Hydrophenoxylation of Alkynes by Cooperative Gold Catalysis**

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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 gemdiaurated 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(µ-OH)]- $[BF_4]$ (1) (NHC = N-heterocyclic carbene), which can be easily prepared from commercially available [Au(NHC)(X)] $(X = OH \text{ or } Cl) \text{ complexes.}^{[8]} \text{ Complexes } 1$ have been shown to be highly active catalysts for silver- and acid-free goldcatalyzed transformations.^[9] We have also recently reported straightforward access to both gem-diaurated and σ,π -diaurated acetylide species by reacting 1A (NHC = IPr = 1,3bis(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 goldcatalyzed 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- $(NHC)_{2}(\mu-OH)$ [BF₄] (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

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and a Brønsted base **3** that could produce a synergistic effect leading to enhanced catalytic activity [Eq. (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 AuCl₃ (3–5 mol%) in the presence of K₂CO₃ or Ag₂CO₃ (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 ¹H NMR spectrum of the isolated product (96%) confirmed the stereospecific formation of Z-isomer **6aa**.^[13] Next, we screened various

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

Ph—≡	<u>≕</u> −Ph +	Днон –	1 (0.5 mol%)	Ph Ph
4	a	5a	80 °C, 1 h	6aa
Entry	NHC	Solvent		Conversion [%] ^[b]
1	IPr	1,4-dioxar	ie	15
2	IPr	CH₃CN		2
3	IPr	DMF		1
4	IPr	1,2-dichlo	roethane	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(μ -OH)][BF₄] 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



Scheme 2. Hydrophenoxylation using various phenols. Conditions: **4a** (0.50 mmol), **5a**–I (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.

desired aryl vinyl ethers 6ab and 6ac in high yields within 1 h (Scheme 2). In contrast, phenols 5d-5g bearing electronwithdrawing 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 (51) afforded the desired product 6al in 67% yield.

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 stereo-specific manner. The hydrophenoxylation of unsymmetrical



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).

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 1phenylpropyne (**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 coworkers (**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, 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, $[{Au(IPr)}_2(\mu-OH)][BF_4]$ (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 \mathbf{II} .^[15] The latter then attacks from the opposite side of I to give a gem-diaurated compound $\mathbf{III}^{[7]}$ or σ -monoaurated compound $\mathbf{IV}^{[17]}$ 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 H₂O 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)][BF₄] (**1A**) and [{Au(SIPr)}₂(μ -



Scheme 5. Proposed reaction mechanism.

Angew. Chem. Int. Ed. 2013, 52, 9767–9771

OH)][BF₄] (**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)][BF₄] (**1C**).^[20] This result strongly supports the existence of the above-mentioned equilibrium.

Next, the use of 2A and 3A as catalysts was investigated (Table 2). Since 2 is not a stable species, [Au(IPr)(CH₃CN)]- $[BF_4]$ (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 $\mathbf{I}^{[14]}$ and gold–phenoxide complex $\mathbf{II}^{[15]}$ 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]

Ph-		Ба -ОН	[Au] toluene 80 ºC, 1 h	Ph 6aa
Entry	Cataly	Conversion [%] ^[b]		
1	(2 A')	40		
2	(3 A) [<1		
3	2A' (1	81		
4 ^[c]	2 A' (1	33		
5	2A' (0	87		
6	I (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. ¹H and ¹³C NMR spectroscopy as well as elemental analysis suggest the new species is [{Au-(IPr)}₂(μ -OPh)][BF₄] (**V**) [Eq. (3)].

$$1A + 4a \xrightarrow[CD_2Cl_2]{} 3A + I$$
(2)
RT 16 h

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 16h 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 ¹H 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 \mathbf{II} is quenched with H₂O, 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.

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