DOI: 10.1002/ange.201304182

Cooperative Catalysis

Hydrophenoxylation of Alkynes by Cooperative Gold Catalysis**

*Yoshihiro Oonishi, Adrián Gómez-Suárez, Anthony R. Martin, and Steven P. Nolan**

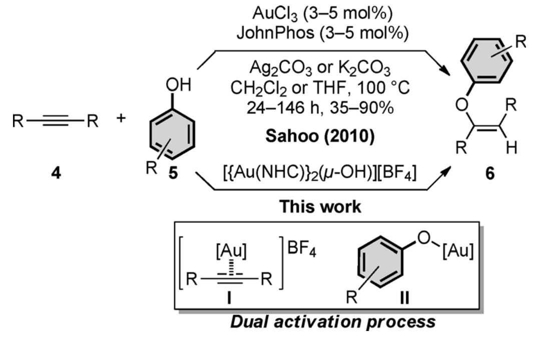
Dedicated to Professor Carl D. Hoff on the occasion of his 65th birthday

Over the past decade, the concept of cooperative or dual catalysis has emerged as an attractive and effective strategy to access unique reactivity and selectivity in synthetic organic chemistry.[1] This type of catalysis has been shown in dual organo-catalyzed,[2] organo- and transition-metal-catalyzed,[3] homobimetallic transition-metal-catalyzed[4] and heterobimetallic catalyzed[5] processes. Recently, it has also received increased attention in gold chemistry owing to the synthesis and isolation of dinuclear organogold species, such as *gem*-diaurated or σ,π-diaurated acetylide complexes.[6] These species were first proposed and later identified as key intermediates or catalyst reservoirs in gold-catalyzed reactions.[7] We recently contributed to this area with the synthesis of dinuclear gold hydroxide species $[\{Au(NHC)\}_2(\mu\text{-}OH)][BF_4]$ (**1**) (NHC = N-heterocyclic carbene), which can be easily prepared from commercially available [Au(NHC)(X)] (X = OH or Cl) complexes.[8] Complexes **1** have been shown to be highly active catalysts for silver- and acid-free gold-catalyzed transformations.[9] We have also recently reported straightforward access to both *gem*-diaurated and σ,π-diaurated acetylide species by reacting **1A** (NHC = IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with aryl/vinyl boronic acids and terminal alkynes, respectively.[10] In addition, complexes **1** exhibited particularly interesting catalytic properties. For example, during our studies of the gold-catalyzed nitrile hydration, the use of **1A** afforded higher conversions to the desired amide than the gold monomer $[Au(IPr)NTf_2]$.[8b] We have previously postulated that $[\{Au(NHC)\}_2(\mu\text{-}OH)][BF_4]$ (**1**) could be considered as a combination of $[Au(NHC)][BF_4]$ (**2**) and [Au(NHC)(OH)] (**3**).[8] We believe that, under the appropriate reaction conditions, this equilibrium could be displaced, thus liberating a Lewis acid **2** and a Brønsted base **3** that could produce a synergistic effect leading to enhanced catalytic activity [Eq. (1)].

$$\underset{\mathbf{1}}{[\{Au(NHC)\}_2(\mu\text{-}OH)][BF_4]} \rightleftharpoons \underset{\boxed{\text{Lewis acid}}}{\underset{\mathbf{2}}{[Au(NHC)][BF_4]}} + \underset{\boxed{\text{Brønsted base}}}{\underset{\mathbf{3}}{[Au(NHC)(OH)]}} \qquad (1)$$

Most gold-catalyzed transformations take advantage of the well-documented ability of gold to activate C−C multiple bonds, typically alkynes, towards nucleophilic attack.[11]

While the addition of primary and secondary alcohols to alkynes is relatively well-known,[12] reports of the addition of tertiary alcohols and phenols remain scarce. To our knowledge, there is only one report dealing with the gold-catalyzed hydrophenoxylation of alkynes.[13] In 2010, Sahoo and coworkers described the reaction between internal alkynes **4** and phenols **5** (2 equiv) using $AuCl_3$ (3–5 mol%) in the presence of K_2CO_3 or Ag_2CO_3 (2 equiv) under very harsh reaction conditions.[13] We envisioned that if **1** could act as a bifunctional catalyst, **2** might react with **4** forming a π-gold–alkyne complex **I**[14] and **3** might react with **5** forming a gold–phenoxide complex **II**[15] (Scheme 1).



Scheme 1. Dual activation in the hydrophenoxylation of alkynes.

We began our studies by reacting diphenylacetylene **4a** and phenol **5a** (1.1 equiv) in 1,4-dioxane at 80 °C using **1A** (0.5 mol %) as catalyst. We were pleased to observe after 1 h an encouraging 15 % conversion to the desired vinyl ether **6aa** by GC. With this result in hand, we proceeded to optimize the reaction conditions (Table 1). Interestingly, the use of less polar solvents allowed for better conversions (Table 1, entries 1–4). In toluene, a 97 % conversion was reached within 1 h at 80 °C (Table 1, entry 5). The ^{1}H NMR spectrum of the isolated product (96 %) confirmed the stereospecific formation of *Z*-isomer **6aa**.[13] Next, we screened various

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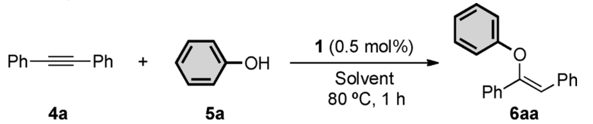
[*] Dr. Y. Oonishi, A. Gómez-Suárez, Dr. A. R. Martin,
Prof. Dr. S. P. Nolan
EaStCHEM School of Chemistry, University of St Andrews
St Andrews, KY16 9ST (UK)
E-mail: snolan@st-andrews.ac.uk
Homepage: http://chemistry.st-and.ac.uk/staff/spn/group/SP_Nolan/Home.html

[**] The ERC (Advanced Investigator Award-FUNCAT), EPSRC and Syngenta are gratefully acknowledged for support. Umicore AG is acknowledged for their generous gift of materials. The EPSRC National Mass Spectrometry Service Centre (NMSSC) is gratefully acknowledged for HRMS analyses. We thank Dr. David J. Nelson and Dr. Alba Collado for helpful discussions. S.P.N. is a Royal Society Wolfson Research Merit Award holder. Y.O. thanks the Uehara Memorial Foundation for a Research Fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304182.

Table 1: Optimization of the reaction conditions.[a]

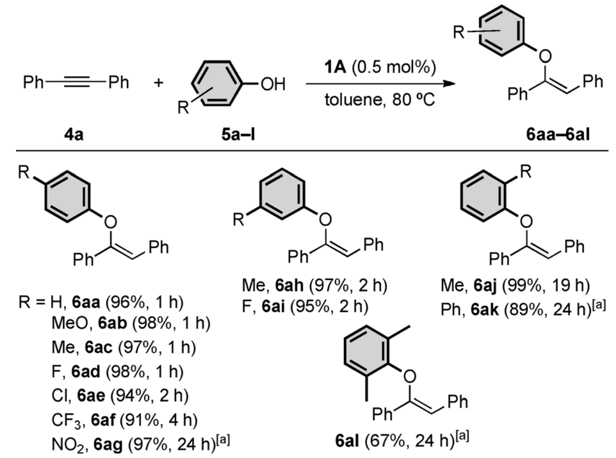


Entry	NHC	Solvent	Conversion [%][b]
1	IPr	1,4-dioxane	15
2	IPr	CH_3CN	2
3	IPr	DMF	1
4	IPr	1,2-dichloroethane	75
5	**IPr**	**toluene**	**97 (96)**
6	SIPr	toluene	45
7	IPr^{Cl}	toluene	94
8	IPent	toluene	86

[a] Conditions: **4a** (0.50 mmol), **5a** (0.55 mmol, 1.1 equiv), [Au] (0.5 mol%), solvent (1 mL), 80 °C. [b] Conversions determined by GC. Average of at least two runs. Yield of isolated product in parentheses.

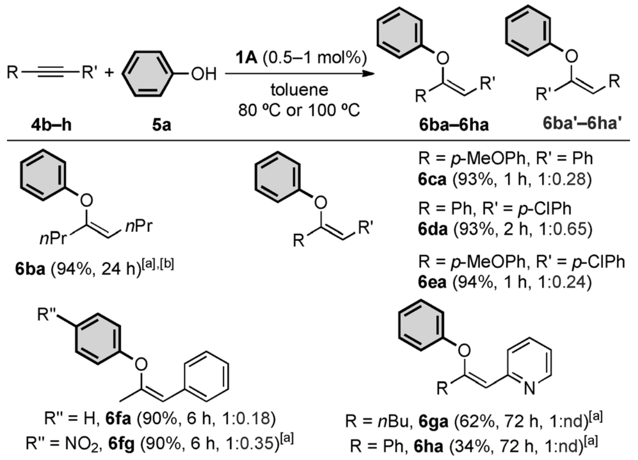
digold hydroxide complexes. While the catalyst bearing SIPr ligands performed poorly, IPr^{Cl} and IPent derivatives[9,16] afforded good to excellent conversions (Table 1, entries 6–8). Since $[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ afforded slightly better conversions and can be easily synthesized from commercially available complexes, 0.5 mol% of **1A** in toluene at 80 °C was selected as our optimized catalytic conditions. This new methodology permits a turnover frequency (TOF) of nearly 4 orders of magnitude greater than the previous state of the art (192 h^{-1} versus 0.05 h^{-1}).[13] Having established the optimized reaction conditions, the scope and limitations of the method were explored.

We first examined the reaction between diphenylacetylene **4a** and several phenol derivatives (Scheme 2). The reaction of phenols **5b** and **5c**, bearing electron-donating groups at the *para*-position, proceeded smoothly to afford the desired aryl vinyl ethers **6ab** and **6ac** in high yields within 1 h (Scheme 2). In contrast, phenols **5d**–**5g** bearing electron-withdrawing groups at the *para*-position needed longer reaction times to reach completion. The corresponding compounds **6ad**–**6ag** were isolated in high yields (91–98%). The reaction time increases as follows: $MeO \approx Me \approx H \approx F < Cl < CF_3 < NO_2$. Interestingly, this trend is the opposite of that observed by Sahoo and co-workers.[13] This observation points to a different reaction mechanism operating in these two systems. The use of sterically hindered substrates was then tested. The reaction with *ortho*-substituted phenols (**5j** and **5k**) afforded the expected ethers (**6aj** and **6ak**) in 99% and 89% yields, respectively, although at a cost of longer reaction times. Surprisingly, even the use of the highly sterically hindered 2,6-dimethylphenol (**5l**) afforded the desired product **6al** in 67% yield.



Scheme 2. Hydrophenoxylation using various phenols. Conditions: **4a** (0.50 mmol), **5a–l** (0.55 mmol, 1.1 equiv), **1A** (0.5 mol%), toluene (1 mL), 80 °C. Yields of isolated products are given. Average of two runs. [a] **1A** (1 mol%), 110 °C.

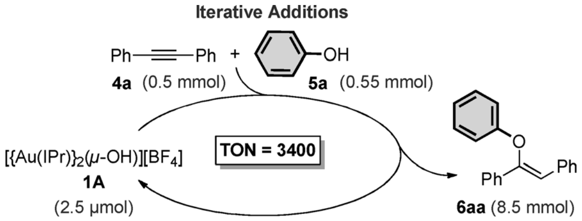
Reactions between various alkynes **4** and phenol **5a** (Scheme 3) were investigated. Dialkyl-substituted **4b** afforded the desired product **6ba** in 94% yield in a stereospecific manner. The hydrophenoxylation of unsymmetrical diaryl-substituted alkynes **4c**–**4e** provided the corresponding products **6ca**–**6ea** stereospecifically in high yields but moderate regioselectivities. Better regioselectivities were observed when one of the aryl moieties bears a methoxy group at the *para*-position (1:0.28 versus 1:0.65). When 1-phenylpropyne (**4f**) was used, the regioselectivity improved to 1:0.18. The reaction of **4f** with 4-nitrophenol (**5g**) instead of **5a** was also investigated. Vinyl ether **6fg** was obtained as the major product. Interestingly, the regioselectivity in this reaction is the opposite of that observed by Sahoo and co-workers (**6fg**/**6fg′** = 1:0.35 versus 0.61:1), thus pointing again towards a different reaction mechanism in each methodology.[13] The reactions using alkynes **4g** and **4h**, having a directing group such as pyridine, were then tested. Gratifyingly, the reaction proceeded with complete regioselectivity,



Scheme 3. Hydrophenoxylation using various unsymmetrical alkynes. Conditions: **4c–h** (0.50 mmol), **5a** or **5g** (0.55 mmol, 1.1 equiv), **1A** (0.5 mol%), toluene (1 mL), 80 °C. Yields of isolated products are given. Average of two runs. Ratio **6**/**6′** was determined by ^1H NMR spectroscopy. nd = not detected. [a] **1A** (1 mol%), 110 °C. [b] **4b** (0.55 mmol) and **5a** (0.50 mmol).

although at lower rates, affording aryl vinyl ethers **6ga** and **6ha** in moderate and low yields of 62 % and 34 %, respectively.

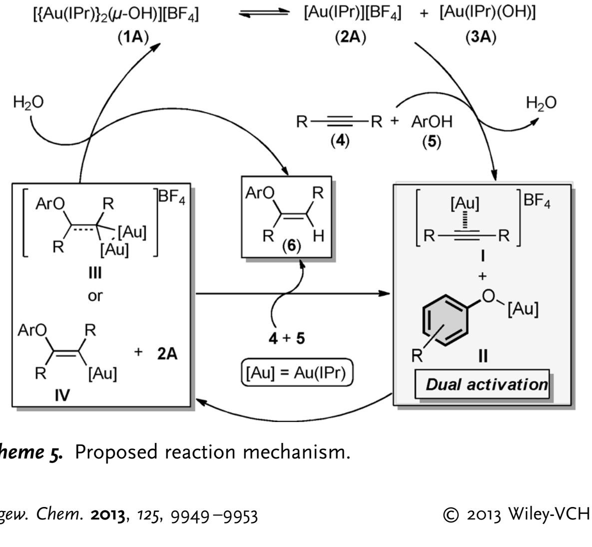
To assess the recyclability of **1A**, once the reaction between alkyne **4a** and phenol **5a** was complete, iterative additions of both substrates (0.5 and 0.55 mmol, respectively) were conducted. As a result, 8.5 mmol of **4a** were converted over 36 h by using 2.5 μmol of **1A** affording an impressive turn over number (TON) of 3400! To relate this to the previous state of the art, the procedure reported by Sahoo and co-workers afforded a TON of 7 for **6aa** (Scheme 4).[13]



Scheme 4. Iterative additions of **4a** and **5a** to the catalytic reaction.

Once the scope and limitations of the system were established, the reaction mechanism was probed. A dual activation mechanism was hypothesized for the hydrophenoxylation of internal alkynes as depicted in Scheme 5. In this mechanistic scenario, [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**1A**) is in equilibrium with [Au(IPr)][BF$_4$] (**2A**) and [Au(IPr)(OH)] (**3A**) under the reaction conditions. [Au(IPr)][BF$_4$] (**2A**) activates alkyne **4** to form the π-gold–alkyne complex **I**,[14] while [Au(IPr)(OH)] (**3A**) reacts with phenol **5** to provide the gold–phenoxide complex **II**.[15] The latter then attacks from the opposite side of **I** to give a *gem*-diaurated compound **III**[7] or σ-monoaurated compound **IV**[17] along with [Au(IPr)][BF$_4$] (**2A**). Similar intermediates have recently been proposed for the addition of MeOH to alkynes.[18] Finally, protodeauration of **III** or **IV** with phenol **5** or H_2O takes place to afford vinyl ether **6** (Scheme 5).

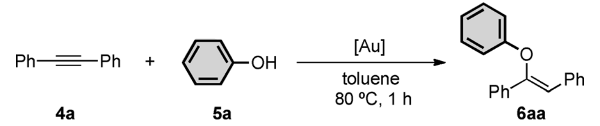
To support this mechanistic proposal, the possible equilibrium between **1A**, **2A**, and **3A** was examined. When mixing [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**1A**) and [{Au(SIPr)}$_2$(μ-OH)][BF$_4$] (**1B**)[16,19] a statistical distribution (1:1:2) was observed between **1A**, **1B**, and the cross-over product [{Au(IPr)}{Au(SIPr)}(μ-OH)][BF$_4$] (**1C**).[20] This result strongly supports the existence of the above-mentioned equilibrium.



Scheme 5. Proposed reaction mechanism.

Next, the use of **2A** and **3A** as catalysts was investigated (Table 2). Since **2** is not a stable species, [Au(IPr)(CH$_3$CN)][BF$_4$] (**2A′**) was employed. **2A′** and [Au(IPr)(OH)] **3A** performed poorly with 40 % and < 1 % conversion, respectively (Table 2, entries 1 and 2). We have previously postulated that **2A′** could lead to in situ generation of **1A** in the presence of water.[8b] Since the reaction was carried out using technical-grade toluene, this could explain the moderate conversions observed using **2A′** as catalyst. To confirm this, the reaction was repeated in the presence of 3 drops of water, where an improved conversion of 81 % was observed, whereas under anhydrous conditions poor conversions were obtained (Table 2, entries 3–4). This series of experiments unequivocally establishes that **2A** or **3A** alone cannot efficiently catalyze the reaction. Nevertheless, the combination of both **2A′** (0.5 mol %) and **3A** (0.5 mol %) showed high conversion (87 %; Table 2, entry 5). Next, π-gold–alkyne complex **I**[14] and gold–phenoxide complex **II**[15] were synthesized following the reported methodologies and tested in catalysis. Gratifyingly, the combination of both **I** (0.5 mol %) and **II** (0.5 mol %) afforded a 97 % conversion (Table 2, entry 6). These results are consistent with our proposal that a digold hydroxide species **1** can act as cooperative bifunctional catalyst to permit the efficient hydrophenoxylation of alkynes.

Table 2: Catalyst studies.[a]



Entry	Catalyst (mol %)	Conversion [%][b]
1	(**2A′**) [Au(IPr)(CH$_3$CN)][BF$_4$] (1)	40
2	(**3A**) [Au(IPr)(OH)] (1)	< 1
3	**2A′** (1) + H_2O	81
4[c]	**2A′** (1)	33
5	**2A′** (0.5) + **3A** (0.5)	87
6	**I (0.5) + II (0.5)**	**97**

[a] Conditions: **4a** (0.50 mmol), **5a** (0.55 mmol, 1.1 equiv), toluene (1 mL), 80 °C. [b] Conversions determined by using GC. Average of two runs. [c] Anhydrous conditions.

To further support our hypothesis of dual gold activation, a number of stoichiometric reactions were carried out.[20] Owing to solubility problems in [D$_8$]toluene, experiments were carried out in CD_2Cl_2.[20] Also, since the presence of water can displace equilibria towards formation of **1A**, anhydrous conditions were used.[20] First we investigated if **1A** could interact with either of the substrates.

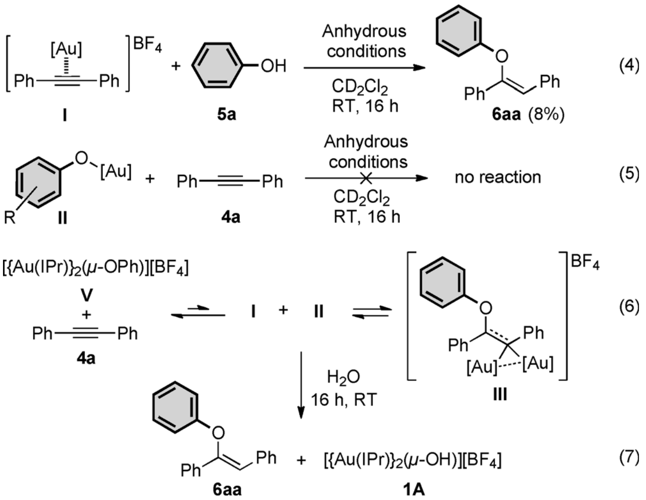
After 16 h at room temperature no reaction was observed between **1A** and alkyne **4a**.[20] However, complete conversion into **1A** and **4a** was observed when mixing **3A** and π complex

I, thus strongly suggesting the existence of an equilibrium between these species [Eq. (2)].[20] When reacting **1A** and phenol **5a**, approximately 50% conversion to a new species could be observed.[20] In the presence of molecular sieves, only one species was observed. ^{1}H and ^{13}C NMR spectroscopy as well as elemental analysis suggest the new species is [{Au(IPr)}$_2$(μ-OPh)][BF$_4$] (**V**) [Eq. (3)].

$$\mathbf{1A} + \mathbf{4a} \xrightleftharpoons[\text{RT, 16 h}]{\text{CD}_2\text{Cl}_2} \mathbf{3A} + \mathbf{I} \qquad (2)$$

$$\mathbf{1A} + \mathbf{5a} \xrightleftharpoons[\text{RT, 16 h}]{\text{CD}_2\text{Cl}_2} \underset{(\mathbf{V})}{[\{\text{Au(IPr)}\}_2(\mu\text{-OPh})][\text{BF}_4]} + \text{H}_2\text{O} \qquad (3)$$

The interactions between **I**, **II**, **4a**, and **5a** were also examined. Only 8% conversion to **6aa** was observed when reacting phenol **5a** and **I** for 16 h at room temperature [Eq. (4)]. Moreover, no reaction was observed between alkyne **4a** and phenoxide **II** under identical reaction conditions, whereas the reaction between π complex **I** and **II** occurred within mixing time [Eq. (5)–(6)]. After 5 min, complete consumption of the starting materials was observed and two new species were detected by ^{1}H NMR spectroscopy in a 1:3 ratio.[20] The minor species was identified as digold phenoxide **V**. We hypothesized that **V** may be in equilibrium with **I**, **II**, and alkyne **4a**. This equilibrium favors formation of the diaurated species **V**, the same as the equilibrium in Equation (2) favoring formation of **1A**.[20] In addition, we postulated that the major species could be the *gem*-diaurated complex **III**, and what is observed is an equilibrium between **V**, **4a**, and **III** [Eq. (6)]. Therefore, when an excess of alkyne **4a** was added to the reaction mixture, **III** and **4a** are observed. Unfortunately, attempts to isolate *gem*-diaurated species **III** were not successful, because once the excess of **4a** is removed a mixture between digold–phenoxide **V**, **4a**, and **III** was obtained, thus further supporting the hypothesis that this step is an equilibrium.[20,21] If the reaction mixture of π complex **I** and gold–phenoxide **II** is quenched with H$_2$O, complete conversion to the desired vinyl ether **6aa** and digold hydroxide **1A** can be observed [Eq. (7)].[20]



In summary, we have developed a mild and straightforward methodology for the hydrophenoxylation of alkynes, using digold–hydroxide complexes, to form various aryl vinyl ethers in good to high yields with good regioselectivities. The current data strongly support a dual activation pathway; digold hydroxide **1A** dissociates into a Lewis acid **2A** and a Brønsted base **3A** and these species will independently react with substrates **4** and **5** respectively. Owing to this synergistic effect, the hydrophenoxylation of alkynes proceeds smoothly under relatively mild conditions. We postulate that diaurated species **III** and **V** can be observed under anhydrous conditions, but we are not able, at this point, to determine their role in reactions conducted under catalytic conditions. These findings provide new insights into the chemistry of gold catalysis and open the door to the development of new catalytic transformations. Further studies to delineate the scope, limitations, and the detailed mechanism of this and related reactions are in progress.

Received: May 15, 2013

Keywords: alkynes · cooperativity · gold · homogeneous catalysis · N-heterocyclic carbenes

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[20] See the Supporting Information for further experimental details.

[21] For another example of reversible C–O bond formation see Ref. [7d].