# Catalytic Cross-Coupling of Vinyl Golds with Diazonium Salts under Photoredox and Thermal Conditions

Dilip V. Patil,<sup>+a</sup> Hokeun Yun,<sup>+a</sup> and Senghoon Shin<sup>a,\*</sup>

<sup>a</sup> Institute for Natural Sciences, CNOS and Department of Chemistry, Hanyang University, 17 Haengdang-dong,Seongdong-gu, 133-791 Seoul, Republic of Korea Fax: (+82)-2-2299-0762; phone: (+82)-2-2220-0948; e-mail: sshin@hanyang.ac.kr

<sup>+</sup> DVP and HY contributed equally to this work.

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**Abstract:** Catalytically generated vinyl gold complexes from *tert*-butyl allenoates were found to undergo an efficient cross-coupling with arenediazonium salts. The gold(I)-gold(III) redox cycle can be accessed under two different conditions, i.e., visible-light photoredox as well as a thermally induced radical chain pathway. The current  $C(sp^2)-C(sp^2)$  cross-coupling protocol that is catalytic in gold, would make available desirable structural diversity to the traditional cross-coupling chemistry.

**Keywords:** cross-coupling; diazonium salts; gold catalysis; radical chain reaction; visible light photo-catalysis

Over the past decade, gold catalysis has evolved into a powerful tool for organic transformations, enabling the formation of C-C and C-X (heteroatom) bonds through diverse cycloisomerization, rearrangements and cycloadditions under mild conditions.<sup>[1]</sup> In majority of these transformations, formation of  $C(sp^2)$ -Au intermediates obtained from the  $\pi$ -activation of alkynes or allenes, is followed by simple protodeauration or halogenation. Combining the complexity-generating power of gold catalysis with C-C cross-coupling in a catalytic fashion would provide a fine prospect for bis-functionalization of  $\pi$ -bonds.<sup>[2]</sup> While conventional C-H functionalization/cross-coupling of arenes relies on directing groups to control regioselectivity (Scheme 1a), vinyl metal species formed from alkynes can couple regiospecifically and also have inherently more diverse structures than the preformed cyclic motifs (Scheme 1b). Toward this goal, reluctance of Au(I) to undergo two-electron oxidation  $[E^{\circ} (Au^{3+}/Au^{+1}) = 1.36 \text{ V}]$  has been a hurdle,<sup>[3]</sup> although use of strong external oxidants such as Selectfluor,  $PhI(OAc)_2$  and NFSI has recently shown some promise in accessing Au(I)/Au(III) cycles, furnishing homo- and hetero-coupling.<sup>[4,5]</sup> However, such external oxidants are generally expensive and/or atom-inefficient and thus there is a clear demand for cleaner oxidants or coupling partners.

Recently, the redox property of gold complexes has gained renewed interest in combination with visible light photoredox catalysis.<sup>[6]</sup> Pioneering works in the groups of Glorius and Toste showed that aryl radicals from diazonium salts<sup>[7]</sup> can oxidize Au(I), enabling  $C(sp^3)-C(sp^2)$  coupling.<sup>[8]</sup> Instead of two-electron redox cycles,<sup>[5h]</sup> these processes are proposed to operate *via* stepwise one-electron transfers, which likely lowers the oxidation barrier of Au(I). Surprisingly, however, cross-coupling of more ubiquitous  $C(sp^2)$ -Au intermediates with arenediazonium salts has so far only rarely been studied,<sup>[8b,9]</sup> presumably due to com-

#### a) C-H functionalization/cross-coupling



Scheme 1. Cross-coupling of in-situ generated organogolds.

Table 1. Optimization study.<sup>[a]</sup>



<sup>[a]</sup> Reactions were conducted with **1a** (0.1 mmol) and **2a** (0.4 mmol) in the presence of 10 mol% of gold complex and 2.5 mol% of photocatalyst in thoroughly degassed solvents (0.1 M) under blue LED irradiation.

<sup>[b]</sup> NMR yields with  $CH_2Br_2$  as an internal standard; yields of **4a** in parenthesis.

<sup>[c]</sup> Prepared *in-situ* from (Ph<sub>3</sub>P)AuCl and AgOTf.

<sup>[d]</sup> 23 Ŵ CFL (hood light) instead of blue LED.

peting protodeauration. Given different propensity of Au(I) and Au(III) complexes toward protodeauration,<sup>[10]</sup> the timing of Au(I) oxidation may affect the competing protodeauration. We therefore investigated photoredox cross-coupling of  $C(sp^2)$ -Au intermediates from *tert*-butyl allenoates,<sup>[11]</sup> for which stable vinyl Au(I) intermediates can be isolated.<sup>[11b]</sup> We report an efficient oxidative tandem cyclization/arylation of tert-butyl allenoates, leading to 3-arylated butenolides for which diverse biological activities have been reported. We found that the Au(I)-Au(III) cycle can be accessed under two different conditions, namely a visible-light photoredox and a thermally induced radical chain pathway and the details are described herein. Such a catalytic process may open up a new, general and mechanistically distinct C-C bond forming processes.

The initial test of tandem cyclization of *tert*-butyl allenoate/cross-coupling was encouraging. The reaction of **1a** with 4-MeO-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (**2a**) in the presence of Ph<sub>3</sub>PAuCl (10 mol%) and [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (2.5 mol%) in thoroughly degassed MeOH under irradiation of blue LED provided 79% of **3a**. Use of the mixed solvent MeOH/CH<sub>3</sub>CN (20:1) somewhat improved the yield to 82% (entry 3). Photocatalysts that are stronger or weaker reductants [ $E_{1/2}$ (M\*/M<sup>+</sup>)] led to poorer yields (entries 4 and 5), indicating that Ru(bpy)<sub>3</sub><sup>2+</sup> is optimal.<sup>[6a]</sup> Change of Au catalysts to those having a bulky and/or a strong  $\sigma$ -donor ligand turned out to be ineffective or led to inferior results

(entries 6 and 7). We were delighted to find that there was substantial improvement in the yield and rate when a cationic Au(I) complex, generated *in-situ* from Ph<sub>3</sub>PAuCl and AgOTf, was used, leading to 92% yield of **3a** in only 1.5 h (entry 9). AuCl<sub>3</sub>, although competent, led to an inferior yield (entry 10). Control experiments indicated that little progress was observed at room temperature in the absence of photocatalyst or gold catalyst (entries 11 and 12). Blue LED light was significantly more effective than fluorescent hood light (entry 13). No reaction was observed in the dark under otherwise identical conditions to entry 9.

Having established mild conditions for the current cyclization/ $sp^2$ - $sp^2$  coupling, we set out to examine the scope. Initial testing was conducted with regard to substitutions on the allenoates 1 (Table 2). Various alkyl groups at R<sup>1</sup> were widely tolerated, giving good to excellent yields of the corresponding butenolides **3a–3e**. Functional groups such as Ph, alkynes and imides and alcohols that can potentially interfere with the formation of **3** were well tolerated to provide **3f–3i**. Substrates having both  $\alpha$ , $\gamma$ -substituents (**3k** and **3l**, **3n** and **3o**) gave somewhat lower yields of the coupled products because of the competing protodeauration. In these cases, use of NaHCO<sub>3</sub> as an additive effectively suppressed this side pathway.

Variations on the structure of arenediazonium salts were subsequently tested (Table 3). Both electron-donating as well as electron-withdrawing arenes turned



- [a] Reactions were performed with 1 (0.2 mmol) and 2a (0.8 mmol), Ph<sub>3</sub>PAuCl (10 mol%), AgOTf (10 mol%) and Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (2.5 mol%) in degassed MeOH:CH<sub>3</sub>CN (20:1, 2 mL) under blue LED irradiation for 1–4 h at room temperature; isolated yields after chromatography.
- <sup>[b]</sup> Without AgOTf under otherwise standard conditions.
- <sup>[c]</sup> An O-TBS protected allenoate was used as substrate.
- <sup>[d]</sup> NaHCO<sub>3</sub> (1 equiv.) as an additive.

out to be equally good. Halogen, nitro and ester substituents were completely compatible (**3p-3u**). The steric environment in the arenediazonium salts did not adversely affect the efficiency as in the formation of **3x-3aa**. Polycyclic (**3ab**) and heteroarenes (**3ac**) was also tested, but in the latter case, only a poor yield was obtained, indicating a limitation of the current coupling.

During the course of our investigation, we were surprised to find that the activation of arenediazonium salts do not necessarily involve the photocatalyst or light source. At room temperature, omitting photocatalyst led to a complete shutdown of the reaction **Table 3.** Variation of the arenediazonium salt.<sup>[a]</sup>



<sup>[a]</sup> Reactions were performed under identical conditions to Table 2, unless otherwise noted; isolated yields after chromatography.

<sup>[b]</sup> Eosin Y (2.5 mol%) was used as a photocatalyst.

MeCO <sub>2</sub> -t-Bu		
1a	Ph <sub>3</sub> PAuCl (10 mol%) <i>in the dark</i>	Ar >=0
+	MeOH:MeCN (20:1)	Me
$ArN_2BF_4$	60 °C	3

Entry	Ar	Time	<b>3</b> , Yield [%] <sup>[b]</sup>
1	$4-MeO-C_6H_4$	4 h	<b>3a</b> , 67
2	2,5-di-MeO-C <sub>6</sub> H <sub>3</sub>	1.5 h	<b>3aa</b> , 70
3	Ph	1.5 h	<b>3v</b> , 0
4	$4-CH_3-C_6H_4$	2 h	<b>3w</b> , 20
5	$3-CH_3-C_6H_4$	h	<b>3</b> y, <2
6	$2-CH_3-C_6H_4$	2 h	<b>3x</b> , 5
7	$4-Cl-C_6H_4$	1.5 h	<b>3r</b> , 84
8	$4-NO_2-C_6H_4$	2.5 h	<b>3t</b> , 82
9	$4-CO_2Me$	1.5 h	<b>3u</b> , 73

[a] 1a (0.2 mmol), 2 (4 equiv.) in the presence of (Ph<sub>3</sub>P)AuCl (10 mol%); no photocatalyst and in the dark.

<sup>[b]</sup> Isolated yields after chromatography.

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(entry 11, Table 1). In sharp contrast, the reaction run at 60 °C with Ph<sub>3</sub>PAuCl *as a sole catalyst in the dark*,



Scheme 2. Control experiments.

proceeded to give 3a in 67% yield (entry 1, Table 4). In this case, a cationic Au(I) complex formed from Ph<sub>3</sub>PAuCl and AgOTf gave extensive proto-demetallation product 4a. This raised an intriguing possibility of thermally induced oxidative addition of arenediazonium salts to Ph<sub>3</sub>PAuCl.<sup>[12]</sup> We then promptly examined the scope under these thermal conditions with various arenediazonium salts (Table 4). In contrast to facile reactions of alkoxy-substituted arenes (entries 1 and 2), phenyl- or methyl-substituted arenes performed poorly under these conditions, providing only extensive biaryl or arylmethyl ether side-products from ArN<sub>2</sub><sup>+</sup> (GC-MS; entries 3-6). In contrast, electron-deficient arenes turned out to be general and excellent coupling partners (entries 7–9). The observed reactivity profile was strikingly consistent to what was observed in the thermal reduction of arenediazonium salts in alcoholic solvents, in which the free-radical chain process is favored in the order of p-MeO > p-NO<sub>2</sub>, p-Br>p-CH<sub>3</sub>>p-H in the diazonium salts.<sup>[16b]</sup> Clearly, these results indicated that a different mechanism is operating, possibly involving a radical chain mechanism or two-electron oxidative addition of arenediazonium salts to LAuCl.[13,16]

A series of control experiments was conducted to further probe the mechanism. Vinyl gold complex 5j prepared according to the literature<sup>[11b]</sup> was coupled with 2a affording 3j [Eq. (1), Scheme 2], with a virtually identical efficiency as the catalytic version (Table 2). This supports an initial, fast cyclization by the cationic [Ph<sub>3</sub>PAu]OTf into **5**j, followed by oxidation into Au(III) species.<sup>[8a]</sup> Formation of vinyl gold complexes and their protodeauration in MeOH was also studied. A cationic [Ph<sub>3</sub>PAu]OTf (1 equiv-; preformed) immediately (<5 min) provided the vinyl gold 5d in a quantitative yield and it remained intact without any protodeauration in CD<sub>3</sub>OD for 24 h at room temperature.<sup>[14]</sup> However, Ph<sub>3</sub>PAuCl (1 equiv.) without AgOTf failed to cyclize 1d at room temperature even in the presence of excess NaBF<sub>4</sub> salt, excluding the possibility of anion metathesis for the formation of cationic gold [Eq. (2), Scheme 2]. Thus, the cyclization of **1a** in the absence of a silver salt (entry 1, Table 1) is attributed to an initial oxidation of Ph<sub>3</sub>PAuCl by photoredox-generated aryl radical,<sup>[8b]</sup> followed by the cyclization of the allenoate by the Au(III) species. Thus it appears that, in the case of cationic gold catalysis (Ph<sub>3</sub>PAu<sup>+</sup>), initial cyclization then photoredox oxidation is the predominant mechanistic route, although possibly not exclusive.<sup>[15]</sup>

From the above experiments, a plausible mechanism is delineated as in Scheme 3. The reactions using cationic [LAu]<sup>+</sup> start with cyclization of 1 to form I. An aryl radical generated from photoredox reaction between excited state Ru(II)\* and diazonium salts would combine with vinyl gold I to form an openshell Au(II) intermediate (II) which then undergo further oxidation by Ru(III) into III.<sup>[8a]</sup> Subsequent reductive elimination closes the Au(I)-Au(III) catalytic cycle. When LAuCl that is incapable of cyclizing 1 is used, oxidation by the photoredox-generated Ar radical should occur first to form Au(II) (IV) which is further oxidized by Ru(III) to Au(III) (V). At 60 °C, oxidation of IV into V may be coupled to a radical chain propagation step via generation of Ar radical from diazonium salts, which explains the formation of 3 in the absence of the photocatalyst in the dark (Table 4). In the latter case, radical initiation may involve SET from solvents.<sup>[16]</sup> Finally, cyclization of 1 by Au(III)  $(\mathbf{V})^{[11a]}$  and reductive elimination would form **3**.

The oxidation state of gold catalyst in the reaction with diazonium salts under photoredox and thermal conditions was probed with XPS (X-ray photoelectron spectroscopy) to support such a mechanism. A mixture of Ph<sub>3</sub>PAuCl (1 equiv.) and PhN<sub>2</sub>BF<sub>4</sub> (3 equiv.) heated at 60 °C for 1 h in CH<sub>3</sub>OH/CH<sub>3</sub>CN (20:1) in the absence of photocatalyst, showed predominantly two peaks at 87.1 eV and 90.9 eV, from  $4f_{7/2}$  and  $4f_{5/2}$ respectively, in good agreement with a reference sample of NaAuCl<sub>3</sub> (87.0 and 90.4 eV), which indicated that an Au(III) species is the predominant form of gold in the mixture.<sup>[17,18]</sup> The corresponding mixture



Scheme 3. Proposed mechanism of cyclization/cross-coupling via dual Au(PPh<sub>3</sub>)OTf/photocatalysis or thermal Au catalysis.

under photocatalytic conditions using Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (2.5 mol%) and blue LED, although less characteristic, also indicated that Au(III) species is prevalent. Moreover, the quantum yield was measured by means of chemical actinometry.<sup>[17,19]</sup> The quantum yield of the photocatalytic reaction using neutral gold complex (Ph<sub>3</sub>PAuCl) was measured to be 0.31, which is consistent with the dual Au/photoredox catalysis (Scheme 3, *left*). However, in the photocatalytic reaction with a cationic gold complex generated from Ph<sub>3</sub>PAuCl and AgOTf, the apparent quantum yield was measured to be 1.21, which suggests that a radical chain process contributes to some extent to the oxidation of **II** to **III** where the photocatalyst functions as a radical initiator.

In summary, we have developed an efficient crosscoupling of *in-situ* generated vinyl gold complexes for the formation of  $C(sp^2)-C(sp^2)$  bonds. Replacing external oxidants with readily available arenediazonium salts and a thermal reaction not requiring a photocatalyst<sup>[20]</sup> are two distinct advantages that offer an economically and mechanistically distinct Au-catalyzed  $C(sp^2)-C(sp^2)$  cross-coupling. The current tandem cyclization/cross-coupling strategy will be particularly valuable since it can combine the structural diversity enabled by gold catalysis with cross-coupling chemistry. Further investigations to demonstrate the generality of the cross-coupling of vinyl gold intermediates with electrophilic partners are currently underway and will be reported in due course.

## **Experimental Section**

### **General Procedure (Photocatalytic Conditions)**

In a flame-dried test tube was placed  $[Ru(bpy)_3](PF_6)_2$  $(4.3 \text{ mg}, 0.005 \text{ mmol}), \text{ diazonium salts } 2 \quad (0.8 \text{ mmol}),$ AgOTf (Ph<sub>3</sub>P)AuCl (9.9 mg, 0.02 mmol), (5.1 mg. 0.02 mmol) and tert-butyl allenoates 1 (0.2 mmol). The mixture was suspended in a mixture of anhydrous MeOH:CH<sub>3</sub>CN (20:1, 2 mL) and was degassed by freezepump-thaw cycles  $(\times 3)$  under argon. The mixture was then allowed to stir at room temperatrure under blue LED irradiation. Upon completion (TLC), the reaction mixture was quenched with water (2 mL) and was extracted with ether  $(3 \times 3 \text{ mL})$ . The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude products were purified by column chromatography over silica gel (ethyl acetate/hexane).

#### **General Procedure (Thermal Conditions)**

To a flame-dried test tube was added diazonium salt 2 (0.8 mmol, 4 equiv.), (Ph<sub>3</sub>P)AuCl (9.9 mg, 0.02 mmol) and *tert*-butyl allenoates 1 (0.2 mmol, 1.0 equiv.) and the tube was wrapped with aluminum foil. In the absence of light, an-hydrous MeOH:CH<sub>3</sub>CN (20:1, 2 mL) was added and the mixture was heated at 60 °C under argon. Similar work-up and purification led to the isolation of **3**.

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