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Internal alkyne regio- and chemoselectivity using a zwitterionic [(NHC)Au(I)] catalyst in a silver-free alkyne hydration reaction

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Abstract. An alkyne hydration of terminal and internal alkynes is reported using a zwitterionic NHC Au catalyst, (BNHC)Au(SMe_2) (**1**), in the absence of silver and Brønsted acid additives. The hydration demonstrates good regioselectivity in alkyne hydration and chemoselectivity for internal alkynes vs. terminal. In addition, (**1**) performs a propargyl alcohol hydration to predominantly form α-hydroxy methyl ketone over the more common Meyer-Schuster rearrangement product. While complex (**1**) is active without silver additives, addition of $AgSbF_6$ increases reaction rate and decreases selectivity for internal alkyne hydration over terminal substrates. To our knowledge, the rate enhancement of (**1**) by $AgSbF_6$ is the first such demonstration of a silver effect for a "halide-free" Au catalyst.

Keywords: alkynes; silver; N-heterocyclic carbenes; regioselectivity; gold

Introduction

Gold catalysts for alkyne functionalization have yielded many valuable methods for organic synthesis,[1-8] but regioselective hydration of internal alkynes remains challenging[9] despite several[10-14] computational and experimental mechanistic explorations of Au alkyne reactions. In general, hydration catalysts are less reactive towards internal alkynes relative to terminal groups and demonstrate low regioselectivity.[9]

One complication in designing selective Au catalysts is the complex role of various additives such as the Ag promoters employed in many Au-catalyzed reactions. Silver salts, assumed to generate $[L\text{-}Au]^+$ via halide abstraction from Au-X, were found to exhibit a further "silver effect" by Shi and coworkers where $[L\text{-}Au]^+$ cannot perform internal alkyne hydration in the absence of a Ag co-catalyst.[10] In constrast, Nolan and co-workers[15-19] have reported a silver-free pre-catalyst ($[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ (**A**) active for the hydration of internal alkynes. Various studies[20-23] have shown Ag can react with gold precatalysts, forming either low-activity chloride-bridged digold complexes as a result of incomplete halide abstraction[21] or Au/Ag heterobimetallic species,[23-24] but to our knowledge Ag has not been shown to directly participate in a Au catalytic cycle. For example, Zhdanko and Maier[20] found Ag effects are limited to influencing concentrations of organogold intermediates or H^+ in Au-catalyzed alkyne hydroalkoxylation. $AgSbF_6$ itself is an active catalyst for terminal alkynes,[25-26] but we are unaware of a monometallic Ag hydration of internal alkynes.

Mechanistic questions and regioselectivity issues extend to Ag-free alkyne hydrations and related functionalization reactions. One of the first Au-catalyzed alkyne hydration systems, an Ag-free mixture of $[(PPh_3)AuCH_3]$ and concentrated sulfuric acid, was poorly reactive towards internal alkynes relative to terminal alkynes.[27] In the absence of additives, $[Ph_3PAuCl]$ is competent for terminal alkyne hydration, but not for hydration of diphenylacetylene.[28] The silver-free $(L)AuNTf_2$[29-30] alkyne hydration system exhibits moderate regioselectivity for internal alkyne substrates. In the related hydrocarboxylation reaction of internal alkynes with benzoic acid catalyzed by **A**, Nolan and coworkers report "good to complete regioselectivity" results from favored addition at the more electrophilic carbon of the alkyne triple bond[18] - similar to the regioselectivity exhibited by alkyne hydration catalyzed by the $[(IPr)AuCl]/AgSbF_6$ system.[5, 31] Given the range of selectivity in these examples, Ag additives appear to be only one of many factors with potential relevance to regioselectivity and chemoselectivity.

Other potential influences of reaction selectivity may include dimer formation. In one case, speciation of a Au hydroalkoxylation catalyst as a monometallic or bimetallic species depends on the steric encumbrance of the ancillary ligand,[14, 32] and different pathways may well demonstrate different reaction selectivity in alkyne hydration. Another complicating issue is the role of counteranions in catalysis.[5, 11, 33-35] Counteranions are commonly

introduced by mixing Au precatalysts with Ag salts of weakly-coordinating anions (WCAs) such as SbF_6. Besides Ag, other salts of WCAs can influence the rate of alkyne hydration (e.g., $KCTf_3$) even in reactions without Au halide precursors.[36] Among other potential roles, anion X may influence reactivity by forming tight [L-Au---X] ion pairs with cationic Au intermediates[37-39] and may facilitate protodeauration in alkyne hydroalkoxylation.[11] Brønsted and Lewis acids can each influence rates of Au-catalyzed hydration.[40] The formation of Brønsted acid HX in situ could also play a role in dictating product distributions, given the known hydration activity of strong acids.[41]

In developing new selective alkyne hydration methods, we sought a Au catalyst system that minimizes complications arising from both Ag additives and WCAs. Since commonly-proposed $[L\text{-}Au(I)]^+$ intermediates are cationic, some weakly-coordinating anionic species is necessary for charge balance. One emerging approach is the use of dative ligands covalently attached to weakly-coordinating anionic residues, rather than relying on an exogenous WCA. Several zwitterionic organometallic complexes of Au[42-45] have now been prepared, each featuring weakly coordinating anionic ligands that bind in a dative fashion. For example, Tamm and coworkers[42] have prepared an anionic *N*-heterocyclic carbene (BNHC) that is covalently attached to a weakly coordinating borato substituent. Zwitterionic organometallic complexes of Au[42] and Ir[46] were successfully used by Tamm in homogeneous catalysis. Given the activity of BNHC-Au catalysts in the rearrangement of an enyne,[42] we chose to study Au alkyne hydration catalysts incorporating the Tamm BNHC ligand.

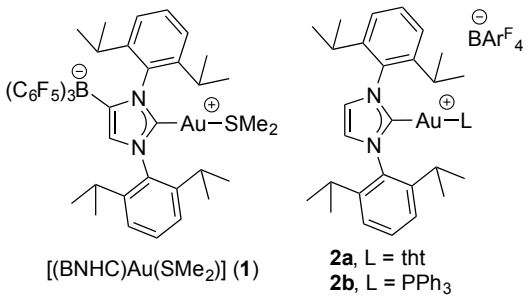


Figure 1. [(NHC)Au(I)] complexes.

We find that the zwitterionic gold (I) complex **1** (Figure 1) featuring Tamm's BNHC ligand is effective in alkyne hydration in the absence of silver and acid additives, and that regioselectivity of internal alkyne hydration with **1** is among the highest reported. Additionally, hydration with **1** demonstrates unusual chemoselectivity compared to existing systems.

Results and Discussion

Zwitterionic [(BNHC)Au(SMe_2)] (**1**) was synthesized following a modified literature procedure.[42] Reaction of commercially available IPr with *n*-BuLi and $B(C_6F_5)_3$ afforded the BNHC as a lithium salt, which was then reacted with Me_2SAuCl to form **1**. The complex in the solid state (Figure 2) demonstrates a near-linear geometry (C(3)-Au(1)-S(1) 176.72(11)°) consistent with BNHC-Au structures reported by Tamm and coworkers.[42]

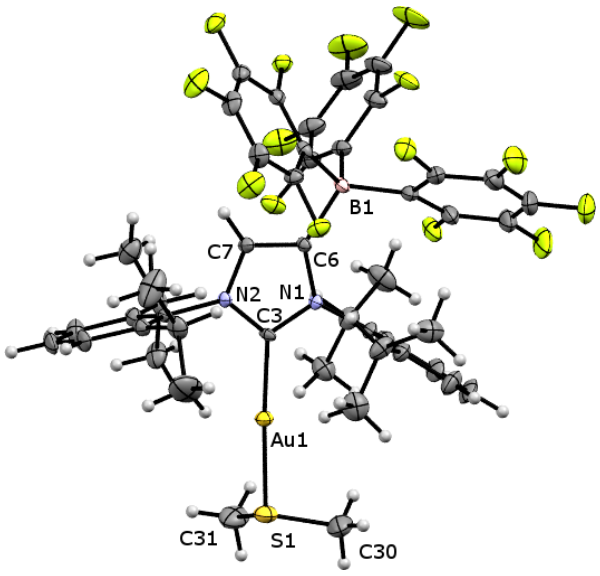


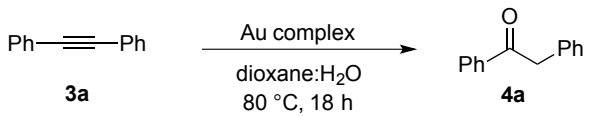
Figure 2. Thermal ellipsoid plot of [(BNHC)Au(SMe_2)] (**1**). Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Au(1)-C(3) 2.022(4), Au(1)-S(1) 2.3077(13), S(1)-C(31) 1.794(6), S(1)-C(30) 1.809(6), N(1)-C(3) 1.354(5), N(1)-C(6) 1.417(5), N(2)-C(3) 1.331(5), N(2)-C(7) 1.385(5), B(1)-C(6) 1.652(6); C(3)-Au(1)-S(1) 176.72(11), C(31)-S(1)-C(30) 100.4(3), C(31)-S(1)-Au(1) 105.9(2), C(30)-S(1)-Au(1) 102.9(2), C(3)-N(1)-C(6) 111.5(3), C(3)-N(2)-C(7) 109.3(3), N(2)-C(3)-N(1) 106.3(3), N(2)-C(3)-Au(1) 128.5(3), N(1)-C(3)-Au(1) 125.1(3), C(7)-C(6)-N(1) 102.7(3), C(7)-C(6)-B(1) 121.7(4), N(1)-C(6)-B(1) 135.5(3), C(6)-C(7)-N(2) 110.1(4).

For catalysis comparison, two [(NHC)Au][X] complexes with a conventional WCA, (BAr^F_4, tetrakis(3,5-bis(trifluoromethyl)phenyl)borate)), were also prepared. [(IPr)Au(tht)][BAr^F_4] (**2a**; tht = tetrahydrothiophene) was prepared by treating (tht)AuCl with $NaBAr^F_4$ and IPr. The synthesis of [(IPr)Au(PPh_3)][BAr^F_4] (**2b**) required the reaction of (tht)AuCl with $NaBAr^F_4$ and PPh_3 followed by the addition of IPr.

To compare the alkyne hydration activity of zwitterionic **1** to other Au catalysts, catalytic runs were performed with diphenylacetylene as the substrate (Table 1), since it has been widely used as a benchmark of activity.[15] Alkyne hydration was

performed in a mixture of 1,4-dioxane and water (2:1) at 80 °C for 18 h, conditions previously optimized with gold(I) systems.[5] **1** converted diphenylacetylene to the corresponding ketone in excellent yield (Table 1). We note that **1** is air stable and reactions were conducted under aerobic conditions.

Table 1. Screen of Au Complexes for Alkyne Hydration.[a]



3a **4a**

Entry	Au complex	Yield (%)[b]
1	[(BNHC)Au(SMe$_2$)], **1**	92
2	None	NR[c]
3	Ph_3PAuCl	NR
4	$Ph_3PAuCl/NaBAr^F{}_4$	NR
5	$Ph_3PAuCl/AgOTf$	2
6	$Ph_3PAuCl/AgSbF_6$	2
7	$Ph_3PAuCl/AgSbF_6/PPh_3$	NR
8	IPrAuCl	NR
9	$IPrAuCl/AgSbF_6$	94
10	$IPrAuCl/NaBAr^F{}_4$	8
11	$IPrAuCl/NaBAr^F{}_4/PPh_3$	NR
12	[(IPr)Au(PPh_3)][$BAr^F{}_4$], **2b**	NR
13	[(IPr)Au(tht)][$BAr^F{}_4$], **2a**	4

[a] Reaction conditions: Au complex (1 mol %) and diphenylacetylene (0.5 mmol) 1,4-dioxane:H_2O (2:1, 1.5 mL), 80 °C, 18 h.
[b] Reaction yield determined by ^{1}H NMR.
[c] NR = no reaction.

Ph_3PAuCl failed as a catalyst even in the presence of $NaBAr^F{}_4$, AgOTf or $AgSbF_6$, with no more than 2% obtained (Table 1, Entries 2-5). Additional PPh_3 did not improve the reaction (Table 1, entry 7). IPrAuCl produced diphenylacetylene hydration in excellent yield in the presence of $AgSbF_6$ (Table 1, entry 9) confirming earlier results of Nolan and coworkers.[5] $NaBAr^F{}_4$ was not effective in activating the IPrAuCl, only affording 8% yield of the corresponding ketone (Table 1, entry 10), and again addition of PPh_3 resulted in no reaction (Table 1, entry 11). **2b** afforded no reaction (Table 1, entry 12) while **2a** produced 4% yield (Table 1, entry 13).

Various catalyst loadings of **1** were also studied. When the catalyst loading was reduced to 0.5 mol%, 1000 ppm, and 100 ppm, reaction yields dropped to 25%, 2%, and 0%, respectively. Changing solvent did not improve the yield, but reaction in the less toxic dioxane alternative[47] cyclopentyl methyl ether produced ketone in very good (85%) yield. Replacing 1,4-dioxane with THF produced 63%, while use of MeOH as solvent resulted in MeOH addition to alkyne. Temperatures below 80 °C reduced the benzyl phenyl ketone yield while elevated temperatures did not produce higher yields.

Unlike many other alkyne hydration precatalysts, Ag salts are not required to activate zwitterionic precatalyst **1** via halide abstraction. Nevertheless, to investigate any further role of silver salts[10] in internal alkyne hydration, $AgSbF_6$ was added to the reaction of **1**. When 1 mol% of $AgSbF_6$ was used with 1 mol% of **1**, the rate of the reaction was significantly increased (Figure 3). A 90-minute induction period was observed in the absence of silver salt, while 1 mol% $AgSbF_6$ shortens the induction period to approximately 1 hour. Increasing the silver loading to 2 mol% did not improve the rate of the reaction further. Addition of $NaSbF_6$ did not appear to accelerate the rate of hydration. We note that $AgSbF_6$ alone does not hydrate internal alkynes under these conditions. In an attempt to isolate a potential Au/Ag bimetallic complex, a 1:1 mixture of **1** and $AgSbF_6$ was stirred in a mixture of 1,4-dioxane and H_2O (2:1, 1.5 mL) at 80 °C for 3 h but no adducts or bimetallic species were observed – only starting material was recovered.

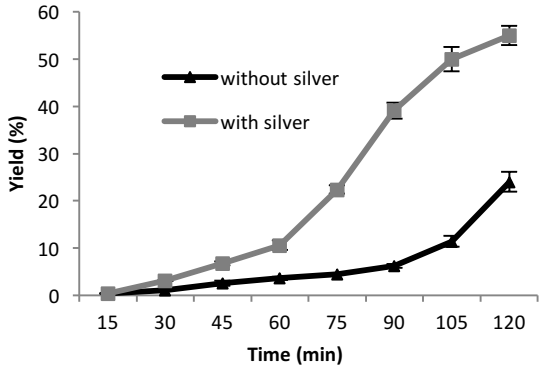
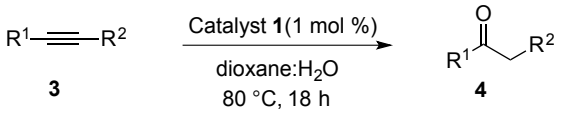


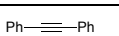
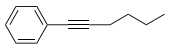
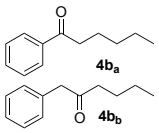
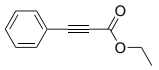
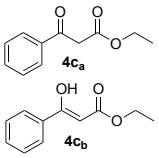
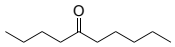
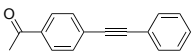
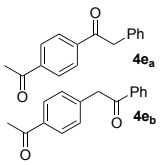
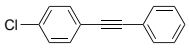
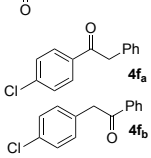
Figure 3. Plot of yield (%) versus time (min) for the hydration of diphenylacetylene using **1** either with or without $AgSbF_6$. Conditions: **1** (5 μmol), $AgSbF_6$ (5 μmol or none) and diphenylacetylene (0.5 mmol), 1,4-dioxane:H_2O (2:1, 1.5 mL), 80 °C. Reaction yield determined by ^{1}H NMR.

With optimized reaction conditions in hand, the substrate scope of catalyst **1** was examined (Table 2). In order to test the regioselectivity of the system, several internal alkyne hydrations were performed. Both **3b** and **3c** converted to products quantitatively (Table 2, entries 2 and 3). Reaction of 1-phenyl-1-hexyne afforded a 1:7.3 **4b$_a$**:**4b$_b$** product ratio (Table 2, entry 2), a relatively high regioselectivity for the hydration of an aryl alkyl substituted alkyne,[9] and the opposite selectivity of that expected under acid-catalyzed hydration conditions.[40] In the case of ethyl phenylpropiolate, only one ketone isomer was formed along with its enol tautomer in a 4.7:1 ratio (Table 2, entry 3). The ester group was retained during this hydration, highlighting the mild nature of the catalytic conditions. An internal aliphatic alkyne, 5-decyne, was also hydrated in very good yield (Table 2, entry 4). Diphenylacetylene with an acyl substituent underwent the hydration to form one

ketone isomer predominantly in a 4.5:1 **4e$_a$**:**4e$_b$** ratio (Table 2, entry 5). A substrate with a chloro substituent was unreactive and may be incompatible with the catalytic protocol (Table 2, entry 6).

Table 2. Substrate Scope of Alkyne Hydration of Internal Alkynes.[a]

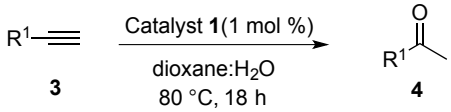


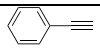
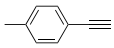
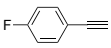
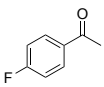
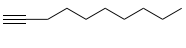
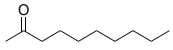
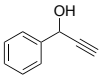
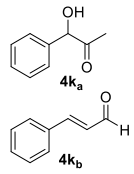
Entry	Substrate	Product	Yield (%)[b]
1			92
2			>99 **4b$_a$**:**4b$_b$** 1:7.3
3			>99 **4c$_a$**:**4c$_b$** 4.7:1
4			86
5			>99 **4e$_a$**:**4e$_b$** 4.5:1
6			0

[a] Reaction conditions: **1** (5 μmol) and substrate (0.5 mmol) in a mixture of 1,4-dioxane and H_2O (2:1, 1.5 mL) were stirred at 80 °C for 18 h.
[b] Reaction yields and regioselectivities determined by ^{1}H NMR.

Reactivity of several terminal alkynes was also tested (Table 3). Relative to internal alkynes, terminal alkynes afforded lower conversions over 18 h using catalyst **1**, contrary to what has been observed with other systems.[27] Phenylacetylene was hydrated to form acetophenone in 62% yield (Table 3, entry 1). Electronic effects strongly influence reactivity with 88% and 38% yield achieved with a methyl-substituted and a fluoro-substituted substrate, respectively (Table 3, entries 2 and 3). An alkyl substituted terminal alkyne, 1-decyne, was converted in excellent yield (Table 3, entry 4). 1-phenyl-2-propyn-1-ol was hydrated and yielded 44% of the corresponding α-hydroxy methyl ketone (Table 3, entry 5) as well as 28% yield of the α,β unsaturated aldehyde, **4k$_b$**, the product expected from the Meyer-Schuster rearrangement.[48] The 1.6:1 ratio of products obtained in entry 5 is informative from a mechanistic standpoint. Shi and co-workers state that gold(I) catalysts are ineffective towards propargyl alcohol hydration to form α-hydroxy methyl ketones,[10] while Nolan and coworkers find [{Au(IPr)}$_2$(μ-OH)][BF_4] an active catalyst to *exclusively* form the Meyer-Schuster rearrangement product.[15]

Table 3. Substrate Scope of Alkyne Hydration of terminal alkynes.[a]



Entry	Substrate	Product	Yield (%)[b]
1			62
2			88
3			38
4			98
5			72 **4k$_a$**:**4k$_b$** 1.6:1

[a] Reaction conditions: **1** (5 μmol) and substrate (0.5 mmol) in a mixture of 1,4-dioxane and H_2O (2:1, 1.5 mL) were stirred at 80 °C for 18 h.
[b] Reaction yields and regioselectivities determined by ^{1}H NMR.

As mentioned above, 18-hour conversions obtained for internal alkynes were higher than for terminal alkynes. To test the chemoselectivity of (**1**), an equimolar mixture of diphenylacetylene and phenylacetylene was reacted under the same reaction conditions as in Table 1 (1 mol% Au loading relative to the sum of alkynes present). The reaction favored hydration of the internal alkyne, producing benzyl phenyl ketone to acetophenone in a 5.2:1 ratio with 59% combined yield. The relative concentrations of phenylacetylene and diphenylacetylene over time (Figure 4**a**) show that initial, slow hydration of phenylacetylene is eventually outpaced by hydration of internal alkyne after 6 hours. The overall reaction rate is considerably slower than internal-only hydration (Figure 3) despite identical Au/alkyne loading (1 mol%). Adding $AgSbF_6$ to the reaction significantly increased the initial rate of phenylacetylene hydration, but like the silver-free reaction terminal hydration eventually slows and is outpaced by internal hydration. The faster initial

phenylacetylene hydration results in a benzyl phenyl ketone to acetophenone ratio of 1.8:1 (77% overall yield). In our hands, the same reaction performed with IPrAuCl/$AgSbF_6$[5] surprisingly produced very low yield (3%) of acetophenone and 0% benzyl phenyl ketone. Since IPrAuCl/$AgSbF_6$ efficiently hydrates phenylacetylene and diphenylacetylene in single-substrate runs, the catalyst inhibition stems from some effect upon combining these two substrates in our competition experiment.

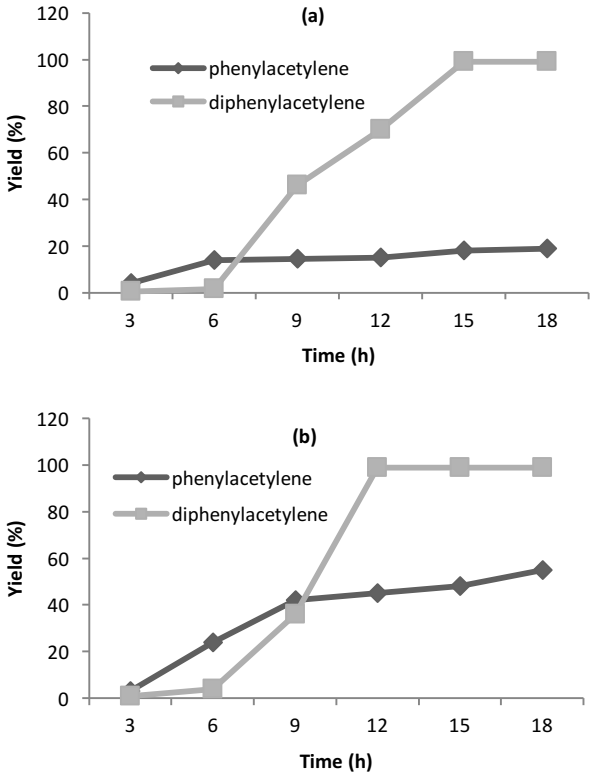


Figure 4. (**a**) Plot of yield (%) vs. time (h) for a 1:1 phenylacetylene:diphenylacetylene competition experiment. Conditions: **1** (2.5 μmol), and diphenylacetylene (0.25 mmol), phenylacetylene (0.25 mmol), 1,4-dioxane:H_2O (2:1, 1.5 mL), 80 °C. (**b**) Plot of yield (%) vs. time (h) for a 1:1 phenylacetylene:diphenylacetylene competition experiment in the presence of $AgSbF_6$. Conditions: as **(4a)**, with $AgSbF_6$ (2.5 μmol). Reaction yield determined by ^{1}H NMR.

Although the ancillary ligand in **1** is a modification of the IPr ligand used in the systems of Nolan and coworkers,[5] the selectivity observed using catalyst **1** differs from that reported by Nolan for the [IPrAuCl]/$AgSbF_6$ system.[5] Particularly surprising is the difference between [IPrAuCl]/$AgSbF_6$ and catalyst **1** when both terminal and internal alkynes are present. Comparing the regioselectivity of **1**-catalyzed alkyne hydration to Nolan's [{Au(IPr)}$_2$(μ-OH)][BF_4] (**A**) system[31] suggests a similar preference for nucleophilic attack at the more electrophilic alkyne carbon, where hydrocarboxylation[18] using **A** shows the same selectivity pattern. A major difference between [{Au(IPr)}$_2$(μ-OH)][X] (**A**) and catalyst **1** is seen for hydration of 1-phenyl-2-propyn-1-ol: **A** exclusively forms the Meyer-Schuster product, while **1** predominantly forms α-hydroxy methyl ketone **4i$_a$** (Table 3, Entry 5). The presence of a silver salt, the structure of the ancillary ligand, and the nature of the weakly coordinating anion may all contribute to the differences in activity between **1** and the Nolan system. Direct structural and reactivity comparisons to **1** via preparation of Au dimers from **1** have thus far not been successful.

While catalyst **1** may be used without external additives, experimental evidence suggests **1** undergoes changes in situ to become kinetically competent for internal alkyne hydration. The induction period apparent in the kinetic profile of catalyst **1** (Figure 3) is consistent with an in situ generation of catalyst active for internal alkyne hydration. Interestingly, the kinetic profile for conversion of a terminal alkyne does not demonstrate an induction period of the same magnitude. Moreover, based on the time course data in Figure 4, the chemoselectivity effect of silver reflects an accelerating influence on the relative rate of terminal hydration relative to internal alkynes. At this stage we do not have evidence to support a direct role for Ag in Au catalysis, nor an informed hypothesis as to the origin of substrate-dependent rate acceleration. Effects previously suggested,[20] such as coordinating to Au poisons or indirect influences upon Au or H^+ concentration are possible. Another possible influence is a counterion effect, where SbF_6 acts as a proton shuttle or a hydrogen bond acceptor.[11] However, $NaSbF_6$ does not accelerate the reaction to the same extent as $AgSbF_6$.

Regardless of the true role of silver in situ, the results from this study suggest that silver effects can influence reaction outcomes, even for reactions of "halide-free" catalysts. Besides the good regioselectivity and unusual chemoselectivity reported here, the influence of $AgSbF_6$ on relative rates and induction periods observed should be of use to others in developing new gold-catalyzed reactions.

Conclusion

Gold complex **1** acts as an efficient catalyst for hydration of terminal and internal alkynes without the need for silver and acid additives. Other gold complexes with exogenous weakly coordinating anions (**2a** and **2b**) were ineffective for silver-free alkyne hydration compared to **1**, highlighting the value of the BNHC ligand to gold catalysis. Regioselectivity for internal alkyne hydration with **1** is among the highest reported, and internal substrates were more efficiently hydrated than terminal. Despite the use of a "halide-free" catalyst precursor, $AgSbF_6$ accelerates the rate of hydration. In a substrate competition experiment, the rate enhancement of

silver was greater for terminal alkynes relative to internal. A mechanistic investigation is now underway to better understand the origin of the unusual behavior of **1**.

Experimental Section

Preparation of (BNHC)Li(THF)$_2$.

This compound was synthesized following a modified literature procedure.[42] To a solution of IPr (0.3965 g, 1 mmol) in 20 mL of toluene was added *n*-butyllithium (0.4 mL, 1 mmol) at – 35 °C. The reaction mixture was allowed to come to room temperature and stir for 4 hours. A solution of $B(C_6F_5)_3$ (0.5389 g, 1 mmol) in 5 mL of toluene was then added to the reaction, and the mixture was stirred at room temperature overnight. THF was slowly added to the resulting suspension until it became a clear solution and stirring was continued for 6 more hours. The resulting white precipitate was vacuum filtered, washed with pentane, and dried in vacuo to afford (BNHC)Li(THF)$_2$; yield: 92%; ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.96 (d, *J* = 7.5 Hz, 6 H), 0.98 (d, *J* = 7.5 Hz, 6 H), 1.11 (d, *J* = 7.0 Hz, 6 H), 1.14 (d, *J* = 7.0 Hz, 6 H), 1.62 (m, 8 H), 2.82 (sept, *J* = 7.0 Hz, 2 H), 3.04 (m, 8 H), 3.11 (sept, *J* = 7.0 Hz, 2 H), 6.25 (br s, 1 H), 7.06 (d, *J* = 7.5 Hz, 2 H), 7.18 (t, *J* = 7.5 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 7.38 (m, 1 H); ^{11}B NMR (500 MHz, CD_2Cl_2): δ -15.8; ^{19}F NMR (400 MHz, CD_2Cl_2): δ -167.3 (t, *J* = 19.6 Hz, 6 F), -162.6 (t, *J* = 21.2 Hz, 3 F), -129.1 (s).

Preparation of (BNHC)Au(SMe$_2$) (1).

A 100 mL round-bottomed flask was charged with (BNHC)Li(THF)$_2$ (0.525 g, 0.500 mmol) and [ClAu(SMe$_2$)] (0.152 g, 0.500 mmol) and toluene (20 mL, cooled to –35 °C) in the absence of light. The reaction mixture was stirred for 2 hours and allowed to warm to room temperature during this time. The resulting mixture was filtered through Celite and the solvent was removed in vacuo. The crude product was recrystallized from dichloromethane/pentane solution at -35 °C to afford (BNHC)Au(SMe$_2$); yield: 45%; ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.93 (d, *J* = 7.0 Hz, 6 H), 1.16 (d, *J* = 7.0 Hz, 6 H), 1.26 (d, *J* = 7.0 Hz, 6 H), 1.31 (d, *J* = 6.5 Hz, 6 H), 2.15 (s, 6 H), 2.65 (sept, *J* = 7.0 Hz, 2 H), 2.90 (sept, *J* = 6.5 Hz, 2 H), 6.45 (s, 1 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR (500 MHz, CD_2Cl_2): δ 21.7, 22.7, 23.6, 24.3, 26.7, 27.5, 28.1, 123.0, 123.7, 129.6, 130.0, 130.3(m), 133.9, 135.5(m), 136.2, 137.5(m), 139.6(m), 146.1, 147.3, 147.7(m), 149.6(m), 174.2. ^{11}B NMR (500 MHz, CD_2Cl_2): δ -16.0; anal. calcd. for $C_{47}H_{41}AuBF_{15}N_2S$: C 48.72, H 3.56, N 2.41; found: C 48.25, H 3.52, N 2.16. Crystallographic data and details of the collection for complex **1** are reported in the Supporting Information. CCDC-1444084 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of [NHCAu(tht)][BAr$^F_4$] (2a).

A dichloromethane solution of AuCl(SC_4H_8) (30.0 mg, 0.102 mmol), NaBAr$^F_4$ (90.0 mg, 0.102 mmol), and IPr (40 mg, 0.103 mmol) were stirred in a vial for 3 hours. The mixture was filtered through Celite and the solvent was removed in vacuo. The crude product was recrystallized from dichloromethane/pentane solution twice to afford [NHCAu(tht)][BAr$^F_4$]; yield: 35%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20 (m, 24 H), 1.66 (br s, 4 H), 2.40 (sept, *J* = 6.5 Hz, 4 H), 2.83 (br s, 4 H), 7.25-7.36 (m, 6 H), 7.48 (br s, 4 H), 7.51 (t, *J* = 7.5 Hz, 2 H), 7.66 (br s, 8 H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 23.6, 24.5, 28.7, 30.2, 38.8, 117.3, 123.4, 124.3(m), 125.5, 128.8(q, *J* = 125.5 Hz), 131.4, 132.8, 134.7, 145.5, 161.6(m), 176.6; anal. calcd. for $C_{63}H_{56}AuBF_{24}N_2S$ (1/2 CH_2Cl_2): C 48.29, H 3.64, N 1.77; found: C 47.95, H 3.30, N 1.94.

Preparation of [NHCAu(PPh$_3$)][BAr$^F_4$] (2b).

A dichloromethane solution of AuCl(SC_4H_8) (30.0 mg, 0.102mmol), NaBAr$^F_4$ (90.0 mg, 0.102 mmol) and PPh_3 (30.0 mg, 0.115 mmol) was stirred in a vial for 3 hours. The mixture was filtered through Celite. To the filtrate was added IPr (40.0 mg, 0.103 mmol). After stirring overnight, the solvent was removed in vacuo. The crude product was recrystallized twice from dichloromethane/pentane solution to afford [NHCAu(PPh_3)][BAr$^F_4$]; yield: 30%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.12 (d, *J* = 7.0 Hz, 12 H), 1.19 (d, *J* = 7.0 Hz, 12 H), 2.47 (sept, *J* = 7.0 Hz, 4 H), 6.92 (m, 6 H), 7.24-7.35 (m, 12 H), 7.42 (t, *J* = 7.0 Hz, 3 H), 7.47 (br s, 4 H), 7.55 (t, *J* = 7.5 Hz, 2 H), 7.67 (br s, 8 H); ^{31}P NMR (500 MHz, $CDCl_3$): δ 39.0; anal. calcd. for $C_{77}H_{63}AuBF_{24}N_2P$: C 54.05, H 3.71, N 1.64; found: C 54.43, H 3.44, N 1.85.

General Procedure for the Alkyne Hydration.

A vial was charged with (BNHC)Au(SMe$_2$) (**1**) (0.0057 g, 0.005 mmol) followed by 1 mL of 1,4-dioxane, diphenylacetylene (0.0909 g, 0.5 mmol) and 0.5 mL of water. The reaction mixture was stirred at 80 °C for 18 hours under aerobic conditions. The solvent was removed under reduced pressure and the reaction yield was calculated by ^{1}H NMR using benzaldehyde as internal standard.

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Internal alkyne regio- and chemoselectivity using a zwitterionic [(NHC)Au(I)] catalyst in a silver-free alkyne hydration reaction

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