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A Au(I)-Precatalyst with a Cyclopropenium Counterion: An Unusual Ion Pair

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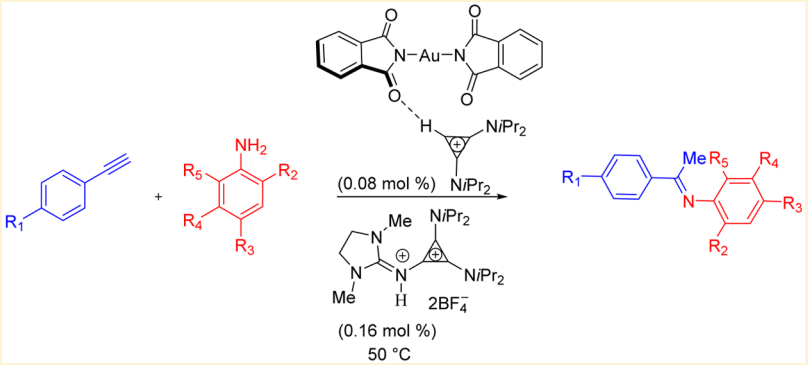
Supporting Information



ABSTRACT: The synthesis and X-ray crystal structure of a novel Au(I)-precatalyst applied to intermolecular alkyne hydroamination is reported. Density functional theory (DFT) calculations revealed the cyclopropenium counterion of this Au(I)-precatalyst imparts stability through H-bonding and other noncovalent interactions.

Catalytic processes are vital for the manufacturing of a myriad of materials this age as witnessed by their use in pharmaceutical, agrochemical, and polymer based manufacturing sectors. Echoing this truth has been the widespread advancement of catalytic transition-metal-mediated protocols, which via judicious selection of an appropriate metal and ligand combination can enable chemo-, regio-, and/or stereoselecitive transformations. In this context, Cu(I) and Ag(I) catalysis has had a historical presence, whereas the use of Au(I) as a catalyst was overlooked until recently owing to a longstanding misconception alleging it was catalytically dead.[1] Notwithstanding, a pioneering Au(I)-catalyzed alcoholysis of alkynes in 1998 by Teles et al.[2] dispelled this presumption and in doing so gave rise to a virtual *catalytic gold* rush[3] that continues to offer innovative transformations benefiting from the 5d orbital expansion and 6s orbital contraction in Au(I) resulting from relativistic effects.[4,5]

Driving these efforts has of course been intellectual curiosity in exploring novel modes of chemical reactivity, while at the same time the robust nature of Au(I) has expedited matters, as it ameliorates the meticulous need for excluding water or oxygen from reactions in many cases.[6] Nevertheless, a recurring shortcoming of Au(I)-catalysis has been the employment of Au(I) precursors, such as the stable linear dicoordinated LAuCl (L is a two-electron donor) precatalyst, that require activation by Ag(I) salts or other additives to access catalytically active unsaturated monocoordinated $[LAu(I)]^+$ complexes. The drawbacks of using silver activators include the following: (1) the formation of gold–silver adducts (e.g., dinuclear gold–silver catalytic resting states)[7] resulting from auro-argentophilic closed shell interactions;[8] (2) the formation of byproducts that can cause side reactions;[9] (3) the fact that many are relatively expensive (e.g., $AgNTf_2$)[10] or unavailable commercially (e.g., $Ag[B(C_6F_5)_4]$)[11] in addition to being difficult to prepare; (4) the ability to act as cocatalyst;[12] and (5) their potential to complicate determination of catalytic active species in a reaction which often makes optimization of a process challenging. Accordingly, to offer alternative strategies for circumventing these impasses and in adding to the works of Teles,[2] Nolan,[13] Hammond,[14] and others,[15] we recently reported a pnictogen based N-centered strong dicationic organic Brønsted acid $\mathbf{1}^+–H^+·2BF_4^-$ (**1**) that served as an activator of a $Ph_3PAu–Pht$ (Pht = phthalimido) (**2**) precatalyst which generated a cationic gold(I) catalyst employed in alkyne hydroamination (Scheme 1a).[16]

Given the success of this strong Brønsted acid/Au(I) catalytic system for hydroamination we envisioned building upon this development by synthesizing a $Au(Pht)_2BACI–H$ (**6**) (BACI = bis(diisopropylamino)cyclopenium) precatalyst that could serve as an in situ derived source of a highly Lewis acidic Au(I)-catalyst (Scheme 1b). As for **6**, it could be secured in a retrosynthetic sense from phthalimide (**7**) and known [Au(BAC)Cl] (**8**) (BAC = bis(diisopropylamino)cyclopenylidene that in turn would be prepared from a synthetic route that ideally was shorter than those previously reported.

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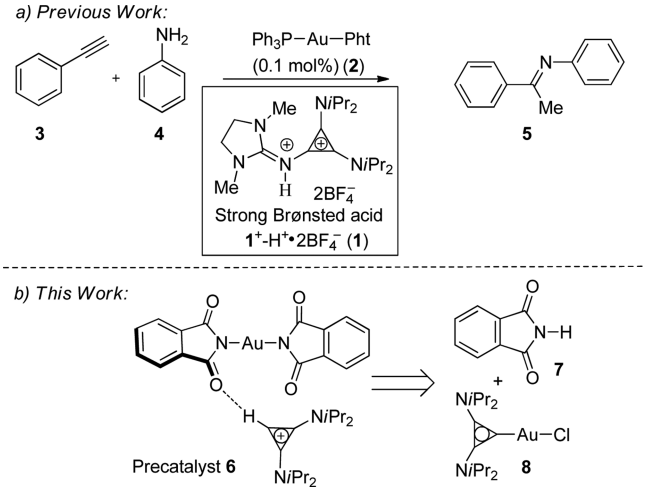
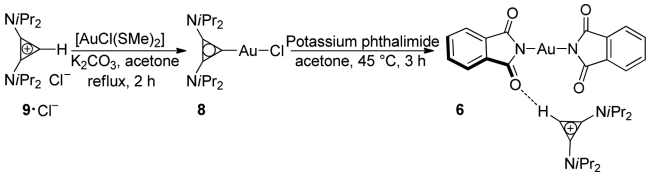
Scheme 1. Retrosynthesis of Au(I) Precatalyst 6



With the above factors in mind, the synthesis of precatalyst **6** was carried out by reacting bis(diisopropylamino)cyclopropenium chloride (**9**·Cl^-) with readily available chloro(dimethylsulfide)gold(I) in the presence of inexpensive and mild base K_2CO_3 to yield known **8**[17] (Scheme 2). From a

Scheme 2. Synthesis of Precatalyst Au(Pht)$_2$BACI−H (6)



preparative standpoint, it is notable that our route to **8** is the shortest to date. Potassium phthalimide in acetone was then added at 45 °C to afford targeted homoleptic Au(I) complex **6** in 87% yield. Subsequently, single-crystal X-ray quality crystals were grown by vapor diffusion of ethyl acetate into an acetonitrile solution of **6**. The X-ray structure of **6** unveiled several interesting features, the most dominant being the presence of a cyclopropenium that apart from balancing the overall charge of the complex engaged in a stabilizing H-bond (C(1)−H(1)···O(1), d = 1.80 Å), Figure 1 (Structure A). To probe the nature of these interactions, a restricted optimization at the B3LYP/LanL2DZ level of theory, wherein all of the heavy atoms were frozen and the hydrogens were left unconstrained starting from the X-ray coordinates of **6**, was performed to provide $\mathbf{6}_{opt}$ (Figure 1). Revealed from a natural

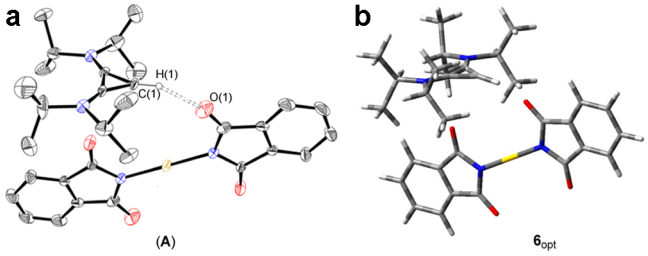


Figure 1. (a) X-ray structure of **6** (Structure A) with 50% ellipsoid probability (see Supporting Information). (b) Computed $\mathbf{6}_{opt}$ optimized at the B3LYP/LanL2DZ level of theory.

bond orbital (NBO) analysis of $\mathbf{6}_{opt}$ was the donation of oxygen O(1) (NBO charge = −0.68) lone pair density into an antibonding σ^*-orbital of the cyclopropeniminium C(1)−H(1) bond (E_{NBO} = 10.06 kcal/mol), which is consistent with a degree of fractional chemical H-bonding or, that is, charge-transfer-based "partial covalent" H-bonding. While in the lexicon of Gilli et al. this same interaction typifies a positive charge-assisted H-bond.[18] To further probe the bonding in $\mathbf{6}_{opt}$, a $(\lambda_2)\rho$ vs σ noncovalent interaction (NCI)[19] plot was computed at the B3LYP-D3/LACVP++**//B3LYP/Lan2DZ level of theory which uncovered the presence of several stabilizing interactions as seen from the highly localized green isosurface areas in $\mathbf{6}_{NCI}$ (Figure 2), where λ_2 equals the second

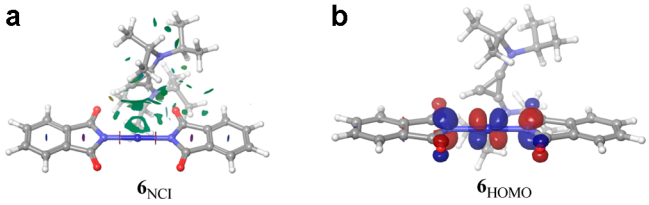


Figure 2. (a) Computed $\mathbf{6}_{NCI}$ corresponding to the noncovalent interactions (NCI) in $\mathbf{6}_{opt}$. (b) Computed $\mathbf{6}_{HOMO}$ corresponding to the HOMO of $\mathbf{6}_{opt}$ (B3LYP-D3/LACVP++**//B3LYP/Lan2DZ level of theory).

eigenvalue of the density Hessian, ρ the electron density, and σ the reduced-density gradient. The origin of these favorable noncovalent interactions derive from H-bond contacts between the phthalimido oxygen O(1) and a well-aligned manifold of partial positive cyclopropenium hydrogens, as well as stabilizing van der Waals contacts. The HOMO of $\mathbf{6}_{opt}$ corresponding to $\mathbf{6}_{HOMO}$ offered additional insight, as it conformed to an antibonding interaction between the $5d_{x,y}$ orbital of Au(I) and the nitrogen 2p(π)-orbital of the phthalimido ligands, thus suggesting the phthalimido ligands would be susceptible to protonalysis (Figure 2).

Having insight into the structure of precatalyst **6** as a proof-of-concept and based on our interest in group 11 catalyzed processes (e.g., imino-alkylation and alkyne/alkene hydroamination reactions),[20] which are an effective stratagem for preparing nitrogen-containing molecules, we were attracted by the possibility of applying Au(I)-precatalyst **6** to alkyne hydroamination reactions.

To this end, using a low precatalyst loading of **6** (0.08 mol %) and strong Brønsted acid $1^+-H^+\cdot 2BF_4^-$ (0.16 mol %), an initial reaction of aniline **4a** and alkyne **3a** was carried out at 50 °C, which to our delight provided imine **5a** in 60% yield (Table 1, entry 1). Notably, the yield of this reaction was approximately 3-fold greater than that obtained under analogous conditions with structurally related precatalyst **2**.[16] Given this promising result a number of different substituted alkynes and amines were subsequently employed to explore the substrate scope of this reaction. Accordingly, the resonance donating and inductively electron-withdrawing 4-bromo substituted aniline **4b** and 2,5-dichloroaniline (**4c**) provided increased product yields of 84% and 93%, and notably, the latter product was obtained in a shorter timespan of 4 h (Table 1, entries 2 and 3). Notwithstanding, the comparative use of 4-fluoroaniline (**4d**) having a powerful inductively electron-withdrawing, less resonance donating, and weakly polarizable halogen afforded imine **5d** in a lower 61% yield. The poor reactivity in this case is thought to derive in large part from the

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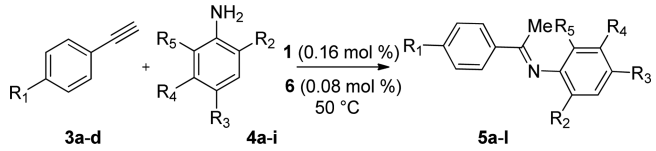
Table 1. Au(I)-Catalyzed Alkyne Hydroamination Using 6



3a-d 4a-i 5a-l

				nucleophile						
entry	R1			R2	R3	R4	R5	time (h)		yield[a,b] (%)
1	**3a**	H	**4a**	H	H	H	H	24	**5a**	60
2	**3a**	H	**4b**	H	Br	H	H	24	**5b**	84
3	**3a**	H	**4c**	Cl	H	Cl	H	4	**5c**	93
4	**3a**	H	**4d**	H	F	H	H	24	**5d**	61
5	**3a**	H	**4e**	H	C_2H_5	H	H	24	**5e**	60
6	**3a**	H	**4f**	H	C_4H_9	H	H	24	**5f**	45
7	**3a**	H	**4g**	C_2H_5	H	H	H	24	**5g**	48
8	**3a**	H	**4h**	Me	Me	H	Me	24	**5h**	49
9	**3a**	H	**4i**	*i*Pr	H	H	*i*Pr	24	**5i**	72
10	**3b**	OMe	**4a**	H	H	H	H	24	**5j**	95
11	**3c**	Me	**4a**	H	H	H	H	24	**5k**	53
12	**3d**	F	**4a**	H	H	H	H	24	**5l**	60

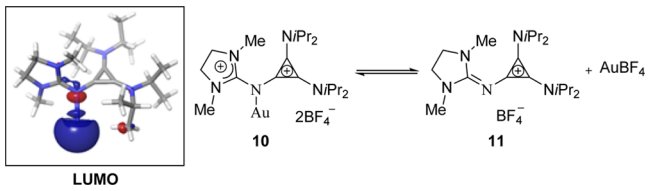
[a]Yields of isolated products after flash chromatography. [b]Reaction conversion after 48 h was insignificant (<1%) based on ^{1}H NMR when the Brønsted acid, metal, or Brønsted acid−metal combination were excluded.

interplay of multipolar C−F interactions (e.g., C−F···H−C, C−F···H−N, or C−F···Au contacts) and reduced amine basicity resulting from the 4-F-substituent of **4d** (Table 1, entry 4).[21]

On the other hand, the use of more electron-rich substrates 4-ethyl- and 4-butylaniline (**4e** and **4f**) having inductively donating para- substituents afforded products in 60% and 45% yield (Table 1, entries 5 and 6). To probe the effect of alkyl substituents and sterics on the reaction, 2-ethylaniline (**4g**) was next investigated, which provided product **5g** in low yield (Table 1, entry 7). The lower yields obtained in the last three cases (i.e., entries 5−7), presumably, arose from the ability of electron-rich anilines to competitively bind gold to generate a less active and/or nonactive catalyst resting state, which in turn would reduce the concentration of the activated η^2-alkyne and subsequently diminish the rate of amine addition. Reasoning from this result the effect of steric inhibition of aniline binding with the catalyst was studied by subjecting 2,4,6-trimethylaniline (**4h**) to the reaction conditions which afforded product **5h** in 49% yield. Notwithstanding, in-keeping with our posit of Au(I)-deactivation via formation of a catalytically inactive resting state, the use of more sterically hindered substrate **4i** was then tested, affording an improved reaction yield of 72% (Table 1, entry 9).

While the actual Au(I) catalyst in these reactions remains elusive at this time, the work of Alcarazo et al.[22] concerning gold(I) coordinated polycationic cyclopropenium-substituted phosphines lends a degree of support to the probable existence of a p-block (group 15) coordinated gold(I) catalyst $[Au(I)\text{-}(\mathbf{1})]^{2+}\cdot 2BF_4^-$ (**10**) having an electron-deficient imidazoliumyl *N*-cyclopropenium ligand (Scheme 3). As for the formation of catalyst **10** it could originate in situ from a domino series of events initiated by the protolysis of **6** by $\mathbf{1}^+-H^+\cdot 2BF_4^-$ to generate conjugate base $\mathbf{1}^+$, which would serve as a ligand for Au(I). Consistent with this prospect and the formation of a reactive Au(I) catalyst was the B3LYP/Lan2DZ computed LUMO of the parent gold complex of **10** with the $2BF_4^-$ counterions removed which conformed predominately to a Au(I) based 6s orbital. Also suggestive of the high gold(I) based reactivity was a computed NBO charge assignment of

Scheme 3. Computed LUMO of 10 and the Relationship of 10 and 11 at B3LYP/Lan2DZ Level of Theory



LUMO

0.599 at gold in envisioned **10**. Notably, the latter term was decidedly larger than that computed for often employed Au(I)-complexes having 1,3-bis(2,4,6-trimethylphenyl)-imidazolium (IMes) and triphenylphosphine ligands (NBO charges = 0.506 and 0.311 at gold). To gain additional insight into conjectural Au(I) catalyst **10**, the relationship of **10** and **11** was evaluated (B3LYP/Lan2DZlevel of theory), revealing a strong preference for **10** vice versa **11** as judged by a 43.0 kcal/mol energy difference.

As for the catalytic cycle of this reaction, it is open to debate given the multiple roles; a weak phthalimide might serve mechanistically, especially in terms of proton shuttling which is a critical event for ensuring effective rates of protodeauration leading to catalytic turnover in Au(I) hydroamination reactions. Moreover, the reaction media of these hydroaminations add a further dimension of complexity, due to the presence of multiple ions (e.g., cyclopropeniminium) capable of stabilize charged intermediates and/or charge buildup, likening it to an ionic liquid, which would arguably have an impact upon acidities. Irrespective, working from a well-established basis of either (1) nucleophilic amine addition to an η^2-$[LAu(I)]^+$-activated alkyne complex occurring in an outer sphere Markovnikov regioselective manner[23] or (2) protodeauration being the rate-determining steps governing catalytic turnover, which is well-known to be a rate-limiting step in many gold(I)-catalyzed hydroaminations,[23] the tentative catalytic cycle in Scheme 4 is offered. As depicted, initial $\mathbf{1}^+-H^+\cdot 2BF_4^-$ (**1**) triggered protonalysis of **6** would generate a putative gold(I) complex $Au(\mathbf{1}^+)_2\cdot 3BF_4^-$ that upon ligand dissociation would

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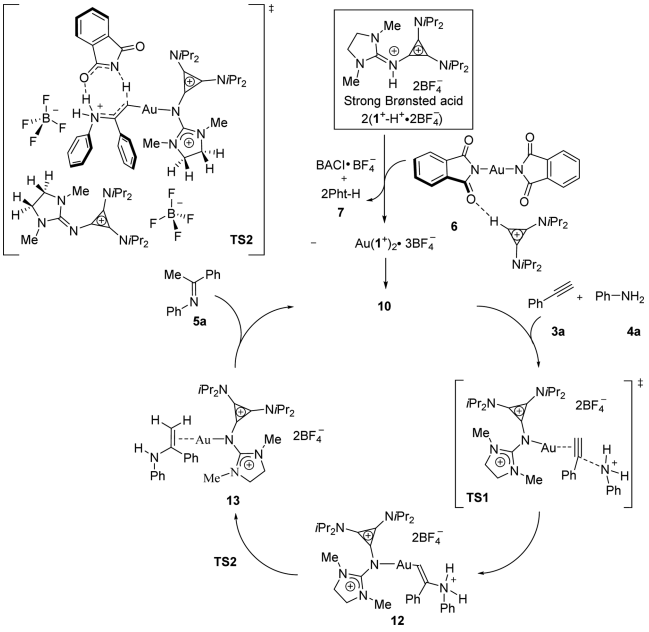
Scheme 4. Proposed Catalytic Cycle for Hydroamination Using Precatalyst 6



afford gold(I) catalyst **10**, which following η^2-alkyne coordination would undergo outer sphere trans-addition of aniline to afford β-anilinium vinylgold species **12**. Thereafter, a subsequent [1,3]-proton shuttling event mediated by phthalimide **7** would then result in protodeauration to give the Au(I) coordinated enamine **13**. Catalytic turnover by dissociation or more probable direct transfer of the Au(I) catalyst to a free alkyne concurrent with enamine tautomerization would then follow to provide imine **5a**.

As for the protodeauration step it is too early to diagnostically confirm how this process occurs; however, one viable possibility is the involvement of phthalimide **7** (a seeming byproduct) as mediators of [1,3]-proton transfer via **TS2** which was computed to have a gas-phase free energy of activation ($\Delta G^{\ddagger}$) of 36.8 kcal/mol, Scheme 4. The role of **7** in this catalytic cycle is notable, as it presents an added mechanistic subtlety given its function as a proton shuttle for protodeauration, which in many Au(I)-catalyzed reactions is a rate-determining step.[24]

To recap, a solid, bench-stable, gold precatalyst prepared by a two-step synthesis was disclosed which as revealed from X-ray structural data and DFT calculations contains a cyclopropenium counterion that stabilizes the complex through H-bonding and other noncovalent interactions. Experimentally, this precatalyst was shown to be an in situ source of a conjectural Au(I)-catalyst that was applied to alkyne hydroamination. Lastly, a proposed catalytic cycle and DFT calculations were provided which revealed a [1,3]-proton transfer event mediated by a phthalimide originating from the precatalyst was involved in catalyst turnover.

EXPERIMENTAL SECTION

1. General Information. Materials were obtained from commercial suppliers and were used without further purification. All reactions were performed under an inert atmosphere. Reactions were monitored by thin layer chromatography (TLC) using TLC silica gel 60 F254. Flash column chromatography was performed over Silicycle ultrapure silica gel (230−400 mesh). NMR spectra were obtained with a 300 MHz spectrometer (^{1}H 300 MHz, ^{13}C 75.5 MHz or ^{13}C 150.9 MHz, ^{19}F 292.4 MHz) in $CDCl_3$, D_2O, and CD_3CN. The chemical shifts are reported as δ values (ppm) relative to tetramethylsilane. FT-IR spectra were obtained with an attenuated total reflectance spectrophotometer from a neat sample.

2. Procedure for Synthesis of Catalyst [AuCl(BAC)] (7). An round bottom flask (RBF) was charged with [AuCl(SMe_2)] (323.9 mg, 1.1 mmol) and K_2CO_3 (3.7 mg, 0.027 mmol). Subsequently, a solution of reported[17] cyclopropenium chloride (**8**·Cl$^-$) (275.4 mg, 1.1 mmol) in acetone (10 mL) was added. It was refluxed for 2 h, after which acetone was removed and the residue dissolved in acetonitrile. The resulting suspension was filtered, and removal of solvent under high vacuum afforded [AuCl(BAC)] (**7**) as a colorless solid (561.8 mg, 91% yield). The spectroscopic data were in full agreement with spectral data for an authentic sample.[17]

^{1}H NMR (CD_3CN, 300 MHz) δ = 3.81−3.96 (m, 4H), 1.52−1.54 (d, J = 4.42 Hz, 12H), 1.27−1.29 (d, J = 5.40 Hz, 12H); ^{13}C NMR (CD_3CN, 150.9 MHz) δ = 144.7, 132.0, 55.9, 48.0, 21.2, 20.0.

3. Procedure for Synthesis of Catalyst Au(Pht)$_2$BACl−H (6). To an RBF charged with **7** (335.5 mg, 0.6 mmol) and potassium phthalimide (233.4 mg, 1.3 mmol), acetone (4 mL) was added. The resulting suspension was stirred at 45 °C for 3 h. The reaction mixture was filtered and washed with a small portion of acetone. Subsequently, filtrate was concentrated, filtered, washed with water, and dried under a high vacuum. Recrystallization from acetonitrile/ethyl acetate at room temperature afforded **6** as a white solid (380 mg, 87% yield). Mp 188−192 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 9.83 (s, 1H), 7.66−7.69 (m, 4H), 7.53−7.55 (m, 4H), 4.01−4.10 (pentet, J = 6.75 Hz, 2H), 4.73−3.82 (pentet, J = 6.81 Hz, 2H), 1.36 (dd, J = 19.02, 6.68 Hz, 24H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ = 178.3, 136.1, 133.9, 131.9, 121.5, 101.1, 56.4, 49.2, 21.3, 20.9.; IR 3087, 2979, 1668, 1568. FAB/EI results indicated that the ion pair dissociates to [Au(I)Pht$_2$]$^-$ and BAC under the conditions of MS.

4. General Procedure for the Gold-Catalyzed Hydroamination of Alkynes with Anilines. In an RBF, gold precatalyst **6** (3.5 mg, 0.005 mmol) and **1**$^+$−H$^+$·2BF$_4^-$ (**1**) (6.0 mg, 0.011 mmol) were added. To this mixture were added phenylacetylene (735.3 mg, 7.2 mmol) and 2,5-dichloroaniline (972.12 mg, 6 mmol), and the resulting mixture was stirred at 50 °C for 4 h. After the reaction mixture cooled to room temperature, flash chromatography (hexanes to ethyl acetate = 20:1) provided **5c** as a colorless oil (1.4 g, 93% yield).

*N-(1-Phenylethylidene)aniline (**5a**).*[16] Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.00−8.03 (m, 2H), 7.50−7.45 (m, 3H), 7.38 (t, J = 8.00 Hz, 2H), 7.10 (t, J = 8.00 Hz, 1H), 6.83 (dd, J = 8.66, 1.40 Hz, 2H), 2.26 (s, 3H).

*4-Bromo-N-(1-phenylethylidene)aniline (**5b**).*[16] Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.94−8.00 (m, 2H), 7.45−7.47 (m, 5H), 6.69 (d, J = 8.52 Hz, 2H), 2.24 (s, 3H).

*2,5-Dichloro-N-(1-phenylethylidene)aniline (**5c**).*[16] Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.02 (dd, J = 7.5, 1.5 Hz, 2H), 7.47−7.54 (m, 3H), 7.37 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.03 (dd, J = 8.40, 2.70 Hz, 1H), 6.87 (d, J = 2.34 Hz, 1H), 2.25 (s, 3H).

*4-Fluoro-N-(1-phenylethylidene)aniline (**5d**).*[16] Light yellow solid. Mp 82−86 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.97−8.00 (m, 2H), 7.37 (t, J = 7.14, 2H), 7.11−7.17 (t, J = 9.81 Hz, 3H), 6.77 (dd, J = 8.59, 4.91 Hz, 2H), 2.26 (s, 3H).

*4-Ethyl-N-(1-phenylethylidene)aniline (**5e**).*[16] Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.99−8.01 (m, 2H), 7.47 (dd, J = 7.45, 2.01 Hz, 3H), 7.20 (d, J = 8.24 Hz, 2H), 6.75 (d, J = 8.2 Hz, 2H), 2.64−2.71 (m, 2H), 2.27 (s, 3H), 1.26−1.31 (m, 3H).

*4-Butyl-N-(1-phenylethylidene)aniline (**5f**).*[16] Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.99−8.02 (m, 2H), 7.47 (dd, J = 5.23, 2.09 Hz, 3H), 7.18 (d, J = 8.37 Hz, 3H), 6.75 (d, J = 8.02 Hz, 2H), 2.63 (t, J = 7.68 Hz, 2H), 2.28 (s, 3H), 1.59−1.69 (m, 2H), 1.34−1.46 (m, 2H), 0.96 (t, J = 7.68 Hz, 3H).

*2-Ethyl-N-(1-phenylethylidene)aniline (**5g**).*[16] Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.04−8.07 m, 1.96, 2H), 7.51 (dd, J = 5.46, 2.18 Hz, 3H), 7.19−7.29 (m, 2H), 7.11 (td, J = 7.42, 1.31 Hz, 1H), 6.68 (dd, J = 7.64, 1.09 Hz, 1H), 2.53 (dd, J = 14.84, 7.86 Hz, 2H), 2.24 (s, 3H), 1.18 (t, 8.08, 3H).

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*2,4,6-Trimethyl-N-(1-phenylethylidene)aniline (**5h**).*[16] Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.09 (d, J = 3.39, 2H), 7.53 (dd, J = 5.28, 2.02 Hz, 3H), 6.93 (s, 2H), 2.34 (s, 3H), 2.12 (s, 3H), 2.05 (s, 6H).

*2,6-Diisopropyl-N-(1-phenylethylidene)aniline (**5i**).*[25] Yellow solid. Mp 73−77 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.14−8.18 (m, 2H), 7.58−7.59 (m, 3H), 7.37−7.44 (m, 1H), 7.28 (d, J = 1.7 Hz, 1H), 7.22 (s, 1H), 2.88 (hept, J = 6.85 Hz, 2H), 2.21 (s, 3H), 1.25−1.29 (m, 12H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 164.8, 146.9, 139.2, 136.1, 132.2, 128.5, 127.2, 123.4, 123.0, 28.3, 23.3, 23.0, 18.1.

*N-(1-(4-Methoxyphenyl)ethylidene)aniline (**5j**).*[16] Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.97 (d, J = 9.05, 2H), 7.32−7.38 (m, 2H), 7.06−7.14 (m, 1H), 6.96−7.00 (m, 2H), 6.81 (dd, J = 8.48,1.25 Hz, 2H), 3.89 (s, 3H), 2.23 (s, 3H).

*N-(1-(p-Tolyl)ethylidene)aniline (**5k**).*[16] Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.93 (d, J = 7.72, 2H), 7.39 (t, J = 6.61, 2H), 7.29 (d, J = 7.72, 2H), 7.12 (t, J = 7.40 Hz, 1H), 6.84 (d, J = 7.44, Hz, 2H), 2.43 (s, 3H), 2.23 (s, 3H).

*N-(1-(4-Fluorophenyl)ethylidene)aniline (**5l**).*[16] Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.96−8.00 (m, 2H), 7.32−7.38 (m, 2H), 7.09−7.15 (m, 3H), 6.78 (dd, J = 8.79, 1.42), 2.21 (s, 3H).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00241.

Crystallographic data of **6** (CIF)

Spectroscopic data for all compounds, computational details for **6**, **10**, and **11** (PDF)

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Notes

The authors declare no competing financial interest.

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