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**Title:** (P,C) Cyclometalated Gold(III) Complexes: Highly Active Catalysts for the Hydroarylation of Alkynes

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# (P,C) Cyclometalated Gold(III) Complexes: Highly Active Catalysts for the Hydroarylation of Alkynes

Charlie Blons, Sonia Mallet-Ladeira, Abderrahmane Amgoune,* and Didier Bourissou*

*Dedicated to Dr. Joaquim Henrique Teles*

**Abstract:** *The first catalytic application of well-defined (P,C) cyclometalated gold(III) complexes is reported. The bench-stable bis(trifluoroacetyl) complexes* **2a,b** *perform very well in the intermolecular hydroarylation of alkynes. The reaction is broad in scope, it proceeds within few hours at 25°C at catalytic loadings of 0.1–5 mol%. The electron-rich arene adds across the C≡C bond with complete regio- and stereo-selectivity. The significance of well-defined gold(III) complexes and ligand design are highlighted in a powerful but challenging catalytic transformation.*

Gold(III) chemistry has progressed very rapidly over the last few years and N-based cyclometalated complexes occupy a forefront position in the field.[1] The luminescent and biological properties of well-defined Au(III) complexes are attracting great interest for opto-electronic and therapeutic applications.[2,3] Comparatively, phosphine-based ligands have been very little exploited in gold(III) chemistry so far, but our work on (P,C) cyclometalated complexes **A** (Figure 1)[4] has challenged the presumed mismatch between soft P donors and hard Au(III) centers. The preparation of complexes **A** is straightforward and actually provided the first example of oxidative addition of aryl–X bonds to gold.[4a,5] In addition, complexes **A** were shown to possess rich reactivity.[4b-d,6] The stability imparted by the (P,C) chelate was also leveraged to prepare and characterize new types of gold(III) species.[4e-g] A forefront goal is now to apply complexes **A** in catalysis, taking advantage of their rich and unique behavior. Despite the increasing variety of stable and reactive well-defined Au(III) complexes, gold(III) catalysis is still in its infancy and lacks well behind gold(I) catalysis.[7,8] Exploring and developing gold(III) catalysis is all the more desirable that the distinct properties of Au(III) complexes[9] may enable to achieve transformations which are difficult to perform or limited in scope and/or efficiency with Au(I) and the other transition metals.

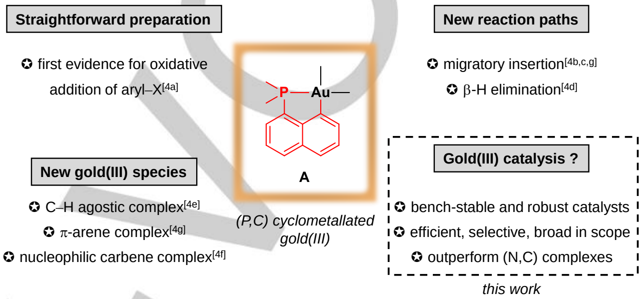

**Figure 1.** (P,C) Cyclometalated Au(III) complexes.

The hydroarylation of alkynes represents an ideal catalytic transformation to test and apply (P,C) cyclometalated Au(III) complexes. Since the seminal discovery of Fujiwara in the 2000's using Pd and Pt complexes,[10] this reaction, *ie* the formal addition of aryl–H bonds to alkynes, has garnered huge interest (Figure 2). It offers a very attractive alternative to the Heck coupling reaction, obviating the use of prefunctionalized aryl–X substrates, and the resulting styrene derivatives are extremely valuable building blocks in organic synthesis and material science.[11]

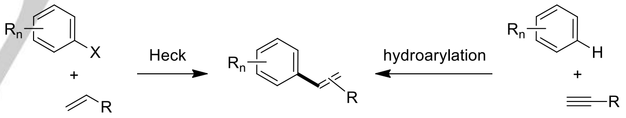

**Figure 2.** Heck and hydroarylation reactions leading to styrene derivatives.

Gold complexes were recognized early on as potent and highly active catalysts for the hydroarylation reaction.[12] Not surprisingly, most studies have focused on gold(I) complexes that actually proved to be extremely powerful for intramolecular hydroarylation reactions, enabling rapid access to biologically relevant (poly)cyclic compounds.[13,14] By comparison and despite the known ability of Au(III) complexes to readily activate C≡C and $C_{sp2}$–H bonds, very few articles deal with the Au(III)-catalyzed hydroarylation of alkynes. In 2003-2004, He and Reetz explored independently simple catalytic systems combining $AuCl_3$ and silver salts.[15,16] These studies stand as rare examples of intermolecular hydroarylation of alkynes, but the $AuCl_3/AgX$ catalysts are only applicable to activated (electron-poor) and/or terminal alkynes, and leave little room for optimization.

Here we report a detailed study of intermolecular hydroarylation of alkynes catalyzed by well-defined Au(III) complexes. (P,C) Complexes of type **A** were discovered to be highly active. The reaction is highly regio- and stereo-selective, it works with a wide scope of alkynes. Comparison with other gold

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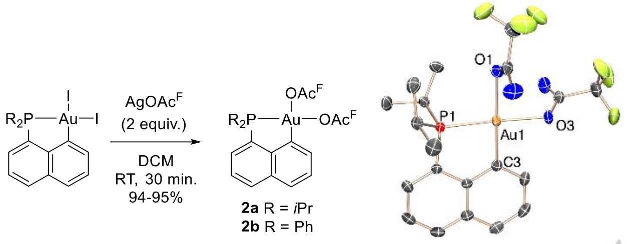
complexes evidences the very strong influence of the ancillary ligand, highlighting the interest and potential of ligand tuning in well-defined gold(III) catalysts.

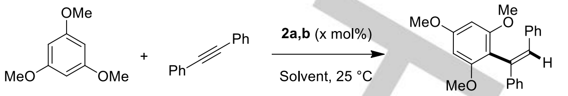
The Au(III) complexes **2a,b** (Scheme 1) were identified as promising precatalysts. They combine the robust (P,C) chelate with labile trifluoroacetate ligands. Reactions of the related (N,C)Au(OAc$^F$)$_2$ complex **B** (Scheme 3) with ethylene and acetylene were reported recently by Tilset *et al*, and the feasibility of catalytic trifluoroacetoxylation of acetylene was demonstrated with TON up to ~20.[17] Iodine to trifluoroacetate exchange readily afforded the desired complexes **2a,b** which were obtained in excellent yields (94%) as bench-stable and analytically pure compounds.[18,19] Their structure was unambiguously assessed by multi-nuclear NMR spectroscopy, high-resolution mass spectrometry (HR-MS) and single-crystal X-ray crystallography (in the case of **2a**).



**Scheme 1.** Synthesis of the (P,C)Au(III) complexes **2a**,**b** and molecular structure of **2a.** Thermal ellipsoids are drawn at 50% probability, hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Au-O1 2.105(3), Au-O3 2.089(2), Au-C3 2.004(3), Au-P1 2.262(1); P1AuC3 84.11(9), P1AuO3 176.88(6), P1AuO1 97.05(7), C3AuO1 177.91(11).

To start our catalytic studies with complexes **2a,b**, we chose as model reaction the hydroarylation of diphenylacetylene, an internal unactivated alkyne, with trimethoxybenzene (TMB) (Scheme 2). The reaction was monitored by $^1$H NMR spectroscopy using hexamethylbenzene as internal standard. The catalytic loading of **2a,b** was initially fixed to 5 mol%. No reaction was observed after 24 h at 25°C in dichloromethane (DCM). Under these silver-free conditions, it is needed to add trifluoroacetic acid (TFA) to activate the gold(III) complex. Using a 20/1 mixture of DCM/TFA, both complexes **2a** and **2b** exhibited high activities, the hydroarylation product being formed in 82 and 90% yields, respectively, within 4 h at 25°C. The (P,C)Au(III) complexes proved to be very robust. The reaction medium was reloaded four times with new substrates and in each case, the hydroarylation product was obtained in quantitative yield.[18] The amount of TFA could be increased to parallel the reaction conditions developed by Fujiwara *et al* for Pd and Pt catalysis (DCM/TFA 1/4).[10] Gratifyingly, the rate of the hydroarylation was significantly increased under these conditions and quantitative yields were obtained with 5 mol% of **2a,b** in only 30 min. It is noteworthy that the catalyst loading could be significantly reduced while retaining high catalytic performance: the hydroarylation product was obtained in 98% yield within 3 h at 25°C, using only 0.1 mol% of **2b**.[15]

Note that the reaction of diphenylacetylene with TMB is fully stereoselective. It affords a single isomer of the triarylethylene product in which the trimethoxyphenyl group and the proton are in *trans* arrangement, as unambiguously established by X-ray diffraction analysis.[18]



| Conditions | Cat. loading (x mol%) | Yields | |
|---|---|---|---|
| | | **2a** | **2b** |
| $CD_2Cl_2$ | 5 | 0 %, 24 h | 0%, 24 h |
| $CD_2Cl_2$/TFA (20/1)$^a$ | 5 | 82 %, 4 h | 90 %, 4 h |
| $CH_2Cl_2$/TFA (1/4)$^b$ | 5 | 99 %, 0.5 h | 99 %, 0.5 h |
| $CH_2Cl_2$/AcOH (1/4)$^b$ | 5 | 0 %, 1 h | 0 %, 1 h |
| $CH_2Cl_2$/TFA (1/4)$^b$ | 1 | 99 %, 1 h | 99 %, 1 h |
| $CH_2Cl_2$/TFA (1/4)$^b$ | 0.1 | 91 %, 4 h | 98 %, 3 h |

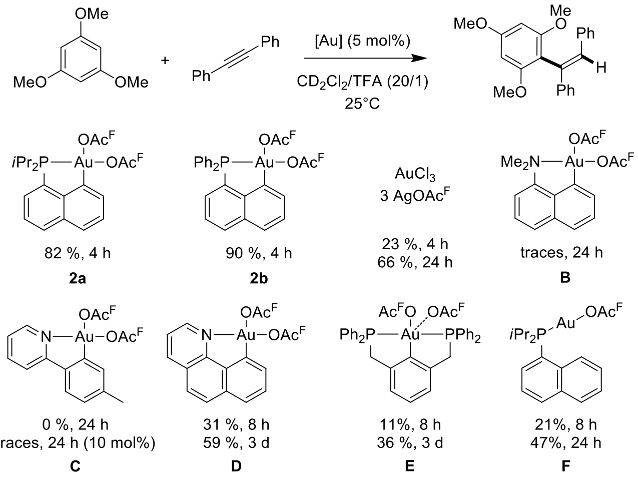
$^a$ 1 eq. of TMB, [alkyne] 0.2 M; $^b$ 2 eq. of TMB, [alkyne] 1 M

**Scheme 2.** Hydroarylation of diphenylacetylene with TMB catalyzed by the (P,C)Au(III) complexes **2a,b**, optimization of the reaction conditions.

The combination of (P,C)Au(III) complexes **2a,b** and TFA thus displays high catalytic activity in the hydroarylation of diphenylacetylene with TMB. To confirm the key role of the two components, some control experiments were carried out. In the absence of gold catalyst, no reaction occurred within 4 h when mixing the two substrates in a DCM/TFA 1/4 mixture, and even after 24 h, only 5% conversion was observed. Conversely, replacing TFA for acetic acid completely shut down the catalytic activity.

At this point, the catalytic behavior of **2a,b** was compared with that of a range of gold complexes with the aim to delineate the influence of the (P,C) ligand (Scheme 3). Because of the limited number of stable but reactive Au(III) complexes available, very little is known yet about how the stereo-electronic effects of ancillary ligands impact gold(III) reactivity, which hinders the rational elaboration and development of highly active and robust Au(III) catalysts. First, it is interesting to compare the two complexes **2a** and **2b**. The presence of Ph instead of *i*Pr groups at phosphorus makes the Au(III) center more electrophilic and less hindered sterically. This results in a slightly higher activity of **2b** in the reaction of diphenylacetylene with TMB, which is most apparent when the catalytic loading is reduced to 0.1 mol% (Table S1).[17]

Then, the positive influence of the (P,C) ancillary ligand and well-defined character of **2a,b** was deduced by using the simple two-component catalytic system AuCl$_3$/3AgOAc$^F$.[15] Only 23 % yield of the hydroarylation product was obtained after 4 h, and 66 % after 24 h. In this case, we noticed the formation of a black precipitate during the course of the reaction, indicating some decomposition of the catalytic system. Complexes **2a,b** are comparatively much more robust under the catalytic conditions. The three (N,C) cyclometalated complexes **B**, **C** and **D** were then evaluated. Strikingly, complexes **B**[18] and **C**[17] proved to be completely inactive, only traces of the hydroarylation product being observed after 24 h. Better results were obtained with the more rigid benzoquinoline fragment, but complex **D**[18,20] gave only 31% yield after 8 h (59 % after 24 h). Thus, the different electronic properties of the (P,C) *vs* (N,C) chelate strongly influence the catalytic activity of the corresponding gold(III) complexes. To complete the survey, the pincer complex **E**[4a] featuring a (P,C,P) ligand was assessed. It also displayed low catalytic activity, only 11 % yield after 8 h (36 % after 3 d), which has most likely to do with the reduced electrophilicity and steric accessibility of the Au(III) center as the result of the coordination of the additional phosphine moiety. Finally, the influence of the gold oxidation state was probed by considering the gold(I) complex **F**[18] bearing di-*isopropyl*-naphthylphosphine. Only 21 % yield was obtained after 8 h (47 % after 24 h). This difference most likely reflects the lower electrophilicity of gold(I) *vs* gold(III) species, making gold(III) complexes unique in catalyzing intermolecular hydroarylation reactions.[21]



1 eq. of TMB, [alkyne] 0.2 M, mesitylene as internal standard, NMR yields

**Scheme 3.** Comparison of the catalytic activities of a range of gold complexes in the hydroarylation of diphenylactelyne with TMB.

Having demonstrated the superior efficiency of complexes **2a,b** for the hydroarylation of diphenylacetylene with TMB, we then screened the scope of alkynes and arenes (Table 1). Two different DCM/TFA ratios were used, namely 20/1 (conditions **A**) and 1/4 (Fujiwara's conditions **B**). The optimal reaction conditions and catalyst (**2a** or **2b**) were selected for each set of substrates to obtain the best compromise between activity and selectivity. As shown by entries 1-8 in which TMB was reacted with a series of alkynes, the reaction proceeds well with internal alkynes featuring aryl, ester, keto and alkyl substituents, but also with terminal alkynes such as phenyl acetylene and methyl propiolate. In all cases, the hydroarylation is fully regioselective.[22] For activated substrates (entries 2, 3, 6 and 8), the alkyne is arylated at the β-position of the electron-withdrawing group. For internal and terminal aryl-alkynes (entries 2, 3, 4, 5 and 7), the arylation proceeds at the α-position and gives *gem*-diaryl alkenes. As in case of diphenylacetylene, the reaction is generally fully stereoselective and affords the *trans* addition product. The only exceptions are ethyl butynoate (entry 6) and methyl propiolate (entry 8), for which the hydroarylation products are prone to isomerize.[15b,21c]

The reaction was then extended to other electron-rich arenes such as 1,3-dimethoxybenzene and 1,2-dialkoxybenzenes (entries 9-11), as well as durene and mesitylene (entries 12-16). Using Fujiwara's conditions, the hydroarylation products were obtained in 62-99% yields in short reaction times (5 min – 2 h). 1,3-Dimethoxybenzene reacts very preferentially at the *o,p* position (entry 9) while 1,2-dialkoxybenzenes react exclusively at the *m,p* positions (entries 10,11). The reaction of mesitylene with diphenylacetylene is noteworthy: $AuCl_3/AgOAc^F$ showed extremely low reactivity (5% yield after 4 h at 50°C),[15] while the hydroarylation product was obtained in 76% yield within 1h30 using complex **2b** (entry 13). To illustrate the efficiency and practical interest of the catalytic transformation, the hydroarylation of mesitylene with ethyl phenylpropiolate (entry 14) was performed in air with technical solvents. Complete selectivity and only slight decrease in activity was noticed. It was also scaled-up to 5 mmol. Using 2 mol% of catalyst **2b**, the reaction was complete in 3 h and the ensuing product was isolated in 94% yield.[18]

From a mechanistic viewpoint, two different scenarios may be envisioned for this gold(III)-catalyzed hydroarylation reaction (Figure S0).[18] The first involves electrophilic C–H auration of the electron-rich arene followed by migratory insertion of the alkyne and protodeauration (**I**). The other involves π-activation of the alkyne at the electrophilic gold(III) center, followed by nucleophilic addition of the electron-rich arene and protodeauration (**II**). All the elementary steps and key intermediates of these two catalytic cycles are precedented in gold(III) chemistry, including $C_{sp2}$–H activation,[23] migratory insertion[4b,c,g] and π-activation of alkynes.[24] No intermediate could be detected upon NMR monitoring, but based on the stereoselectivity of the reaction in favor of *trans* addition of the aryl group and H atom across the alkyne, we assume that the transformation proceeds *via* the outer-sphere mechanism **II**.

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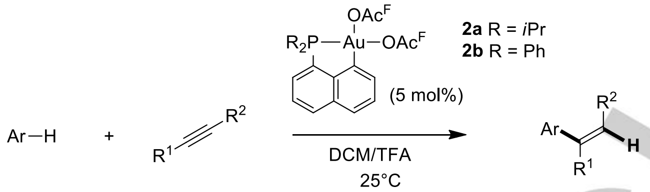
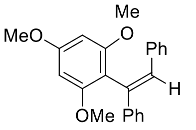
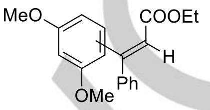
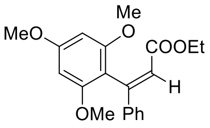
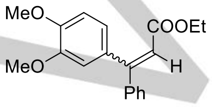
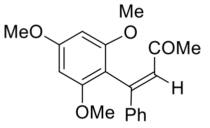
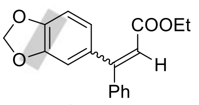
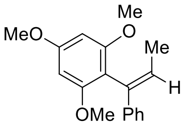
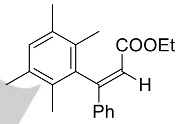
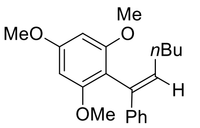
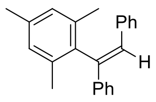
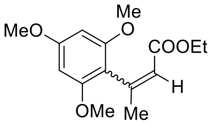
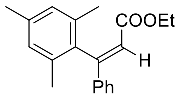
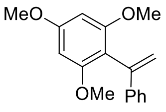
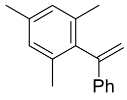
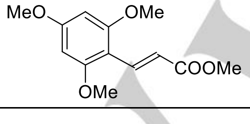
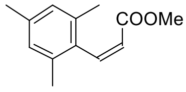
**Table 1**. Scope of the gold(III)-catalyzed hydroarylation of alkynes using **2a,b**.[a]



| Entry | Product | cat, conditions | yield[b] | Entry | Product | cat, conditions | yield[b] |
|---|---|---|---|---|---|---|---|
| 1 |  | **2b**, Cond. **A**<br>**2b**, Cond. **B** | **90%** (4 h)<br>**99%** (30 min), **79%**[c] | 9 |  | **2b**, Cond. **B** | **89%** (0.5 h), **77%**[c]<br>*o,p*/*o,o*: 92/8 |
| 2 |  | **2b**, Cond. **A**<br>**2b**, Cond. **B** | **90%** (3 h)<br>**99%** (1 h) | 10 |  | **2b**, Cond. **B** | **81%** (2 h), **58%**[c]<br>*E*/*Z*: 62/38 |
| 3 |  | **2a**, Cond. **A**[d] | **65%** (24 h), **60%**[c] | 11 |  | **2b**, Cond. **B** | **62%** (1 h), **60%**[c]<br>*E*/*Z*: 61/39 |
| 4 |  | **2a**, Cond. **A** | **87%** (1 h) | 12 |  | **2b**, Cond. **B** | **94%** (1 h), **92%**[c] |
| 5 |  | **2a**, Cond. **A**[d]<br>**2a**, Cond. **B** | **94%** (8 h), **74%**[c]<br>**99%** (30 min) | 13 |  | **2b**, Cond. **B** | **76%** (1h30) |
| 6 |  | **2b**, Cond. **B** | Z: **54%** (1 h), **45%**[c]<br>E: **27%** (1 h), **22%**[c] | 14 |  | **2b**, Cond. **B** | **99%** (1 h) |
| 7 |  | **2b**, Cond. **A** | **66%** (15 min), **63%**[c] | 15 |  | **2b**, Cond. **B** | **69%** (5 min) |
| 8 |  | **2a**, Cond. **A** | **E: 61%** (2 h)<br>**Z: 7%** (2 h) | 16 |  | **2b**, Cond. **B** | **99%** (30 min) |

[a] Conditions **A**: DCM/TFA (20/1), 1 eq. arene, [alkyne] = 0.2 M, Conditions **B**: DCM/TFA (1/4), 2 eq. arene, [alkyne] = 1 M
[b] Spectroscopic yield; [c] Isolated yield; [d] 2 eq. of alkyne

In summary, the (P,C)Au(OAc$^F$)$_2$ complexes **2a,b** were found to efficiently catalyze the intermolecular hydroarylation of alkynes. The reaction proceeds rapidly at 25°C with a broad scope of terminal and internal alkynes. These (P,C) cyclometalated species are very robust and their catalytic performance is far superior to that of "naked" gold(III) salts, as well as classical (N,C) cyclometalated Au(III) complexes. These results demonstrate that (P,C) cyclometalated complexes **A** are not only useful tools to study gold(III) organometallic chemistry, but also competent and actually powerful catalysts.

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**Keywords:** alkynes • catalysis • cyclometalation • gold(III) • hydroarylation • P-based ligands

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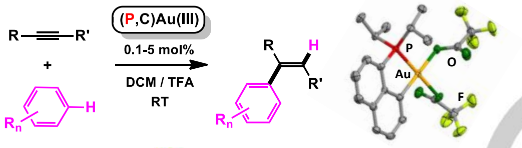
## Entry for the Table of Contents

COMMUNICATION

**Yes, Au(III) can do it and the ancillary ligand counts!** The first catalytic application of (P,C) cyclometalated gold(III) complexes is reported. They perform very well in the hydroarylation of alkynes, surpassing all known gold catalysts.



Gold(III) catalysis

✓ Key influence of the ancillary ligand: (P,C) outperforms (N,C)

✓ Unprecedented substrate scope (16 examples)

✓ High regio and stereoselectivity

*Charlie Blons, Sonia Mallet-Ladeira, Abderrahmane Amgoune* and Didier Bourissou**

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**(P,C) Cyclometalated Gold(III) Complexes: Highly Active Catalysts for the Hydroarylation of Alkynes**