \ (dt, J = 8.8, 2.6 \text{ Hz}, 2H), \ 7.43 - 7.34 \ (m, 5H), \ 7.22 \ (d, J = 8.7 \text{ Hz}, 2H), \ 7.09 \ (t, J = 5.1 \text{ Hz}, 2H), \ 3.14 \ (pd, J = 7.2, 2.6 \text{ Hz}, 4H), \ 2.34 \ (s, 6H), \ 1.58 - 1.48 \ (m, 12H), \ 1.41 - 1.30 \ (m, 12H); \ ^{31}P\{^1H\} \text{NMR} \ (162 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm}): \delta \ 77.5 \ (s); \ ^{13}C\{^1H\} \text{NMR} \ (126 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm}): \delta \ 159.7 \ (t, J = 6.9 \text{ Hz}), \ 135.8 \ (s), \ 133.6 \ (t, J = 2.3 \text{ Hz}), \ 132.0 \ (t, J = 4.7 \text{ Hz}), \ 131.6 \ (s), \ 129.0 \ (s), \ 128.9 \ (s), \ 124.4 \ (s), \ 117.4 \ (t, J = 5.7 \text{ Hz}), \ 114.3 \ (s), \ 112.8 \ (t, J = 25.7 \text{ Hz}), \ 27.2 \ (t, J = 15.2 \text{ Hz}), \ 20.3 \ (s), \ 18.2 \ (s), \ 18.1 \ (s); \ ^{19}F \text{NMR} \ (282 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm}): \delta \ -79.0 \ (s); \ ^{19}F \text{MS} \ (\text{CSI}) \text{ ccalcd for [M-OTf]}^+ \text{C}_{34}\text{H}_{45}\text{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. Absorption correction and scaling was performed with SADABS. The structures were solved using intrinsic phasing with the program SHELXT. Least-squares refinement was performed with SHELXL-2013 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 Ueq of the attached C atoms.
5.7 References


[12] Although the postulated mechanism explains the observed intermediates and the required amount of AgN(Tf), 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 AuIII-AuII species. One-electron oxidation of the PNP ligand by a AuII 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.


134–141.


