

Gold Catalysis

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

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Abstract: The synthesis, reactivity, and potential of well-defined dinuclear gold complexes as precursors for dual gold catalysis are explored. Using the preorganizing abilities of the ditopic $\text{PN}^{\text{H}}\text{P}^{\text{Pr}}$ (L^{H}) ligand, dinuclear $\text{Au}^{\text{I}}\text{--Au}^{\text{I}}$ complex **1** and mixed-valent $\text{Au}^{\text{I}}\text{--Au}^{\text{III}}$ complex **2** provide access to structurally characterized chlorido-bridged cationic species **3** and **4** upon halide abstraction. For **2**, this transformation involves unprecedented two-electron oxidation of the redox-active ligand, generating a highly rigidified environment for the Au_2 core. Facile reaction with phenylacetylene affords the σ,π -activated phenylacetylide complex **5**. When applied in the dual gold heterocycloaddition of a urea-functionalized alkyne, well-defined precatalyst **3** provides high regioselectivities for the anti-Markovnikov product, even at low catalyst loadings, and outperforms common mononuclear Au^{I} systems. This proof-of-concept demonstrates the benefit of preorganization of two gold centers to enforce selective non-classical σ,π -activation with bifunctional substrates.

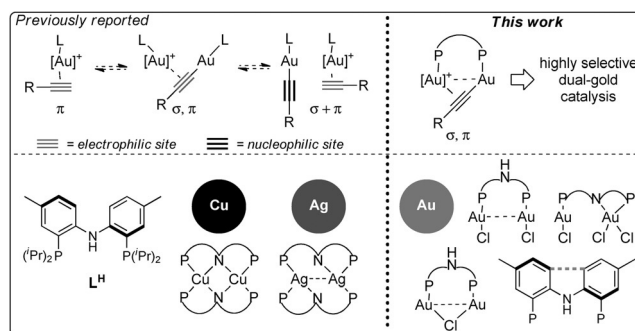
Gold catalysis has flourished over the past 15 years, enabling a wide range of transformations.^[1] More recently, dual gold catalysis has been developed successfully.^[2] Whereas “traditional” mono-gold catalysis relies on π -activation of a substrate by a cationic Au^{I} center, dual gold catalysis typically involves both σ - and π -activation (of one or two functionalities, such as $\text{C}\equiv\text{C}$ bonds) by two gold centers. The prevailing strategy utilizes mononuclear Au^{I} complexes to induce this mode of activation (Scheme 1).^[3] However, this strategy offers no handles to induce preorganization of both gold centers to specifically target well-defined σ,π -activation of, for example, unsaturated hydrocarbon $\text{C}\text{--}\text{C}$ multiple bonds whilst avoiding π - or $\sigma + \pi$ -coordination. Furthermore, no control over the selective binding of bifunctional substrates (such as heterocyclizations) can be achieved in this manner.

The synthesis, coordination chemistry and catalytic applications of dinuclear Au^{I} complexes are well-developed.^[4,5]

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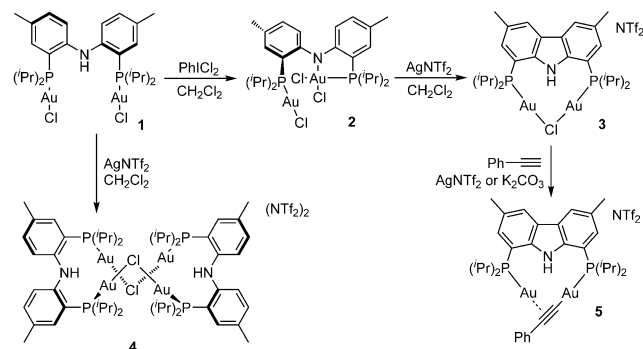


Scheme 1. Top: coordination of $\text{C}\equiv\text{C}$ bonds on mononuclear Au^{I} species and a strategy to induce selective σ,π -activation using well-defined diphosphine-supported dinuclear $\text{Au}^{\text{I}}\text{--Au}^{\text{I}}$. Bottom: known (left) and novel (right) coinage metal coordination chemistry of $\text{PN}^{\text{H}}\text{P}^{\text{Pr}}$ ligand L^{H} , including unprecedented ligand-based reactivity.

The proximity of both gold centers has occasionally been credited to enhance reactivity.^[6] However, to the best of our knowledge the competence of well-defined dinuclear σ,π -alkynide complexes in dual gold catalysis has never been reported, despite the potential benefits of two pre-organized gold centers with respect to chemoselectivity and activity for this type of reaction. Additionally, facile access to dinuclear mixed-valent gold complexes might be an interesting target in the context of cascade and $\text{Au}^{\text{I}}/\text{Au}^{\text{III}}$ cooperative catalysis.^[7]

The ditopic tridentate ligand $\text{PN}^{\text{H}}\text{P}^{\text{Pr}}$ (L^{H} ; Scheme 1) displays versatile coordination chemistry with respect to a wide range of transition metals,^[8] including Cu^[9] and Ag.^[10] Strikingly, no single complex of gold with this type of ditopic framework is known to date. Furthermore, chemistry related to the redox-active nature^[11] of L^{H} has been well-established in nickel, manganese, and rhenium complexes,^[12] 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 **L** backbone.^[9a] 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 and to selectively bind and activate bifunctional substrates. To address these challenges, we herein 1) uncover the versatile coordination chemistry of gold using the redox-active ditopic $\text{PN}^{\text{H}}\text{P}^{\text{Pr}}$ ligand, 2) disclose the interesting ligand and metal-based reactivity of (mixed-valent) dinuclear species, and 3) establish well-defined precatalyst systems ideally suited for σ,π -activation of alkynes and demonstrate their use in highly selective dual gold catalysis.

The straightforward reaction of **PN^HP^{Pr}** with AuCl(SMe₂) in a 1:2 ratio provides white solid **1** (³¹P NMR: δ 40.9 ppm) with a ¹H NMR spectrum suggestive of a C₂ symmetric species (Scheme 2). Single crystal X-ray diffraction analysis



Scheme 2. Synthesis of well-defined Au₂-complexes **2–5** from Au^I–Au^I precursor **1**, generated by reaction of ligand L^H with AuCl(SMe₂) (2 equiv).

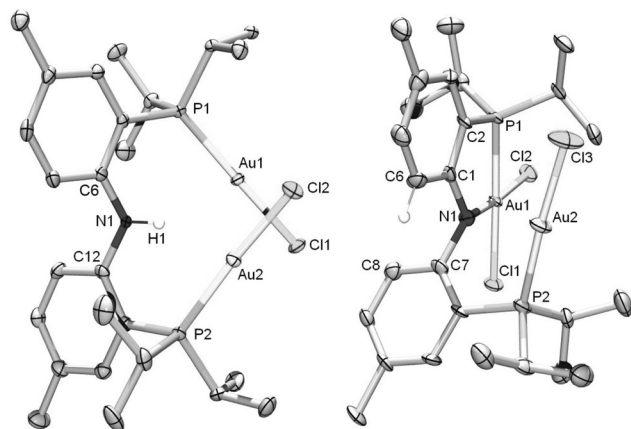


Figure 1. Displacement ellipsoid plots (50% probability level) of **1** (left) and **2** (right). For clarity, the counterion and hydrogen atoms are not shown. Selected bond lengths (Å) and angles (°), for **1**: Au1–P1 2.2495(8), Au1–Cl1 2.3010(7), Au1–Au2 3.23791(17), P1–Au1–Cl1 173.45(3), C6–N1–C12 126.3(3). For **2**: 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), Au1–Au2 4.641, P1–Au1–Cl1 178.39(8), P1–Au1–N1 84.51(19), N1–Au1–Cl2 172.66(20), C1–N1–C7 116.4(7), torsion ∠ C6–C1–C7–C8 76.4(8).

reveals an intramolecular Au1–Au2 distance of 3.23791(17) Å, which suggests an aurophilic d¹⁰–d¹⁰ interaction^[13] in the solid state (Figure 1). Reaction of **1** with one equivalent of dichloro-λ³-(iodanyl)benzene (PhICl₂) in CH₂Cl₂ instantaneously generates a dark purple solution that shows two signals in the ³¹P NMR spectrum at δ 44.3 (P2) and 105.3 ppm (P1). The strongly downfield shifted signal for P1 supports coordination to a Au^{III} center by site-selective two-electron Au^I oxidation with formation of Au^I–Au^{III} derivative **2**. Mass spectrometry supports an overall Au₂Cl₃(L) configuration. The ¹H NMR spectrum contains one strongly upfield shifted aromatic signal at δ 5.90 ppm but no –NH signal could be identified. X-ray structure

determination confirms the sole formation of species **2**, with the central deprotonated amido nitrogen coordinating to the square-planar Au^{III} center (Figure 1).

The PNP-ligand backbone in **2** is severely twisted, with a C6–C1–C7–C8 torsion angle of 76.4(8)°. 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 intramolecular Au–Au distance of 4.641 Å excludes an aurophilic d⁸–d¹⁰ interaction. Cyclic voltammetry does not indicate reversible oxidation of the potentially redox-active ligand scaffold in **2**.

A prerequisite for catalysis with a AuX(L) precursor (X is a halide) is the generation of a vacant coordination site by halide abstraction with, for example, Ag⁺ salts or a suitable Lewis acid. Addition of one equivalent of AgNTf₂ (or related silver salts or GaCl₃; see the Supporting Information) to **2**, which bears multiple chlorido fragments, leads to a mixture of species according to ³¹P NMR spectroscopy. However, addition of two equivalents results in rapid decoloration of the reaction solution and generation of a single symmetric product (³¹P NMR: δ 40.4 ppm), suggestive of the presence of only Au^I–phosphine fragments. The ¹H NMR spectrum shows only one methyl signal for the ditolylamine backbone and chemically identical isopropyl groups at phosphorus. Most notably, only two instead of the anticipated three aromatic hydrogen signals are observed, together with a downfield signal at δ 10.53 ppm. This signal integrates for one hydrogen and is attributed to an –NH fragment. ESI-MS data suggest that the dinuclear complex, bearing only one chlorido ligand, remains intact during this transformation. The structure of complex **3** could be elucidated by X-ray structure determination of single crystals grown from CH₂Cl₂–pentane (Figure 2).

Clearly, halide abstraction by AgNTf₂, related silver salts, or GaCl₃, induces a highly unusual metal-based reduction of mixed-valent species **2** to yield Au^I–Au^I species **3**

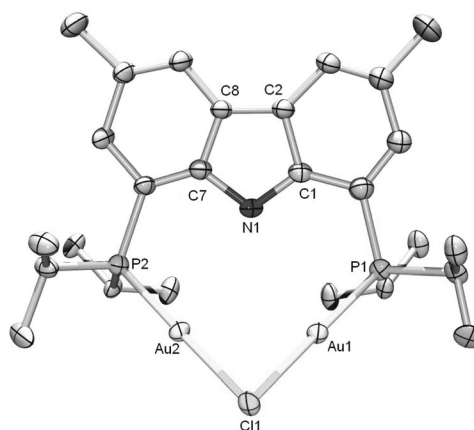


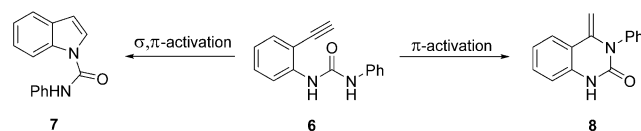
Figure 2. Displacement ellipsoid plot (50% probability level) for the cationic part of **3**. The NTf₂ counterion, lattice solvent molecules, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Au1–P1 2.2500(12), Au2–P2 2.2500(12), Au1–Cl1 2.3484(12), Au1–Au2 3.0758(3), C2–C8 1.449(7), P1–Au1–Cl1 178.53(4), Au1–Cl1–Au2 81.74(4).

(concomitant with oxidative C–C coupling of the two C–H groups *ortho* to the nitrogen in the ligand backbone), to generate a carbazole framework wherein the nitrogen is reprotonated. The gold centers are bridged by a single chlorido ligand, leading to an acute $\angle \text{Au1-Cl1-Au2}$ of $81.74(4)^\circ$. Relative to “open” complex **1**, the intramolecular Au–Au distance decreased by approximately $0.16 \text{ \AA}$ in this “closed” derivative, as a result of increased directional positioning of the phosphine lone pairs, despite the larger natural bite angle.^[14] To the best of our knowledge, this is the first report of redox-chemistry occurring at the *ortho* C–H positions of the **PNP** framework within the coordination sphere of any transition metal. The existence of a single chlorido bridgehead between two Au^{I} centers is relatively rare.^[15] Notably, no single example exists of an intramolecular Au–Cl–Au bridge stabilized by a single dinucleating ligand. Reaction of **1** (featuring the “open” ligand) with one equivalent of AgNTf_2 generates tetranuclear bis(chlorido)-bridged complex **4** as a crystalline solid ($\angle \text{Au1-Cl1-Au2}$ $96.78(4)^\circ$). This species is likely in equilibrium with the dinuclear monomer in solution (see the Supporting Information for details about complex **4**).

Substitution of the chlorido bridge in these dinuclear gold species might release a masked Au^{I} -cation. Reaction of **3** with excess phenylacetylene leads to broadening of the ^{31}P NMR signal and appearance of an additional singlet at $\delta 43.3 \text{ ppm}$, which converts to a single product **5** (with complete conversion) upon addition of one equivalent of AgNTf_2 or K_2CO_3 . No signal corresponding to the terminal CH of the alkyne was observed for this species by ^1H NMR spectroscopy, suggesting formation of a gold(acetylide) fragment. The overall symmetry of the complex appears to be retained during this transformation, which points to rapid exchange of the phenylacetylide between the two gold centers.^[16] Single crystal X-ray structure determination corroborates the dual interaction of the $-\text{C}\equiv\text{CPh}$ ligand with the $\text{Au}^{\text{I}}-\text{Au}^{\text{I}}$ complex, that is, σ -coordination of the terminal phenylacetylide carbon C(15) to Au(1) and π -coordination of the triple bond system

to Au(2) (Figure 3). This is the first crystallographically characterized intramolecular $\text{Au}_2(\sigma,\pi\text{-acetylide})$ complex with a diphosphine ligand, and serves to illustrate that preorganization of two gold centers may lead to selective substrate coordination. Complex **4** reacts in a similar fashion, leading to the well-defined species **5'** that was characterized by NMR spectroscopy and mass spectrometry (see the Supporting Information).

Having established that dinuclear complex **3** engages in well-defined σ,π -activation of C–C triple bond systems, the heterocyclization (intramolecular hydroamination) of urea-functionalized alkyne **6** was selected as a proof-of-concept reaction to probe the catalytic competence of this well-defined Au_2 species. Markovnikov addition to generate a six-membered ring (**8**) involves π -activation by a single gold species, whereas dinuclear σ,π -activation results in anti-Markovnikov addition to give a five-membered ring (**7**; Scheme 3).^[17] Using 2.5 mol % of **3** in DMF at 60°C for five



Scheme 3. Heterocyclization of 1-(ethynylphenyl)urea (**6**) into either anti-Markovnikov product **7** or Markovnikov addition product **8**.

hours leads to full conversion and high regioselectivity for the five-membered indole **7** (85 %), in accordance with a selective σ,π -acetylide mechanism. External base (such as K_2CO_3) inhibits the reactivity, while addition of one equivalent of AgNTf_2 with respect to the catalyst provides slightly higher regioselectivity for **7** (90 %); presumably this is due to faster generation of the σ,π -acetylide species. In the absence of additives (Ag^+ or base), bis(chlorido)-bridged tetranuclear complex **4** displays a similar preference for formation of **7**. The high regioselectivity achieved with dinuclear catalysts **3** and **4** is attributed to the ligand-enforced proximity of both Au^{I} centers. Stoichiometric reaction of **3** and **6** shows sole formation of the σ,π -activated substrate by ESI-MS (Supporting Information, Figure S27).

Dilution studies were performed to investigate the effect of decreased catalyst loading on the level of regiocontrol for the conversion of **6** to **7** and **8**. The findings clearly validate our hypothesis, as the high regioselectivity for **7** obtained with catalyst **3** is independent of the catalyst concentration (Figure 4). In contrast, dilution experiments with mononuclear $\text{AuCl}(\text{P}^t\text{Bu}_3)$ —reported as the best catalyst to form **7** by σ,π -activation^[17]—result in a sharp drop in selectivity.^[18] These results demonstrate the benefits of well-defined preorganization of two gold centers to enforce selective σ,π -activation and to mediate regioselective dual gold catalysis with functionalized alkynes, even at low catalyst loadings.

In summary, we have demonstrated that the redox-active $\text{PN}^{\text{H}}\text{P}^{\text{I}}\text{Pr}$ ligand is a suitable framework to preorganize two gold centers for selective σ,π -activation of functionalized alkynes. Halide abstraction from mixed-valent $\text{Au}^{\text{I}}-\text{Au}^{\text{III}}$ complex **2** using AgNTf_2 results in highly unusual reactivity

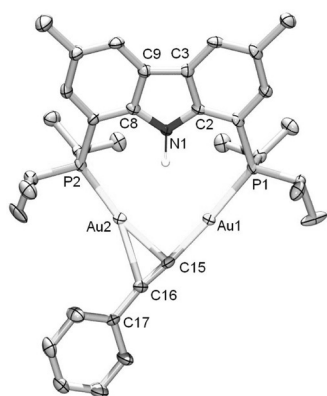


Figure 3. Displacement ellipsoid plot (50% probability level) for the cationic part of **5**. The NTf_2 counterion, lattice solvent molecules, and hydrogen atoms are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Au1–P1 2.2899(10), Au2–P2 2.2676(11), Au1–C15 2.019(5), Au2–Ct(C15–C16) 2.201, C15–C16 1.227(6), Au1–Au2 3.1110(2), P1–Au1–C15 $176.81(13)$, Au1–C15–C16 $174.2(4)$, P2–Au2–Ct(C15–C16) 174.99 , C15–C16–C17 $170.0(5)$.

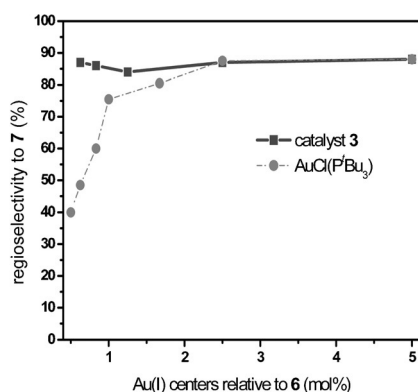


Figure 4. Comparison of regioselectivity toward indole **7** with dinuclear catalyst **3** vs. mononuclear benchmark catalyst AuCl(PtBu₃) under dilution conditions.

involving two-electron ligand oxidation, generating chlorido-bridged Au^I–Au^I species **3** bearing a highly rigidified carbazolyl backbone. Reaction with phenylacetylene enabled the first crystallographically characterized intramolecular dual gold σ,π -acetylide complex (**5**) supported by a single diphosphine ligand. The well-defined dinuclear Au^I complexes are excellent precatalysts for dual gold catalysis involving selective σ,π -activation, inducing high regioselectivity in the gold-catalyzed heterocyclization of urea **6**, without the need to add base or silver salts. Dilution experiments show that dinuclear catalyst **3** 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. The detailed mechanism behind the surprising conversion of **2** into **3** is currently under investigation. This ligand-to-gold two-electron transformation appears to involve several digold intermediates, including the dinuclear “monomer” of complex **4**, as well as a unique Au^{III}–Au^{III} species supported by one PNP ligand.^[19]

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Keywords: σ,π -activation · bridging acetylide · dinuclear gold complexes · dual gold catalysis · redox-active ligand

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