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Intramolecular Anti-Phosphinoauration of Alkynes – An FLP-**Motivated Approach - Synthesis of Stable Aurated Phosphindolium Complexes**

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Abstract: The synthesis of aurated phosphindolium complexes from easy accessible 1,5-alkynylphosphine derivatives has been studied by using gold(I) complexes featuring carbene and phosphine ligands as initiators. Upon formation of the mixed phosphine NHC/phosphine phosphine gold species, elevated temperatures induced the cyclization to give stable aurated phosphindolium salts which is supported by DFT calculations. The key elementary step that comprises a yet unknown anti-phosphinoauration of an unactivated alkyne is favored if bulky NHC ligands are used which was analyzed by kinetic measurements. This concept could furthermore be extended to neutral (phosphindolium)AuCl complexes featuring the yet unknown phosphindole ligand.

In the past decades, numerous applications have been found for homogeneous gold-catalysts.¹ In most cases, the reactions include the addition of a nucleophile such as amines,² alcohols/water,³ or carbon based nucleophiles,⁴ onto a gold-activated multiple bond as key elementary step.5 However, taking into account the reported manifold of nucleophiles employed in gold catalysis, phosphines have been largely unexplored which stands in stark contrast to their common use as ligands in these transformations. One reason might be the assumption that in the case of stoichiometric amounts of phosphine a strong coordination to the free binding site of the gold catalyst can inhibit the catalysts activity. So far, only one report by Kuniyasu and Kambe deals with the gold-mediated *cis*-addition of phosphines from RSAuPPh₃ complexes.⁶ But due to the special electronic nature of the applied electron-deficient alkyne dimethylacetylendicarboxylate (which itself is a powerful electrophile known to be attacked by phosphines) no general information can be obtained regarding the tolerance of phosphines in gold catalysis; for example generally cisadditions are extremely rare which indicates that triggered by the nature of this specific alkyne an unusual pathway takes place.⁶ Therefore, a general study of a phosphinoauration reaction with electronically non-activated alkynes which are usually applied in gold-catalyzed reactions is still missing. Other reports on the connection of a C-P bond by means of homogeneous gold catalysts are restricted to the addition of a phosphite onto an imine⁷ or by reductive elimination from an intermediate gold(III) species.⁸ Several phosphine-alkyne

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addition reactions have been reported,⁹ which attracted our curiosity if the elementary step of a phosphinoauration was feasible. As mentioned before, the lack of reports on phosphines as nucleophiles in gold catalysis might be attributed to the strong affinity of P/Au to engage in the soft/soft Lewis pair combination Au(I)/PR₃ leading to a catalytically inactive LAuPR₃ species. Interestingly, Bertrand et al. reported on the stoichiometric aminoauration reaction (Scheme 1a),¹⁰ however as nitrogen is much less likely to form stable adducts with Au(I) centers than phosphorus, this process is obviously much easier and fits into the reactivity observed in the plenty of reported catalytic hydroamination reactions.¹¹ However, to the best of our knowledge, no report on any gold catalyzed hydrophosphination reaction,¹² clearly demonstrates the challenges attributed with phosphorus nucleophiles compared to nitrogen.

To overcome the problem of strong P/Au coordination, we were inspired by the trans-phosphinoboration of non-activated alkynes with frustrated Lewis pairs (FLPs).13 While phosphorus also forms strong adducts with Lewis acidic boranes, the combination of a sterically bulky phosphine and borane (FLP) can easily activate alkynes in a trans-phosphinoboration reaction (Scheme 1b).14,15 Based on the analogy of the soft Lewis acidity of boron and gold(I) we assumed that steric bulkiness for either the phosphine or/and the gold species might enable a weakening of the Au-P bond and reinstalling unquenched Lewis acidity and basicity. In the following work we will analyze this initial idea for an intramolecular trans-phosphinoauration reaction (Scheme 1c).

a) Anti-Aminoauration





c) This study



^tBu₂P

Scheme 1. Reported aminoauration reaction (1) and comparison between intermolecular frustrated Lewis-pair (1b) and intramolecular gold mediated activation of alkynes (1c).

 $B(C_6F_5)_3$

Initial attempts aimed for the synthesis of frustrated Lewis pairs containing a cationic Lewis acidic gold center in the presence of a non-coordinating Lewis basic phosphine. However, even the combination of the bulkiest so far reported NHC ligand (IPr**)¹⁶ with tris-o-tolyl phosphine led to the formation of the [(NHC)Au(PR₃)][NTf₂] adduct 1 verified by X-ray diffraction

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(Figure 1). ¹⁷ Also the synthesis of bulky phosphine ligands containing tolane substituents led to the corresponding



Figure 1. Solid state structure of compound 1; and 2. Hydrogen atoms, the counter-anion $(NTf_{2}{}^{\text{-}})$ and co-crystallized solvent molecules are omitted for clarity.

[(R₃P)Au(PR₃)][NTf₂] adduct **2**, clearly verifying the high tendency of phosphines to coordinate to the soft gold(I) center. Even though the synthesis of Au/P frustrated pairs seemed challenging, we were curious if this is necessary as phosphine dissociation might be reversible at elevated temperatures. In order to investigate an intramolecular gold(I)-mediated phosphino-alkyne addition, we prepared *ortho*-phosphine-substituted phenylacetylene derivatives **3** following a procedure of Mathey.¹⁸ In our initial experiment the addition of a stoichiometric amount of IPrAuNTf₂ at room temperature led to the quantitative and fast formation of the Lewis acid/base adducts **4**, but in contrast to the Bertrand's system, no further conversion was monitored (Scheme 2).



Scheme 2. Synthesis of mixed phosphine NHC complexes.

As a next step, phosphine gold complex **4a** was heated at 140 °C in bromobenzene-d₅ as solvent (40.7 mM) under inert conditions (Scheme 3). A complete consumption of the starting material was observed [*in situ* ³¹P NMR monitoring from δ = 38.8 ppm (**4a**) to δ = 26.5 ppm (**5a**)] after 12 h and **5a** assigned as phosphindolium could be isolated in 80% yield by crystallization. The NMR monitoring also revealed that the rearrangement is irreversible and that the evolving phosphindolium species was stable against air and moisture. Crystals of **5a** suitable for X-ray analysis were obtained by recrystallization from CH₂Cl₂Br/pentane (Figure 2). The molecular

structure confirms the *trans*-phosphinoauration product exhibiting a stable vinyl gold moiety. $^{\rm 19}$



Scheme 3. a) Initial cyclization experiment with 4a; b) mesomeric structures for the phosphindolium core.



Figure 2. Solid-state structure of 5a. Hydrogen atoms, the counter-anion (NTf₂⁻) and co-crystallized solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) for 5a: Au1-C2 2.042(6), Au1-C7 2.025(3), C1-C2 1.359(8), C2-C3 1.531(7), C3-C4 1.3900, P1-C1 1.814(6), P1-C4 1.771(5), P1-C5 1.812(5), P1-C6 1.845(4); C7-Au1-C2 170.18(18), C4-P1-C1 94.2(3), C5-P1-C1 112.8(2), C4-P1-C5 113.0(2); C4-P1-C1 94.2(3); C4-P1-C6 118.0(2); C5-P1-C6 106.16(18); C1-C2-C3 112.4(5).

Interestingly, the so far unknown phosphinindolium-3-yl ligand can be described ranging from a phosphoniovinyl gold compound (5a), carbene λ^5 -phosphindole (5a'), carbene ylide (5a'') up to a mesoionic carbene (5a''') (Scheme 3b). Note, in the case of Bertrand's indole derived vinyl gold compounds such mesomeric structures cannot be formulated. The bond length of the C1-C2 bond [1.359(8) Å] is in the upper range for the phospha-indene type double bond [1.348-1.362 Å], 20 while the P1-C1 bond distance 1.814(6) Å] is in agreement with a P-C single bond observed in similar systems [1.775-1.794 Å]²⁰ and significant longer than for a λ^5 -ylen structure [1.695 Å].²¹ The Au-C2 bond length [2.04 Å] is in a typical range of other vinyl gold compounds, $^{\rm 19}$ indicating resonance structure ${\bf 5a}$ as the major contribution for the electronic description.²² This is further supported by Natural Resonance Theory calculations (NRT) employing the NBO6.0 program,²³ clearly indicating **5a** as the leading resonance structure containing a vinyl gold moiety and a

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3-center-4-electron bond between C2-Au-C7 (~96%), while ylide resonance form **5a**" accounts only to 1-3%.

As a next step, we evaluated the scope of the transformation with various phenylacetylene derivatives **4a-4m** (Scheme 4). All of the tolane precursors **4a-4e** showed clean reactions and the corresponding products were obtained in high yields no matter if electron-rich (**4b**, **c**), sterically bulky (**4d**) or electron-poor (**4e**) aromatic substituents attached to the triple bond were applied. It is noteworthy that the rearrangement for the electron-poor aryl alkyne (**4e**) proceeded much slower than for the electron-rich substrates (**4b**, **c**), which might be attributed to the stronger tendency of the electron-rich alkyne to form a gold alkyne complex, that is necessary for the activation of the substrate. Aliphatic alkynes turned out to be suitable substrates as well. Cyclic (**4f**), sterically bulky (**4g**) and linear (**4h**) alkyl groups were all tolerated and the corresponding vinyl gold compounds (**5f-5h**) were obtained in moderate to excellent yields.







Figure 3. Solid state structure of compound 5I (left) and 6 (right). Counteration NTf₂ and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for 5I: P2-Au1 2.3081(9), Au1-C1 2.032(4), C1-C2 1.329(5), C2-C3 1.535(5), C2-P1 1.798(4), P2-Au1-C1 174.8(1), Au1-C1-C2 125.9(3), C1-C2-P1 124.4(3), C3-C2-P1 107.2(3); and 6 Au1-C2 2.042(16), C1-C2 1.36(2), C1-P1 1.795(16), C2-Au-C2' 180.0, Au1-C2-C1 127.2(13).



Scheme 6. Scrambling: dual role of phosphines - ligand and nucleophile.

After evaluation of the scope with regard to the alkyne fused ligand, we turned our focus on variations of robust ligand structures that surrounds the cationic gold center (Scheme 7). Besides IPr and phosphines ('BuXPhos, P'Bu₃) ligands that were used for the upper examples, rearrangements using the sterically more demanding IPr^{*24} (**3m**) and IPr^{*16} (**3n**) were conducted. Both test reactions delivered full conversion accompanied with high yields (Scheme 7). Despite the steric bulk of the applied ligands, the cave-like structure of the applied NHCs perfectly fits to the organic substituent of the product. The result of the X-ray analysis of compound **5n** underlines this assumption (Figure 4).¹⁴ Switching to less hindered ligands was also possible which was demonstrated by using IMes as NHC ligand (**5o**).

Scheme 4. Reaction Scope. Triflimide (NTf_2^-) as counter-anion (omitted); (a) X-ray structure analysis¹⁴; (b) reaction time 48 h.

Following the FLP idea of weakening the Au-P bond by increasing the steric bulk of the phosphine moiety we prepared ortho-tolyl substituted phosphine derivative 4i that could be converted to the corresponding aurated phosphindolium 5i in good yield (see SI for the result of an X-ray analysis). Variations of the aromatic backbone were also possible but yields for a dimethyl-substituted benzene backbone (5k) and for a thiophene backbone (5j) turned out to be significantly lower than for the other test substrates. Importantly, these transformations are not limited to internal alkynes featuring a phenyl backbone. While it might be possible to generate the corresponding gold acetylide with the phosphine acting as a base, we observed in case of terminal alkyne featuring an alkyl tether (31) the generation of the corresponding 5-exo phosphino-auration product 51. An X-ray analysis is in agreement with this assignment (Figure 3; left). Importantly, it should be noted that while previous transformations contained an NHC ligand on gold this product bears two phosphines. Interestingly, when phosphine ligands are employed both as ligand and as nucleophile there are more options available as ligand scrambling is possible. This is demonstrated with adduct 4c* featuring the phosphaalkyne 3c and a bulky phosphine ligand (P^tBu₃). Heating this complex in bromobenzene led to the formation of the phosphindole dimer 6 and dimer 7 which can be explained by ligand scrambling (Scheme 6). The unique structure of a bisphosphindolium ligated metal could be clearly verified by X-ray diffraction (Figure 3; right). It should be noted that in the previous cases with NHC ligands on gold no ligand scrambling processes were observed, presumably a result of the stronger carbene-Au bond.

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 $\begin{array}{l} \textbf{5c} 80\%, R = CH_3, R' = H; (NHC = IPr) \\ \textbf{5m} 96\%, R = Ph, R' = CH_3; (NHC = IPr^*) \\ \textbf{5n} 80\%, R = 4\text{-}tBu\text{-}Ph, R' = CH_3; (NHC = IPr^{**}) \\ \textbf{5o} 87\%, R = H, R' = CH_3; (NHC = IMes) \end{array}$

Scheme 7. Variations of the NHC ligand.



Figure 4. Solid state structure of compound 5n. Hydrogen atoms, the counteranion (NTf₂-) and co-crystallized solvent molecules are omitted for clarity.

In a next step we investigated our initial idea of a frustrated Au/P Lewis pair system. We were curious if bulkiness could affect a weakening of the P-Au bond and hence speed up the cyclization reactions. Therefore, we performed kinetic measurements with alkyne **3c** in the presence of varying NHC ligands in order to evaluate the effect of ligand size on the transformation (see SI). Indeed, we found an enhanced reaction rate for the sterically more demanding IPr* ligand compared to the less hindered IPr ligand. In the course of this measurement, we also recognized that a decent temperature of 60 °C is sufficient for the rearrangement of substrate **3c**, leading to full conversion after 24 h. Noteworthy, with this electron-rich substrate a slow conversion can even be observed at room temperature.

A primary experiment concerning the reactivity of the obtained vinyl gold species was performed with substrate **5c** (Scheme 8). In the presence of stoichiometric amounts of HNTf₂ a fast protodemetallation was observed giving rise to the phosphindolium **8** accompanied by the released cationic gold fragment. X-ray diffraction unambiguously established the structure of **8** (Figure 5).



Scheme 8. Protodemetalation experiment.

Even though the concept of frustrated Lewis pair chemistry is valid for large ligands we were curious about small ligands in which the Au-P dissociation is independent of steric bulk. We were specifically interested in just AuCl as the resulting phosphinoauration product should give access to neutral unprecedented gold phosphindole complexes.²⁵ Upon mixing (dms)AuCl with ligands **3a-c** the gold complexes **4a**-4c**** were instantaneously formed. Interestingly, under forcing conditions (160 °C) we were able to generate a mixture of starting material and the desired phosphinoauration products **5a**-5b****. The starting materials and cyclization products could clearly be verified by X-ray diffraction (Figure 6; see also SI). Note, that similar compounds featuring an intact Au-Cl bond were not prepared with Bertrand's aminoauration system, but might be very interesting targets for further catalytic studies.



Scheme 9. Phosphinoauration leading to neutral gold phosphindole complexes.







Figure 6. Solid state structure of compound **4b**^{**} (left) and **5b**^{**} (right). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) for **5b**^{**} (°): Au1-Cl1 2.3098(8), Au1-C2 1.999(3), C2-C1 1.374(4), C1-P1 1.802(3), P1-C4 1.785(3), C4-C3 1.408(4), C3-C2 1.487(4), P1-C5 1.801(3).

This result prompted us to investigate the *trans*phosphinoauration from a theoretical point of view. DFT calculations at the B3LYP-D3BJ/cc-pVDZ level of theory indicate

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that the novel free singlet phosphindole-yne ligand (Singlet/Triplet gap Δ S/T = 25.5 kcal/mol) is only stable bound to a transition metal center. Upon dissociation of the metal a low lying transition state of ca. Δ G[‡] = 1 kcal/mol leads back to the thermodynamically more favorable phosphaalkyne (Δ G = -29.2 kcal/mol) (see SI; Figure S1). Interestingly, the transition state energy for the cyclization event is similar high (Δ G[‡] = 29.7 kcal/mol) employing the Au⁺-NHC fragment, taking into account the non-favored dissociation of the P-Au bond (Figure 7). However, in this case the phosphindole-yne ligand is trapped at the transition metal therefore leading to a more stable complex (Δ G = -3.9 kcal/mol).



Figure 7. Calculated energy profile at the B3LYP-D3BJ/cc-pVDZ level.

When calculating the energy profile employing the AuCl precursor it should be noted that the initial cyclization complex was

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calculated to be endergonic by +6.5 kcal/mol at the same level of theory (B3LYP-D3BJ/cc-pVDZ) (see SI; Figure S3). Taking into account the polar reaction medium (SMD calculation with bromobenzene) leads to a similar thermodynamic stability of the starting material compared to the cyclization product ($\Delta G = -0.1$ kcal/mol) highlighting the importance of the polarity of the solvent in this transformation.

In summary, we could demonstrate that the elementary step of an *anti*-phosphinoauration is feasible leading to a novel class of phosphindolium ligands. This new elementary step for gold chemistry might open up new synthetic perspectives also with regard to catalytic processes. For the best conversion rates it was found that sterically bulky ligands surrounding the gold center are beneficially in conclusion with an FLP approach. However, at elevated temperatures even the cyclization with AuCl takes place to generate the new phosphindolium ligand framework. The reaction provides structurally and valuable phosphindolium complexes in high yields and selectivity.

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