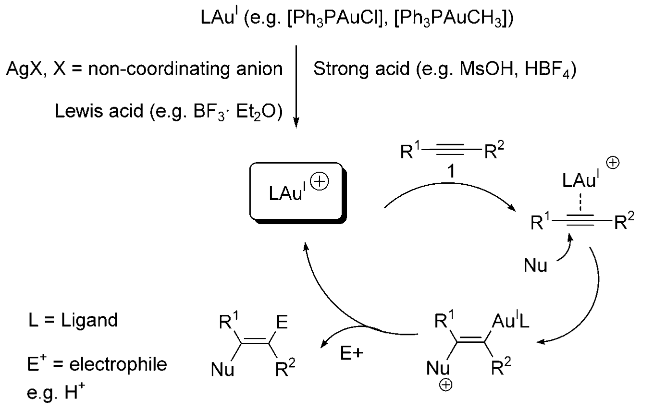
DOI: 10.1002/ange.201003593

Fluorine-Enabled Cationic Gold Catalysis: Functionalized Hydration of Alkynes**

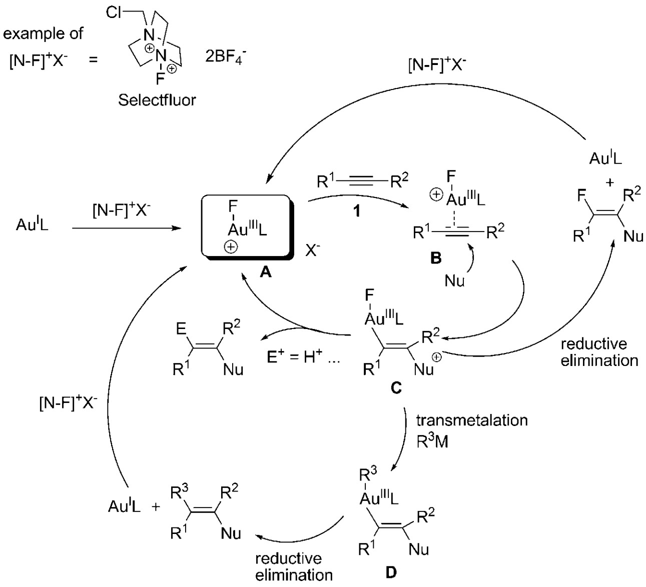
Weibo Wang, Jacek Jasinski, Gerald B. Hammond, and Bo Xu**

Dedicated to Professor Donald J. Burton

Transition-metal catalysis plays a major role in chemical synthesis.[1] Many transition metals need to be in cationic form to be catalytically active; a case in point is gold.[2] Cationic gold species have been regarded as the most powerful catalysts for electrophilic activation of alkynes toward a variety of nucleophiles.[2,3] Simply put, a nucleophilic attack on a $[AuL]^+$-activated alkyne proceeds through a π complex to give a *trans*-alkenyl gold complex intermediate capable of reacting with an electrophile (E^+), usually a proton, to yield the final product through protodeauration (Scheme 1). A common cationic gold precursor, such as $[Ph_3PAuCl]$, is not catalytically active by itself. It is typically treated with a silver salt of a non-coordinating anion (e.g. $AgBF_4$) to generate the active cationic gold complex (Scheme 1). We sought an alternate mode of catalysis arising from a fluorine-enabled cationic metal species, generated by fluorination of a low-valence metal complex (e.g. $[ClAu^IL]$) with an ammonium $[N{-}F]^+$ type fluorination reagent containing a poorly coordinating counterion (Scheme 2). Such species (intermediate **A**) is expected to have a Lewis acidity that is stronger than for the corresponding metal catalyst prior to fluorination. This is due to the higher oxidation state of the metal and the presence of a non-coordinating counter anion (e.g. BF_4^- in the case of Selectfluor) (Scheme 2). Our premise is that this cationic gold–fluorine species **A** would be able to catalyze not only well-known reactions of $[Au^IL]^+$ (e.g. hydration or cyclization of alkynes) (Scheme 2, inner cycle), with similar or even higher efficiency, but that it could also mediate additional transformations not traditionally associated with $[Au^IL]^+$. This is illustrated in Scheme 2 (outer circle). For example, the fluoro–gold vinyl intermediate **C** may undergo reductive elimination to give a vinyl fluoride, or transmetalation with an organometallic reagent R^3M (e.g. M = B, Si, Sn, etc.). The weak Au–F bond[4] and the strong B–F, Si–F, and Sn–F bonds would drive the transmetalation. After reductive elimination, the low-valence gold(I) complex is re-fluorinated to resume



Scheme 1. Traditional methods for the generation of $[LAu^I]^+$ and its catalytic cycle.



Scheme 2. Fluorination-enabled cationic gold complex and its catalytic cycle.

---

[*] W. Wang, Prof. Dr. G. B. Hammond, Prof. Dr. B. Xu
Department of Chemistry, University of Louisville
Louisville, KY 40292 (USA)
Fax: (+1) 502-852-5998
E-mail: gb.hammond@louisville.edu
bo.xu@louisville.edu
Dr. J. Jasinski
Materials Characterization
Conn Center for Renewable Energy Research
University of Louisville, Louisville, KY 40292 (USA)

[**] We are grateful to the National Science Foundation for financial support (CHE-0809683). We acknowledge the support provided by the CREAM Mass Spectrometry Facility (University of Louisville) funded by NSF/EPSCoR grant no. EPS-0447479.

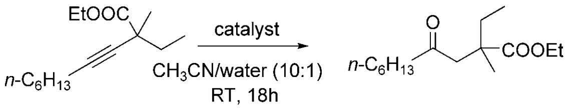
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201003593.

its catalytic cycle. Overall, this approach should deliver a diversity of fluorinated and non-fluorinated building blocks or targets.

It is well known that alkynes do not undergo hydration using solely AuCl or [ClAuPPh$_3$]. Zhang and others have developed an oxidative coupling chemistry involving a Au^I/Au^{III} catalytic cycle.[5] In Zhang's proposed mechanism for the gold-catalyzed coupling reaction of arylboronic acids with propargyl esters,[5b] cationic Au^I initiates the activation of alkyne in a propargyl ester, and Selectfluor is used to oxidize the resulting vinyl Au^I intermediate to a Au^{III} species. In this report, Zhang and co-workers also showed that cationic P–Au^I complexes were poor catalysts, which would seem to hint that Au^I is oxidized to cationic Au^{III} prior to the addition of nucleophiles to alkynes. In their most recent communication on the gold-catalyzed carboheterofunctionalization of alkenes,[5a] Zhang and co-workers have indeed revised their earlier mechanistic proposal and proposed the initial oxidation of Au^I to Au^{III} with Selectfluor. Of late, fluorination reagents have become the oxidant of choice in transition-metal-mediated C–H activation, fluorination, oxidation, and coupling reactions, as demonstrated by Ritter,[6] Sanford,[7] Gouverneur,[8] Michael,[9] Yu,[10] and Liu[11] among others. In most of those reports, the fluorination reagent (e.g. Selectfluor)[12] acts as a powerful oxidant that increases the oxidation state of the transition-metal intermediate within the catalytic cycle. We propose that fluorine enables new modes of cationic gold catalysis, and, depending on the application, the fluorinated reagent can be even used as an activator in catalytic amounts.

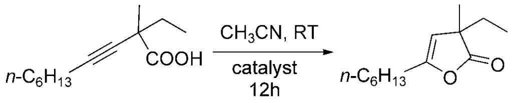
The hydration of alkynes is a straightforward method for preparing carbonyl compounds.[13,14] We used a gold-catalyzed synthesis of γ-keto esters through regioselective hydration of 3-alkynoate[15] to test our cationic fluorine–gold complex (Table 1). Traditional gold(I) catalysts, like AuCl or [PPh$_3$AuCl], do not catalyze this hydration (Table 1, entries 1 and 2), whereas [PPh$_3$AuCl]/AgBF$_4$ gave moderate yield of the ketoester. As expected, gold(III) led to a better yield (Table 1, entry 4) but our gold(I)/Selectfluor system (both components in catalytic amounts) produced the best results (Table 1, entry 5). The mechanism of this hydration is illustrated in Scheme 2 (inner cycle); water, acting as nucleophile (Nu = H$_2$O), attacks the activated alkyne (intermediate **B**), followed by protodeauration of the vinyl–gold complex **C** to furnish the ketone product. The cyclization of alkynoic acid is also an example of transformations catalyzed by gold (Table 2). In the cyclization of an alkynoic acid, [PPh$_3$AuCl] or Selectfluor alone did not enable the cyclization, but, when combined in catalytic amounts, the resulting lactone was obtained in high yields. These results support the synergism that exists between the gold catalyst and Selectfluor.

Table 1: Hydration of internal alkyne.



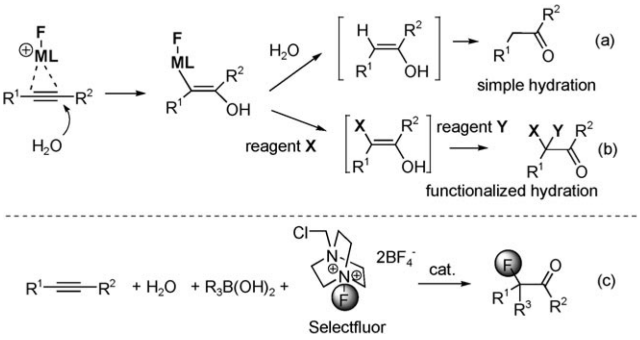
Entry	Catalyst (equiv)	Yield
1	AuCl (2%)	no reaction
2	[ClAuPPh$_3$] (2%)	no reaction
3	[ClAuPPh$_3$] (2%)/AgBF$_4$ (2%)	45%
4	NaAuCl$_4$ (2%)	81%
5	[ClAuPPh$_3$] (2%)/Selectfluor (4%)	85%

Table 2: Cyclization of alkynyl acid.



Entry	Catalyst (equiv)	Yield
1	[ClAuPPh$_3$] (5%)	no reaction
2	Selectfluor (100%)	no reaction
3	[ClAuPPh$_3$] (5%)/Selectfluor (10%)	88%

A major shortcoming of a transition-metal-catalyzed hydration is that it only adds the elements of H$_2$O to an alkyne (Scheme 3a).[16] We believe that the fluorine-enabled cationic gold catalysis could do more than simple hydration. We propose that the vinyl–metal complex hydration intermediate (obtained by the reaction of fluorine-generated cationic metal species **A** with an alkyne) can react further during the hydration process to give an α,α-disubstituted ketone (Scheme 3b) in a one-pot reaction. We coined this process "functionalized hydration". We speculated that our fluorine–gold intermediate could react with organoboronic acid (reagent **X**) and an electrophilic fluorine source such as Selectfluor (reagent **Y**) to give α-aryl-α-fluoroketone (Scheme 3b). A proof of principle is the synthesis of functionalized α-fluoroketones—well-known targets and important synthetic intermediates.[17] Tertiary α-fluorinated ketones have received much attention recently because compounds having an α-fluorocarbonyl moiety are biologically active, they are effective mimics of α-hydroxy ketones, useful probes in various biological processes, and also enzyme inhibitors.[17a,c] They also provide configurationally stable substituents for molecules containing a tertiary chiral

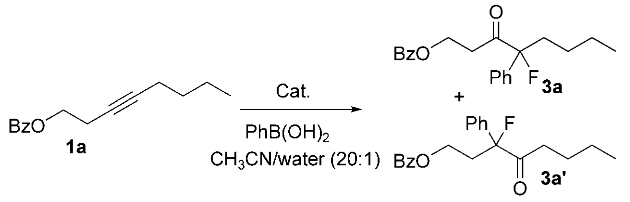


Scheme 3. Concept of functionalized hydration.

carbon atom next to a carbonyl group, an important structural motif in medicinal chemistry.[17c] This one-pot tandem addition/oxidative coupling/fluorination sequence using readily available starting materials (alkyne, water, organoboronic, acid and Selectfluor) would have clear advantages over literature methods, all of which require multiple synthetic steps.[16]

We examined the reaction of **1a** with phenyl boronic acid (Table 3). Various metal catalysts were screened. Without additives, AuCl or [Ph_3PAuCl] could not catalyze the reaction of **1** with phenyl boronic acid (Table 3, entries 1 and 2), but in combination with Selectfluor (1.5 equiv), we obtained a 50% yield of **3** (Table 3, entry 4). Increasing the amount of Selectfluor further increases the yield (Table 3, entry 5). Reducing the loading of [Ph_3PAuCl] from 5% to 2% had no deleterious effect (Table 3, entry 7). Replacing Selectfluor with NFSi was not effective (Table 3, entry 8). We tested other gold(I) catalysts, but they were less efficient (Table 3, entries 9–11). We also tested gold(III) catalysts ($AuCl_3$ and $AuCl_3$/AgOTf, Table 3, entries 12 and 13), but they gave much lower yields. Other transition metals like copper, silver, and palladium could not catalyze this transformation under similar conditions (Table 3, entries 14–16). On exploring the scope of this novel functionalized hydration, we found that functionalized and unfunctionalized internal alkynes reacted with aryl boronic acid, giving very good yields of α-substituted ketones, with moderate regioselectivity (Table 4, entries 1–12). With electron-rich 4-methoxy- or 3,4-dimethoxyphenylboronic acids, we observed by-products arising from fluorination or oxidation of the electron-rich aromatic rings by Selectfluor.[12] Steric and electronic effects determine the regioselectivity.[13,14] For internal alkynes possessing a nucleophilic site nearby (e.g. the ester group in **1a**), this site may influence the regioselectivity through neighboring-group participation.[13–15]

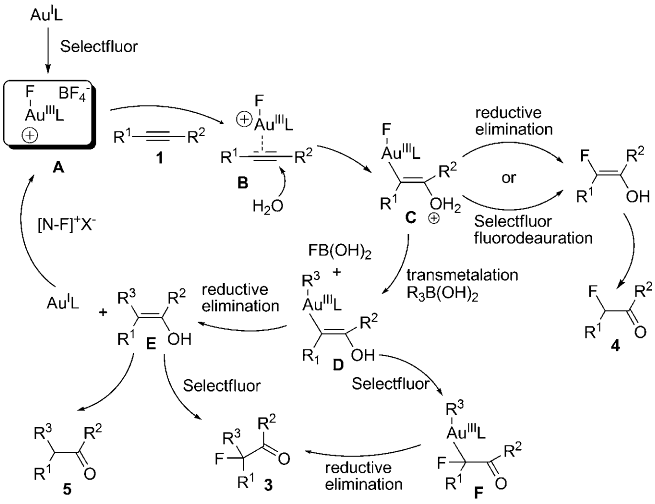
Table 3: Functionalized hydration: screening of conditions.[a]



Entry	Catalyst	Selectfluor (equiv)	Yields [%] (**3a**/**3a'**)
1	AuCl	none	no reaction
2	[PPh_3AuCl]	none	no reaction
3	[PPh_3AuCl]	0.1	no reaction
4	[PPh_3AuCl]	1.5	50 (5.1 :1)
5	[PPh_3AuCl]	2.2	57 (4.7:1)
6	[PPh_3AuCl]	2.5	88 (6.7:1)
7[b]	[PPh_3AuCl]	2.5	83 (5.7:1)
8[c]	[PPh_3AuCl]	2.5	no reaction
9	[(o-Tol)$_3$PAuCl]	2.5	75 (6.5:1)
10	[(*p*-CF$_3$-C$_6$H$_4$)$_3$PAuCl]	2.5	78 (5.0:1)
11	AuCl	2.5	65 (4.7:1)
12	$AuCl_3$	2.5	41 (5.7:1)
13	$AuCl_3$/AgOTf (15%)	2.5	29 (5.6:1)
14	CuBr	2.5	complex mixture
15	AgOTf	2.5	complex mixture
16	$PdCl_2$	2.5	complex mixture

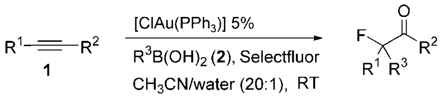
[a] 5% catalyst loading, RT, 18 h. Bz = benzoyl. [b] 2% catalyst loading, RT, 24 h. [c] NFSi was used instead of Selectfluor; Selectfluor: 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate); NFSi: *N*-fluorobenzenesulfonimide.

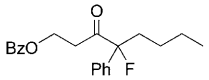
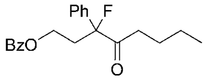
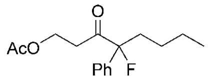
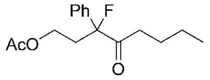
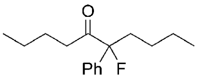
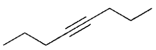
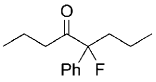
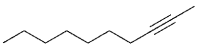
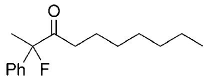
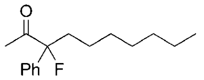
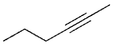
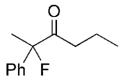
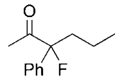
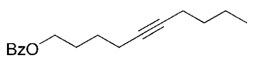
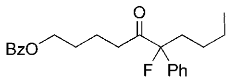
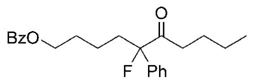
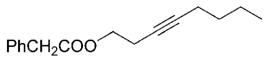
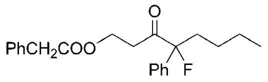
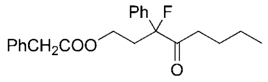
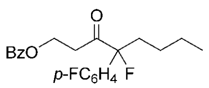
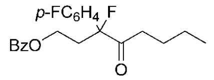
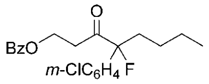
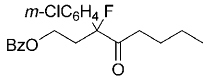
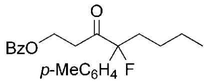
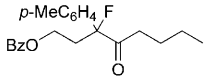
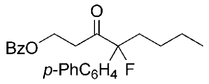
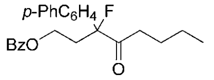
Our proposed mechanism, shown in Scheme 4, resembles the reaction of boronic acid with alkynes.[18] Initially, water attacks the gold-activated alkyne to form a vinyl–gold complex **C**,[19] which reacts with a metal reagent RM (e.g., $PhB(OH)_2$) through a transmetalation process, to give intermediate **D**. We believe that the strong B–F bond and the weak Au–F bond[4] are the driving forces behind this transmetalation. Reductive elimination of **D** gives **E**. The reaction does not stop at this stage; instead **E** can be fluorinated by Selectfluor to give the functionalized ketone **3**.[20] Because we had never isolated **5**, it is also possible that intermediate **D** reacts with Selectfluor first to give **F**, and, following reductive elimination, gives the final product **3**. The transmetalation of Au^{I}–Cl complex with boronic acid has been demonstrated by Hashmi and co-workers in a recent paper.[21] The transmetalation of Au–F with boronic acid has also been proposed by Zhang and co-workers in their gold-catalyzed cross-coupling reaction of propargylic acetate.[5b] To probe the proposed mechanism in Scheme 4 we conducted two control experiments (Scheme 5). According to Scheme 4, fluoroketones **4** could be formed in the absence of a coupling partner R^{3}M, in which case, the vinyl–metal complex **C** undergoes reductive elimination or fluorodemetalation[15] to give fluoroketone **4**. This was the case experimentally, although so far only moderate yields have been obtained (Scheme 5a). The reaction of terminal alkyne **1i** with **2a** gives the oxidative coupling product **6**.[22] The formation of **6** hints towards a tandem mechanism that involves fluorination of the gold complex, transmetalation with boronic acid or terminal



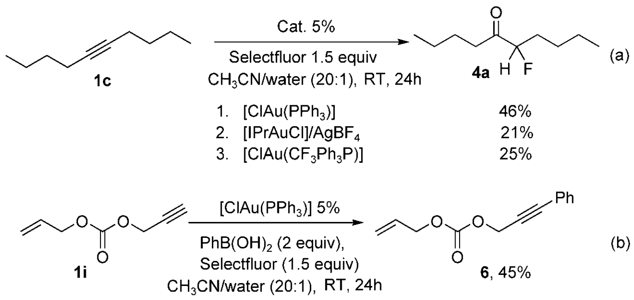
Scheme 4. Proposed mechanism for the functionalized hydration.

Table 4: Scope of the functionalized hydration.[a]



Entry	1		2	Products 3	Yield (ratio)
1		**1a**	PhB(OH)$_2$ (**2a**)	 	**3a**, 88% (6.7:1)
2		**1b**	**2a**	 	**3b**, 88% (4.6:1)
3		**1c**	**2a**		**3c**, 63%
4		**1d**	**2a**		**3d**, 79%
5		**1e**	**2a**	 	**3e**, 85% (2.2:1)
6		**1f**	**2a**	 	**3f**, 47% (2.1:1)
7		**1g**	**2a**	 	**3g**, 83%(5:1)
8		**1h**	**2a**	 	**3h**, 70% (5.0:1)
9		**1a**	*p*-F-C$_6$H$_4$B(OH)$_2$ (**2b**)	 	**3i**, 88% (5.3:1)
10		**1a**	*m*-Cl-C$_6$H$_4$B(OH)$_2$ (**2c**)	 	**3j**, 71% (3.4:1)
11		**1a**	*p*-Me-C$_6$H$_4$B(OH)$_2$ (**2d**)	 	**3k**, 88% (6.7:1)
12		**1a**	*p*-Ph-C$_6$H$_4$B(OH)$_2$ (**2e**)	 	**3l**, 90% (5.3:1)

[a] **1** (0.4 mmol), **2** (0.8 mmol), Selectfluor (1.0 mmol), [ClAuPPh$_3$] (5%), 3 mL CH$_3$CN/water (20:1), RT, 18–24 h.



Scheme 5. Synthesis of fluoroketones and the oxidative coupling of alkynes.

alkyne, and reductive elimination, as shown in Scheme 4. It is interesting to note that gold catalysts undergo transmetalation and reductive elimination readily, although they are not able to undergo oxidative insertion—as Pd does in coupling reactions.

The key step of this mechanism is the generation of cationic gold species **A** by fluorination (Scheme 4). Our preliminary experiments show that Selectfluor did react with gold(I) complex at room temperature. For example, when CH$_3$CN was used as solvent, AuCl readily reacted with Selectfluor at room temperature; the net result being the transfer of fluorine from Selectfluor to gold (Scheme 4). This process could be monitored by ^{19}F NMR spectroscopy. After addition of Selectfluor to AuCl in CD$_3$CN, a new peak (br. s, $\delta = -184$ ppm) appeared and its intensity increased with time (see the Supporting Information for spectral analyses). When we added $PhB(OH)_2$ to the system, this peak disappeared immediately and biphenyl was detected in the reaction mixture (see the Supporting Information). We believe that the new peak represents a reactive metal–fluoride species, which we tentatively assigned as $[Au^{III}ClF(L)]^+$ ($L = CH_3CN$). The formation of biphenyl can be rationalized by a transmetalation with phenylboronic acid, followed by reductive elimination to give biphenyl (see the Supporting Information). The high reactivity rules out the possibility that it is a simple fluoride anion. $[Ph_3PAuCl]$ can also be oxidized under the same conditions but at a lower rate; however, in this case the phosphine ligand Ph_3P was also oxidized (by the high-valence gold or Selectfluor) after prolonged times. $Ph_3P{=}O$ was detected in the reaction mixture (confirmed by ^{31}P NMR and ESI-MS analysis).[5b,c]

Although the oxidation of Au^I to Au^{III} by Selectfluor has been postulated as a reasonable process, it has never been confirmed experimentally in the literature. As the Au^I to Au^{III} oxidation was a key step in our mechanism, we studied this process using X-ray photoelectron spectroscopy (XPS).[23] XPS has been used in the determination of the chemical states of supported gold catalysts.[24] The binding energy (BE) of the Au $4f_{7/2}$ electron in each gold oxidation state is usually large enough to be differentiated (for $[ClAu^IPPh_3]$, Au $4f_{7/2} = 85.7$ eV, for $Na[Au^{III}Cl_4]$, Au $4f_{7/2} = 87.6$ eV).[23] We used this technique to investigate the valence change of gold in the reaction. First, we tested two gold standards ($[ClAu^IPPh_3]$ and $Na[Au^{III}Cl_4]$, Figure 1); the Au $4f_{7/2}$ photoelectron peak is located at a BE value of 85.7 and 87.5 eV, respectively, which is quite consistent with the literature.[23] We investigated our samples A–C using the same conditions as for the standards. Sample A appears as a mixture of two gold oxidation states (Figure 1). We then tested the chloride-stabilized samples (chloride reacts with the gold(III) complex to give a more stable chloroaurate); they gave similar spectra but with a higher percentage of gold(III) species (see Table S2 in the Supporting Information). Because the BE difference between Au 4f peak of two gold states is large (ca. 3.0 eV), we assigned them to be Au^0 and Au^{III} species, respectively. The spectra of these Au 4f peaks are very similar to a literature report,[24] and have been ascribed to be a mixture of Au^0 and Au^{III} (see Supporting Information for more details). Thus, our XPS measurements confirm the existence of gold(III) (BE of Au $4f_{7/2} = 87.6$ eV) in the reaction mixture of gold(I) catalyst and Selectfluor (Figure 1). The existence of gold(0) can be explained by disproportionation of unreacted Au^I complexes or decomposition/reduction of Au^{III} species in high vacuum during XPS measurements. Because the Au^{III} species is the major component in all tests, the existence of Au^{III} species cannot be attributed to a disproportionation of unreacted Au^I complexes alone.

We also conducted other investigations on the potential valence change of gold in the reaction, using high-resolution ESI mass spectrometry (see the Supporting Information). We were able to detect various cationic Au^{III} species, but $[Au^{III}(L)ClF]^+$ itself was not detected; this may be because metal–fluorine bonds tend to be labile and reactive. The fluoride ion, according to hard/soft acid–base theory, is mismatched with the cations formed by late transition metals, especially gold.[25]

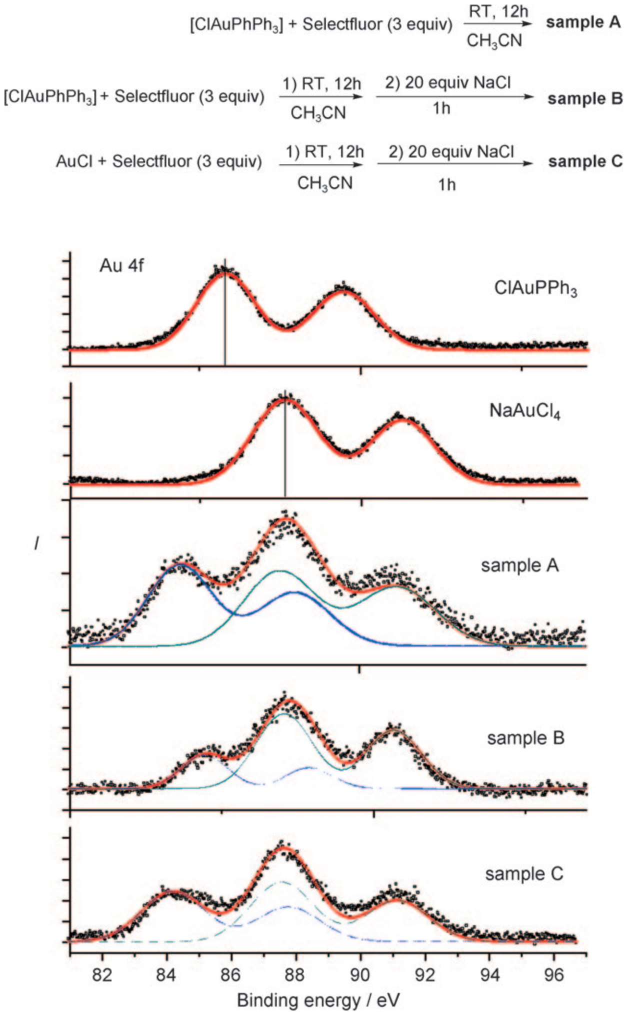


Figure 1. XPS curve fitting of the Au 4f photoelectron peaks.

In summary, a potentially new role for fluorine in cationic gold catalysis is proposed, an example of which is the hydration of alkynes to give α-substituted α-fluoroketones, in one pot and under mild conditions. The ready availability of alkynes and organoboronic acids, and the current interest in α-fluoroketones make this reaction quite attractive. Studies probing the broader implications of cationic metal species enabled by fluorine are underway in our laboratory.

Experimental Section

General procedure for preparation of **3**. Selectfluor (354 mg, 1.0 mmol, 2.5 equiv) was added into a solution of alkyne **1a** (92 mg, 0.4 mmol), $[Ph_3PAuCl]$ (9.8 mg, 0.02 mmol, 5% equiv), and phenylboronic acid (98 mg, 0.8 mmol, 2 equiv) in 3 mL $MeCN/H_2O$ (20:1). The reaction was stirred at room temperature for 18 h. The reaction mixture was quenched with saturated NH_4Cl solution, the resulting aqueous mixture was extracted with diethyl ether (3 × 15 mL), and then the combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure to give the crude product, which was purified by flash silica gel chromatography (30% dichloromethane in hexane/60% dichloromethane in hexane) to give

3a as a mixture of two regioisomers (**3a**/**3a′** = 6.7:1); 118 mg (88 %). IR (neat): 2958, 1724, 1450, 1275, 1116, 711 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), major isomer: $\delta = 0.87$ (t, $J = 6.5$ Hz, 3 H), 1.29–1.31 (m, 4 H), 2.03–2.18 (m, 1 H), 2.22–2.38 (m, H), 3.08–3.1 (m, 2 H), 4.55 (t, $J = 6$ Hz, 2 H), 7.31–7.53 (m, 8 H), 7.82 ppm (d, $J = 7.5$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$), major isomer: $\delta = 14.0$, 22.8, 22.5, 36.6, 37.8 (d, $J = 22$ Hz), 59.4, 103.5 (d, $J = 186$ Hz), 124.5 (d, $J = 10.5$ Hz), 128.4, 128.8, 129.7, 133.1, 137.6(d, J=22 Hz), 166.4, 208.5 ppm (d, $J = 30$ Hz); ^{19}F NMR (470 MHz, $CDCl_3$): major isomer: $\delta = -170.04$ ppm (t, $J = 25.4$ Hz); GC/MS (EI) m/z: 221, 201, 177, 135, 77; anal. calcd. for $C_{21}H_{23}FO_3$: C 73.66, H 6.77; found: C 73.42, H 6.75.

Received: June 12, 2010
Revised: July 13, 2010

Keywords: alkynes · fluorination · fluoroketones · gold

---

[1] G. P. Chiusoli, P. M. Maitlis, *Metal-Catalysis in Industrial Organic Processes*, RSC, Cambridge, **2008**.

[2] a) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; b) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266; c) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351; d) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239.

[3] a) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482; b) R. A. Widenhoefer, *Chem. Eur. J.* **2008**, *14*, 5382; c) E. Jiménez-Nuñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326; d) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766; e) P. Garcia, M. Malacria, C. Aubert, V. Gandon, L. Fensterbank, *ChemCatChem* **2010**, *2*, 493.

[4] T. Okabayashi, Y. Nakaoka, E. Yamazaki, M. Tanimoto, *Chem. Phys. Lett.* **2002**, *366*, 406.

[5] a) G. Zhang, L. Cui, Y. Wang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 1474; b) G. Zhang, Y. Peng, L. Cui, L. Zhang, *Angew. Chem.* **2009**, *121*, 3158; *Angew. Chem. Int. Ed.* **2009**, *48*, 3112; c) Y. Peng, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 5062; d) W. E. Brenzovich, Jr., D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard III, F. D. Toste, *Angew. Chem.* **2010**, *122*, 5651; *Angew. Chem. Int. Ed.* **2010**, *49*, 5519; e) A. D. Melhado, W. E. Brenzovich, A. D. Lackner, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 8885.

[6] a) T. Furuya, H. M. Kaiser, T. Ritter, *Angew. Chem.* **2008**, *120*, 6082; *Angew. Chem. Int. Ed.* **2008**, *47*, 5993; b) T. Furuya, T. Ritter, *J. Am. Chem. Soc.* **2008**, *130*, 10060; c) T. Furuya, T. Ritter, *Org. Lett.* **2009**, *11*, 2860.

[7] a) K. L. Hull, W. Q. Anani, M. S. Sanford, *J. Am. Chem. Soc.* **2006**, *128*, 7134; b) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2009**, *131*, 9651; c) N. D. Ball, M. S. Sanford, *J. Am. Chem. Soc.* **2009**, *131*, 3796.

[8] M. Schuler, F. Silva, C. Bobbio, A. Tessier, V. Gouverneur, *Angew. Chem.* **2008**, *120*, 8045; *Angew. Chem. Int. Ed.* **2008**, *47*, 7927.

[9] C. F. Rosewall, P. A. Sibbald, D. V. Liskin, F. E. Michael, *J. Am. Chem. Soc.* **2009**, *131*, 9488.

[10] X. Wang, T.-S. Mei, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 7520.

[11] a) T. Wu, G. Yin, G. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 16354; b) S. Qiu, T. Xu, J. Zhou, Y. Guo, G. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 2856.

[12] a) P. T. Nyffeler, S. G. Duron, M. D. Burkart, S. P. Vincent, C.-H. Wong, *Angew. Chem.* **2005**, *117*, 196; *Angew. Chem. Int. Ed.* **2005**, *44*, 192; b) M. Schueler, *Spec. Chem. Mag.* **2006**, *26*, 20.

[13] L. Hintermann, A. Labonne, *Synthesis* **2007**, 1121.

[14] N. Marion, R. S. Ramon, S. P. Nolan, *J. Am. Chem. Soc.* **2009**, *131*, 448.

[15] W. Wang, B. Xu, G. B. Hammond, *J. Org. Chem.* **2009**, *74*, 1640.

[16] a) G. E. Heasley, C. Codding, J. Sheehy, K. Gering, V. L. Heasley, D. F. Shellhamer, T. Rempel, *J. Org. Chem.* **1985**, *50*, 1773; b) R. S. Neale, *J. Am. Chem. Soc.* **1964**, *86*, 5340; c) L. Benati, P. C. Montevecchi, P. Spagnolo, *Tetrahedron Lett.* **1988**, *29*, 2381; d) K. Tamao, K. Maeda, *Tetrahedron Lett.* **1986**, *27*, 65.

[17] a) Y. Guo, B. Twamley, J. n. M. Shreeve, *Org. Biomol. Chem.* **2009**, *7*, 1716; b) K.-Y. Kim, B. C. Kim, H. B. Lee, H. Shin, *J. Org. Chem.* **2008**, *73*, 8106; c) G. K. S. Prakash, P. Beier, *Angew. Chem.* **2006**, *118*, 2228; *Angew. Chem. Int. Ed.* **2006**, *45*, 2172; d) M. Nakamura, A. Hajra, K. Endo, E. Nakamura, *Angew. Chem.* **2005**, *117*, 7414; *Angew. Chem. Int. Ed.* **2005**, *44*, 7248.

[18] a) Y. Harada, J. Nakanishi, H. Fujihara, M. Tobisu, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2007**, *129*, 5766; b) C. Zhou, R. C. Larock, *J. Org. Chem.* **2006**, *71*, 3184; c) Y. Chen, C. Lee, *J. Am. Chem. Soc.* **2006**, *128*, 15598; d) C. H. Oh, H. H. Jung, K. S. Kim, N. Kim, *Angew. Chem.* **2003**, *115*, 829; *Angew. Chem. Int. Ed.* **2003**, *42*, 805.

[19] L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.* **2008**, *130*, 17642.

[20] The fluorination of a ketone bearing an aromatic ring has been reported: D. Enders, M. R. M. Huttle, *Synlett* **2005**, 991.

[21] A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592.

[22] F. Yang, Y. Wu, *Eur. J. Org. Chem.* **2007**, 3476.

[23] J.-H. Choy, Y.-I. Kim, *J. Phys. Chem. B* **2003**, *107*, 3348.

[24] M. P. Casaletto, A. Longo, A. Martorana, A. Prestianni, A. M. Venezia, *Surf. Interface Anal.* **2006**, *38*, 215.

[25] D. S. Laitar, P. Muller, T. G. Gray, J. P. Sadighi, *Organometallics* **2005**, *24*, 4503.