PNP pincer ligands in late transition metal nitrido chemistry and gold catalysis
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Citation for published version (APA):
Vreeken, V. (2016). PNP pincer ligands in late transition metal nitrido chemistry and gold catalysis
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.\textsuperscript{[1]} More recently, the discovery of catalysis involving novel dual-activation mechanisms has led to a new range of possible transformations.\textsuperscript{[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 Au\textsuperscript{I}/Au\textsuperscript{III} of ± 1.4 V.\textsuperscript{[3]} Nevertheless, recent advances show the feasibility of performing elementary reactions on gold complexes provided well-designed strategies are employed.\textsuperscript{[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.\textsuperscript{[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).\textsuperscript{[5]} The prevailing strategy utilizes mononuclear Au(I) complexes to induce dual-activation, which sometimes have been developed specifically for this purpose.\textsuperscript{[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).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{activation_modes.png}
\caption{Reported activation modes in gold(I)-catalysis. \textcolor{red}{Red} = nucleophilic site, \textcolor{blue}{Blue} = electrophilic site}
\end{figure}
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 σ,π-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 PN\(^{H}P^{\text{Pr}}\) (L\(^H\)) and its congeners display versatile coordination chemistry to a wide range of transition metals,\(^{10}\) including Cu\(^{11}\) and Ag\(^{12}\) (Figure 2). Furthermore, chemistry related to the redox-active nature\(^{13}\) of 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 PN\(^{H}P^{\text{Pr}}\) ligand. The ligand enforced proximity of Au-nuclei may result in selective binding and activation of bifunctional substrates in a σ,π-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 (σ+π-activation).

![Figure 2](image-url)  
**Figure 2.** Reported Group 11 TM-complexes containing a monoanionic PNP ligand (left). Concept of enforced σ,π-activation (right).

In this Chapter we aim to investigate the potential of the PN\(^{H}P^{\text{Pr}}\) ligand in dinuclear Au\(^I\) 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 σ,π-activation. We will therefore first describe exploratory studies on the versatile coordination chemistry of
gold with the redox-active ditopic PN\textsubscript{H}PiPr ligand. This will be complemented by studies demonstrating the catalytic abilities of the described dinuclear Au\textsuperscript{I} complexes.

4.2 Results and discussion

4.2.1 Synthesis and characterization

The straightforward reaction of PN\textsuperscript{H}PiPr with AuCl(SMe\textsubscript{2}) in a 1:2 ratio provided complex 1 as a white solid (Figure 3). The \textsuperscript{31}P NMR spectrum shows a slightly broadened singlet at δ 40.9 and the \textsuperscript{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\textsuperscript{[15]} of 1 (Figure 4, left), which displays Au-P and Au-Cl distances that are within the range for typical Au\textsuperscript{I}-phosphine complexes. The orientation of the PNP backbone results in a dihedral angle between the two phenyl rings of 99.7(5)°, with both phosphine donors on the same side of the ligand backbone. This allows for an intramolecular Au\textsuperscript{I}---Au\textsuperscript{II} distance of 3.23791(17) Å, which indicates an aurophilic $d^{10}$-$d^{10}$ interaction exists in the solid state.\textsuperscript{[16]}

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

Crystals of 1 were also obtained by slow diffusion of pentane into a CDCl\textsubscript{3} solution of the complex. Surprisingly, these crystals were colored purple. X-ray diffraction studies gave polymorph structure B\textsuperscript{[15]} of 1 (Figure 4, right). Interestingly, the Au\textsuperscript{I}--Au\textsuperscript{II} 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)°). 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\textsuperscript{I}Au\textsuperscript{III} complex, vide infra.
To assess the possibility of selectively abstracting a single chloride from the complex, 1 was reacted with one equivalent of AgNTf₂. Selective formation of compound 2 was indeed observed (Figure 3), as indicated by a singlet at δ 40.6 ppm in the ³¹P NMR spectrum and slightly shifted signals in the ¹H 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 AuI structure featuring two μ-Cl bridges (Figure 5). The angle ∠Au-Cl-Au in 2 is around 97°, while the general orientation of the PN²Pr 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.
The residual Au$^1$Au$^{III}$ structure found in the crystal lattice of polymorph B of 1 is intriguing, as it signifies an entry into mixed-valent Au$^1$Au$^{III}$ species. In an attempt to selectively generate such a species, colorless 1 was reacted with one molar equivalent of dichloro-$\lambda^3$-(iodanyl)benzene (PhICl$_2$) in dichloromethane. Addition of this oxidant led to instantaneous formation of an intensely purple colored solution with a strong UV-vis absorption at $\lambda$ 573 nm ($\varepsilon = 1.1 \times 10^3$ L mol$^{-1}$ cm$^{-1}$). Furthermore, two signals were present in the $^{31}$P NMR spectrum at $\delta$ 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 Au$^{III}$ center via site-selective two-electron oxidation of one of the Au(I) centers. The $^1$H NMR spectrum, which is also indicative of an asymmetric compound, contains one remarkably upfield shifted aromatic signal at $\delta$ 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 Au$^1$-Au$^{III}$ species 3, with the deprotonated central secondary amine of PNP coordinating to the square
planar Au\textsuperscript{III} 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 \textsuperscript{1}H 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 $d^8$-$d^{10}$ interaction.

![Figure 6. Left: Displacement ellipsoid plots (50% probability level) of complex 3\textsuperscript{[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-C1 2.354(2); Au1-C12 2.3039(22); Au2-P2 2.2401(23); Au2-C13 2.2948(24); Au1---Au2 4.641; P1-Au1-C11 178.39(8); P1-Au1-N1 84.51(19); N1-Au1-C12 172.66(20); P1-Au1-C11 176.30(11); C1-N1-C7-C12 75(1). Right: \textsuperscript{1}H NMR spectrum (top) and \textsuperscript{31}P NMR spectrum (bottom) of 3.]

Generation of a vacant coordination site on a gold-halide precursor is generally, but not always,\textsuperscript{[9d]} a prerequisite for Au-catalysis. This can be achieved by halide abstraction with e.g. Ag\textsuperscript{+}-salts or a suitable Lewis acid. With the mixed-valent Au\textsuperscript{I}-Au\textsuperscript{III} 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 AgNTf\textsubscript{2} as halide abstracting agent to 3 led to a mixture of species, according to \textsuperscript{31}P NMR spectroscopy. However, addition of two equivalents of this reagent (or other Ag\textsuperscript{+}-salts or Lewis acid GaCl\textsubscript{3}) led to rapid decoloration of the reaction solution and generation of a single product with a signal at δ 40.4 in the \textsuperscript{31}P NMR spectrum, suggesting the formation of Au\textsuperscript{I}-phosphine fragment(s). Furthermore, the \textsuperscript{1}H 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 Au¹-Au³ mixed-valent species to a Au¹-Au¹ 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 ∠Au1-Cl1-Au2 of 81.74(4)°. 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. 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 (°) 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 Au¹ 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\(\text{I}\) complexes, we selected three known and one new substrate that give rise to different products depending on the mode of activation - π, σ+π or σ,π - of the C≡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.

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

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 10.** Au$^+$-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 $\sigma,\pi$-acetylide mechanism (Table 1). Use of external base (K$_2$CO$_3$) resulted in catalyst deactivation. On the other hand, addition of one equivalent AgNTf$_2$ with respect to the catalyst provided slightly higher regioselectivity to 7 (90%). Presumably this is due to faster generation of the $\sigma,\pi$-acetylide species. The bis(chlorido)-bridged tetranuclear complex 2 displayed similar preference to form 7 without additives (Ag$^+$ or base). The addition of K$_2$CO$_3$ 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 AgNTf$_2$.

Table 1. Au$^+$-catalyzed heterocyclization of 6$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Au-catalyst</th>
<th>Additive</th>
<th>7 (%)</th>
<th>8 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>2.5 mol% K$_2$CO$_3$</td>
<td>$_[^{[c]}]$</td>
<td>$_[^{[c]}]$</td>
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<tr>
<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% AgNTf$_2$</td>
<td>90</td>
<td>10</td>
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<tr>
<td>4</td>
<td>1</td>
<td>-</td>
<td>$_[^{[c]}]$</td>
<td>$_[^{[c]}]$</td>
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<tr>
<td>5</td>
<td>2$^{[d]}$</td>
<td>2.5 mol% AgNTf$_2$</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>2$^{[d]}$</td>
<td>2.5 mol% K$_2$CO$_3$</td>
<td>$_[^{[c]}]$</td>
<td>$_[^{[c]}]$</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>5 mol% AgNTf$_2$</td>
<td>94</td>
<td>6</td>
</tr>
</tbody>
</table>

[a] conditions: [6] = 1.0 $\times$ 10$^2$ 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 $^1$H NMR spectroscopy. [c] conversion below detection limit. [d] [cat] = 1.25 mM (2 is considered as a tetragold complex).

To attain the $\sigma,\pi$-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 $\sigma,\pi$-mode, similarly to the phenylacetylide moiety found in complex 5. A minor signal at $m/z = 1911$ is observed that could indicate $\pi$-activation involving a tetranuclear complex.
Figure 11. Mass spectrum 5 minutes after mixing 4 and 6 in a 1:1 ratio in DMF.

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(P^tBu_3) – reported as the best catalyst to form product 7 via $\sigma,\pi$-activation$^{[5a]}$ – resulted in a drop in selectivity. These results demonstrate the benefits of well-defined preorganization of two gold centers to enforce selective $\sigma,\pi$-activation and to mediate highly regioselective dual-gold catalysis with functionalized alkynes, even at low catalyst loadings.

Figure 12. Comparison of regioselectivity to indole 7 obtained with dinuclear catalyst 4 vs. mononuclear benchmark AuCl(P^tBu_3) 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 \textit{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.\(^{[5a]}\)

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 α-15 and β-14 (in a 2:1 ratio). The formation of α-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 β-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 β-8 (ratio α-7:β-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 an 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 \( \beta-14 \).\[^{24}\] The reaction was therefore repeated with 7.5 mol\% \( \text{NEt}_3 \) 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.\[^{20}\] 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\(^{1+}\)-phenoxide and a \( \pi \)-activated diphenylacetylene. Nucleophilic attack by the \( \sigma \)-activated phenoxide ultimately leads to the hydrophenoxylated 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 hydrophenoxylated 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 PNHPipPr 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$^1$ 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 the exception of the compounds shown below, all reagents were purchased from commercial suppliers and used without further purification. Ligand $L^H (PN^H PiPr)$, bis(2-diisopropylphosphine-4-methylphenyl)amine) was 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

Synthesis of complex 1

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

$^1$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 m/z: 858.1734, found 858.1720.
Synthesis of complex 2

A vial was loaded with 1 (46.1 mg, 0.05 mmol) and AgNTf$_2$ (20 mg, 0.05 mmol). To the vial was added 2 mL CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$-pentane mixture.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ 7.54 (s, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 6.9 Hz, 2H), 2.91 – 2.79 (m, 2H), 2.48 (h, J = 6.9 Hz, 2H), 2.36 (s, 6H), 1.45 (dd, J = 19.8, 6.7 Hz, 6H), 1.37 – 1.12 (m, 18H); $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 40.6 (br. s); $^{13}$C{$^1$H} NMR (126 MHz, CD$_2$Cl$_2$, ppm): δ 146.0 (d, J = 5.5 Hz), 134.9 (d, J = 2.3 Hz), 133.5 (d, J = 8.6 Hz), 133.3 (d, J = 3.4 Hz), 123.4 (d, J = 6.8 Hz), 120.4 (q, J = 321.7 Hz), 113.6 (d, J = 54.3 Hz), 28.0 (d, J = 34.4 Hz), 23.6 (d, J = 37.1 Hz), 20.9 (s), 20.9 (d, J = 2.2 Hz), 20.4 (d, J = 5.5 Hz), 19.7 (s), 18.1 (d, J = 1.8 Hz); HR-MS (CSI) calcd for [0.5 M-NTf$_2$]$^+$ C$_{26}$H$_{41}$Au$_2$ClNP$_2$ m/z: 858.1734, found 858.1763.

Synthesis of complex 3

Under an argon atmosphere, 1 (641 mg, 0.717 mmol) was dissolved in 30 mL dichloromethane. To this colorless solution, PhICl$_2$ (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.

$^1$H NMR (300 MHz, CD$_2$Cl$_2$, ppm): δ 7.43 (d, J = 8.1 Hz, 1H), 7.24 (dd, J = 8.7, 0.9 Hz, 1H), 7.08 (dd, J = 8.1, 4.8 Hz, 1H), 7.01-6.92 (m, 2H), 5.90 (dd, J = 8.6, 4.8 Hz, 1H), 3.26 (dp, J = 10.0, 7.0 Hz, 1H), 3.10 (dp, J = 9.5, 7.0 Hz, 1H), 2.84 (dp, J = 11.0, 7.1 Hz, 1H), 2.46 (s, 3H), 2.35 (dp, J = 10.2, 7.1 Hz, 1H), 2.24 (s, 3H), 1.80-1.58 (m, 6H), 1.51-1.24 (m, 12H), 1.21-1.08 (m, 6H); $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, ppm): δ 105.3 (s), 44.3 (s); $^{13}$C{$^1$H} NMR (126 MHz, CD$_2$Cl$_2$, ppm): δ 165.5 (d, J = 11.6 Hz), 153.1 (d, J = 6.3 Hz), 137.7 (d, J = 7.6 Hz), 136.7 (d, J = 3.0 Hz), 134.3 (d, J = 2.2 Hz), 133.7 (d, J = 6.1 Hz), 132.5 (d, J = 2.8 Hz), 131.9 (d, J = 2.3 Hz), 131.2 (d, J = 9.6 Hz), 126.6 (d, J =
(54.5 Hz), 116.9 (d, J = 13.1 Hz), 104.0 (d, J = 58.2 Hz), 29.4 (d, J = 30.2 Hz), 29.1 (d, J = 34.0), 25.4 (d, J = 19.8 Hz), 25.1 (d, J = 20.1 Hz), 21.6 (s), 21.4 (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_2Cl_3NP_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_2Cl_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_2Cl_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.

^1H NMR (500 MHz, CD_2Cl_2, ppm): δ 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); ^31P{^1H} NMR (202 MHz, CD_2Cl_2, ppm): δ 40.4 (s); ^13C{^1H} NMR (126 MHz, CD_2Cl_2, ppm): δ 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_2ClNP_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_2Cl_2. Subsequently, the mixture was added to a vial loaded with K_2CO_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.

^1H NMR (400 MHz, CD_2Cl_2, ppm): δ 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); ^31P{^1H} NMR (162 MHz, CD_2Cl_2, ppm): δ 43.3 (s); ^13C{^1H} NMR (126 MHz, CD_2Cl_2, ppm): δ 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 (dp, 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, Rₜ = 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, 125.7, 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), 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 ¹H NMR spectroscopy and confirmed at least in duplo. NMR spectra of both products have been reported in literature. 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 ¹H 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 ¹H 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 F² 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 Ueq 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 F² 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 Ueq 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-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 DBFPPhos 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 DBFPPhos (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 (SbF$_6$ and PF$_6$). However, no appreciable reactivity to form the desired product was found.


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