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Redox Gold Catalysis **Hot Paper**

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Ligand-Assisted Gold-Catalyzed Cross-Coupling with Aryldiazonium Salts: Redox Gold Catalysis without an External Oxidant[**]

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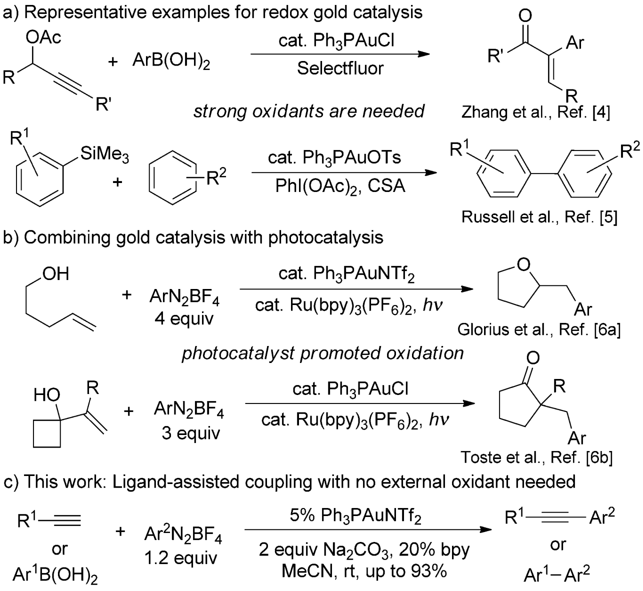
Abstract: *Gold-catalyzed C(sp)–C(sp^2) and C(sp^2)–C(sp^2) cross-coupling reactions are accomplished with aryldiazonium salts as the coupling partner. With the assistance of bpy ligand, gold(I) species were oxidized to gold(III) by diazonium without any external oxidants. Monitoring the reaction with NMR and ESI-MS provided strong evidence for the nitrogen extrusion followed by Au^{III} reductive elimination as the key step.*

Homogeneous gold catalysis has grown rapidly during the past decade. Within this enduring field, the π-activation mode has gained far more attention than redox gold catalysis.[1] This reluctance is likely due to concerns regarding the high redox potential between Au^{I} and Au^{III}.[2] The "seal of hesitation" was clearly broken in the past few years with some breakthrough examples.[3]

For example, Zhang reported the propargyl ester rearrangement and sequential coupling with boronic acid using Selectfluor as the oxidant.[4] Russell also developed the arene cross-coupling with PhI(OAc)$_2$ (PIDA) as the oxidant (Scheme 1 a).[5] In these representative cases, strong oxidants were required to facilitate the Au^{I}/Au^{III} catalytic cycle. More recently, the groups of Glorius and Toste demonstrated that the Au^{I}/Au^{III} catalytic cycle could be alternatively accessed through the combination of a photocatalyst and a radical precursor, such as aryldiazonium salts (Scheme 1 b).[6] As proposed by the authors, the oxidation of the gold catalyst was achieved through the initial combination of an aryl radical and a gold(I) species, and sequential single-electron transfer from the resulting gold(II) intermediate to the photocatalyst.

Our group recently disclosed a gold-catalyzed cross-coupling between aromatic and aliphatic terminal alkynes, and it was achieved through the selective formation of gold acetylide.[7] With the aid of a strong oxidant (PIDA) and phenanthroline ligand, rapid reductive elimination of the Au^{III} intermediate led to facile and selective diyne formation. Encouraged by this success and inspired by recent works from the groups of Glorius and Toste (Scheme 1 b), we were intrigued by the possibility of C(sp)–C(sp^2) cross-coupling using aryldiazonium salts as the coupling partner under mild photocatalytic conditions.[8]

To test this hypothesis, the alkyne **1a** and diazonium salt **2a** were selected as the model substrates. As shown in Table 1 (entry 1), the reaction of **1a** and **2a** in the presence of both a photocatalyst and gold catalyst gave none of the desired coupling products (low conversion of **1a**). Considering that the formation of a gold acetylide could be critical, a base (Na$_2$CO$_3$) was added to assist the alkyne deprotonation. As expected, the cross-coupling product **3aa** was formed, though in modest yield (entry 2). In the control experiments (entries 3–5), almost identical kinetics and yields were observed under either standard or dark conditions in the absence of the photocatalyst, and thus negated the involvement of a photocatalytic process. This result was exciting since it implied that the diazonium salt alone, in this reaction, might be fully capable of oxidizing the active gold(I) species into gold(III). To optimize the reaction conditions, various additives and catalysts were tested (see the Supporting Information for details). Through extensive screening, a conversion as high as 74% could be achieved by simply increasing the reaction concentration (entry 7). Eventually, using an organic



Scheme 1. Redox gold catalysis. CSA = camphorsulfonic acid, Tf = trifluoromethanesulfonyl, Ts = 4-toluenesulfonyl.

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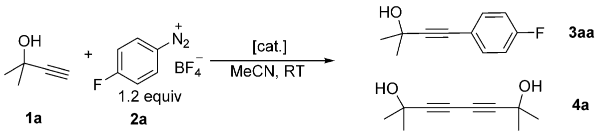
Table 1: Optimization of reaction conditions.[a,b]



Entry	Catalyst (%)	Additive (equiv)	*t* [h]	Conc. [м]	Conv. [%][c]	Yield [%] 3 aa[d]	4 a[c]
1	$[Ru(bpy)_3](PF_6)_2$ (2.5), $[Ph_3PAuNTf_2]$ (5)	–	10	0.2	9	0	0
2	$[Ru(bpy)_3](PF_6)_2$ (2.5), $[Ph_3PAuNTf_2]$ (5)	Na_2CO_3 (2)	10	0.2	46	41	0
3	$[Ru(bpy)_3](PF_6)_2$ (2.5)	Na_2CO_3 (2)	10	0.2	0	0	0
4	$[Ph_3PAuNTf_2]$ (5)	Na_2CO_3 (2)	10	0.2	44	41	0
5	$[Ph_3PAuNTf_2]$ (5)[e]	Na_2CO_3 (2)	10	0.2	40	36	0
6	–	Na_2CO_3 (2)	10	0.2	0	0	0
7	$[Ph_3PAuNTf_2]$ (5)	Na_2CO_3 (2)	10	0.5	74	62	0
8	$[Ph_3PAuNTf_2]$ (5)	bpy (2)	8	0.5	100	83	8
9	$[Ph_3PAuNTf_2]$ (5)	Na_2CO_3 (2), bpy (0.2)	4	0.5	100	94	2
10	$[Ph_3PAuNTf_2]$ (2)	Na_2CO_3 (2), bpy (0.2)	10	0.5	53	40	2
11	$PdCl_2$ (5)	bpy (2)	10	0.5	0	0	0
12	$PdCl_2$ (5), $[Ph_3PAuNTf_2]$ (5)	bpy (2)	10	0.5	86	56	13

[a] Reaction conditions: **1** (0.1 mmol), **2** (0.12 mmol), catalysts, and additives in acetonitrile at RT for 10 h. [b] Less than 5 % of the homocoupling product 4,4′-difluorobiphenyl (**5 a**) was detected. [c] Determined by ^1H NMR spectroscopy using *p*-xylene as the internal standard. [d] Determined by ^{19}F NMR spectroscopy using benzotrifluoride as the internal standard. [e] Under dark conditions.

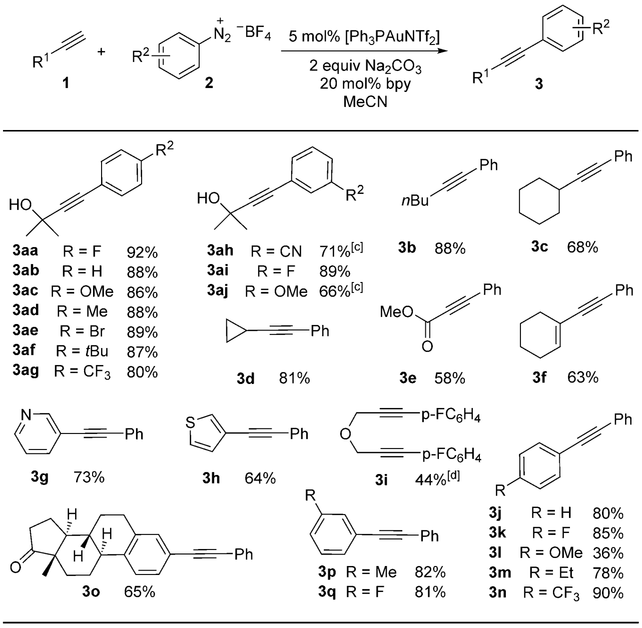
base, 2,2′-bipyridine (bpy), resulted in complete consumption of **1a** (**3aa** in 83 % yield; entry 8).[9] We reasoned that the bpy served both as a base and an ancillary ligand.[10] Finally, the combination of Na_2CO_3 as the base and bpy as the ligand gave the best result with **3aa** obtained in 94 % yield (entry 9). Reducing the catalyst loading led to lower conversion, and is likely due to gold decomposition. It has been reported that trace amounts of Pd^{II} in gold salts might contribute to Sonogashira-type coupling.[11] To rule out this possibility, $PdCl_2$ was tested as the catalyst either by itself or combined with gold (entries 12 and 13). The results confirmed that this reaction proceeds through a gold-catalyzed process.[12]

With the optimized conditions in hand, we explored the reaction scope (Table 2). An electron-deficient diazonium (see product **3aa**; 4 h) reacted faster than a non-electron-deficient diazonium (see product **3ab**; 6 h). On the contrary, an electron-rich diazonium (product **3ac**) reacted more slowly (8 h). *Ortho*-substituted phenyldiazonium salts gave lower conversion and yield (< 30 %), which hinted at the steric sensitivity of this reaction. Various terminal alkynes (both aliphatic and aromatic) with different functional groups such as hydroxy (**3a**), ester (**3e**), heterocycles (**3g**, **3h**), and estrone derivative (**3o**) were well tolerated under these mild and efficient reaction conditions.[13] In general, aliphatic alkynes reacted faster than aromatic alkynes, thus suggesting that the gold oxidation likely occurred after the formation of gold acetylide.

To study the reaction mechanism, experiments were monitored by NMR spectroscopy. First, no decomposition of **2a** and $Ph_3PAuNTf_2$ occurred without bpy, even after 18 h [Figure 1 A(a,b)]. In another NMR tube bpy was added, and the $[Ph_3PAu(bpy)]^+$ complex (^{31}P NMR: δ31.6 ppm) was formed instantly [Figure 1 A(c)]. Interestingly, this gold complex decomposed during the reaction with ArN_2^+, thus forming the phosphonium **M** overtime [Figure 1 A(d,e)].[14] After complete conversion of the gold, **2a** was no longer consumed, thus refuting the possibility of **M** being an active species.

It is known that cationic Au^I complexes can react rapidly with terminal alkynes to form gold acetylides, especially under basic conditions.[15] To prove that the gold acetylide was the reaction intermediate, the complex **6a** was prepared and treated with the diazonium **2b** (1.1 equiv; Figure 1). As shown

Table 2: Substrates scope screening.[a,b]



[a] Reaction conditions: **1** (0.4 mmol), **2** (0.48 mmol), $[Ph_3PAuNTf_2]$ (0.02 mmol), bpy (0.08 mmol), and Na_2CO_3 (0.8 mmol) in 0.8 mL acetonitrile at RT. [b] Yield of the isolated product. [c] 10 % of $[Ph_3PAuNTf_2]$ was used. [d] 3 equiv of **2a** was used.

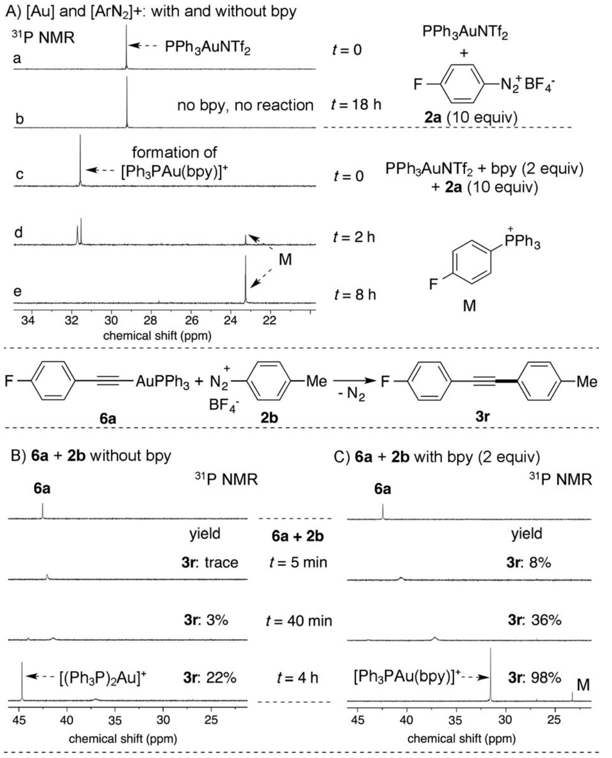


Figure 1. Exploring the reaction mechanism with ^{31}P NMR spectroscopy.

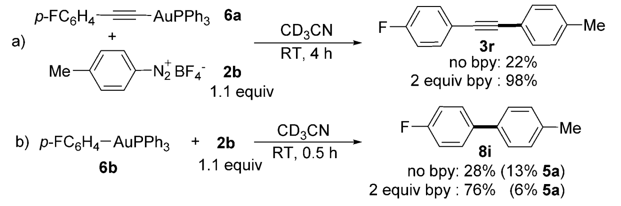


Figure 2. Direct reactions of gold complexes and diazonium salts.

in Figure 1B, without bpy, the gold acetylide **6a** decomposed overtime with only 22% of the cross-coupling product **3r** forming (no further conversion after 4 h). The formation of a gold mirror and $[(Ph_3P)_2Au]^+$ (^{31}P NMR: δ 44.9 ppm) was observed within 1 hour. Impressively, with the addition of bpy, **3r** was formed instantly and the reaction was completed in a nearly quantitative yield (Figure 1C). After reaction completion, the $[Ph_3PAu(bpy)]^+$ complex was confirmed as the final gold species.[16]

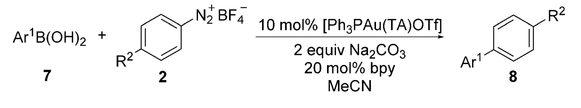
These NMR experiments revealed important mechanistic insights. Firstly, the $Ph_3PAuNTf_2$ catalyst alone could not promote diazonium decomposition. The addition of bpy is crucial in assisting the nitrogen extrusion. However, the gold acetylide itself could react with the diazonium without bpy, thus generating the cross-coupling products, albeit in low yield. In the presence of bpy, a significantly faster reaction rate was observed (Figure 1C). Considering the fact that **M** ($[Ph_3P\text{-}Ar]^+$) was formed after reaction completion, it is clear that the oxidation of Au^I occurs after the formation of gold acetylide. This discovery was rather exciting since it suggested that $[Ph_3P\text{-}Au\text{-}R]$ complexes were more feasible than cationic gold in diazonium-promoted oxidation. By forming the $[Ph_3P\text{-}Au\text{-}R]$ intermediate in situ, similar cross-coupling reactions could be achieved under the proper conditions. To test this hypothesis, reactions of aryl and alkyl gold complexes with diazonium were performed.

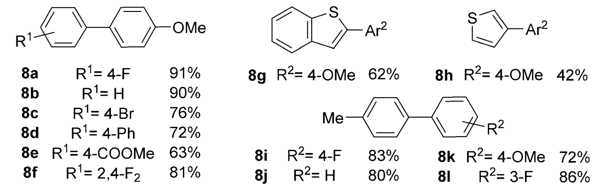
Compared to the C(sp)–C(sp^2) coupling (Figure 2a), the C(sp^2)–C(sp^2) coupling with aryl gold was faster (Figure 2b). Rapid gas evolution was observed almost simultaneously after the addition of the diazonium salt into the mixture of **6b** and bpy in CD_3CN. Similar to the C(sp)–C(sp^2) coupling, addition of bpy was critical for the reaction progress (gold mirror was observed within 10 min if bpy was absent). A complex reaction mixture was observed with the alkyl gold complex $[PPh_3AuMe]$ under the same reaction conditions even with the addition of bpy.

According to literature, aryl boronic acids can react with Au^I under basic conditions to form the corresponding aryl gold complexes.[17] Thus, it is reasonable to envision a catalytic C(sp^2)–C(sp^2) cross-coupling between aryl boronic acids and diazonium salts. Under previously optimized reaction conditions, the desired cross-coupling product **8** was successfully obtained (around 40% yield), presumably because of the faster gold catalyst decomposition. Applying the more stable triazole gold complex [Ph$_3$PAu(TA)OTf], developed by our group,[18] higher yields were obtained (up to 86%, see the Supporting Information for details). Under these new reaction conditions, various substituted aryl boronic acids and diazonium salts were tested. Overall, good to excellent yields were obtained for most of the tested substrates (Table 3). Considering the importance of C–C bond formation in organic synthesis, this new approach is of great interest since it offers an alternative strategy for cross-coupling.[19]

To verify whether the reaction proceeded through a radical mechanism, the diazonium salt **2c** was prepared. As shown in Figure 3, the reaction of **2c** with **1a** was quite sluggish with only 25% of the desired coupling product **9a** formed. The radical trapping product 3-methyldihydrobenzofuran was not detected, and thus confirmed that the aryl radical formation, if applicable, was not the key step in this cross-coupling.[20]

Table 3: Substrate screening of the C(sp^2)–C(sp^2) coupling.[a,b]





8a	R^1= 4-F	91%
8b	R^1= H	90%
8c	R^1= 4-Br	76%
8d	R^1= 4-Ph	72%
8e	R^1= 4-COOMe	63%
8f	R^1= 2,4-F$_2$	81%
8g	R^2= 4-OMe	62%
8h	R^2= 4-OMe	42%
8i	R^2= 4-F	83%
8j	R^2= H	80%
8k	R^2= 4-OMe	72%
8l	R^2= 3-F	86%

[a] Reaction conditions: **7** (0.4 mmol), **2** (0.48 mmol), [Ph$_3$PAu(TA)OTf] (0.04 mmol), bpy (0.08 mmol), and Na_2CO_3 (0.8 mmol) in 0.8 mL acetonitrile at RT. [b] Yields determined by NMR spectroscopy.

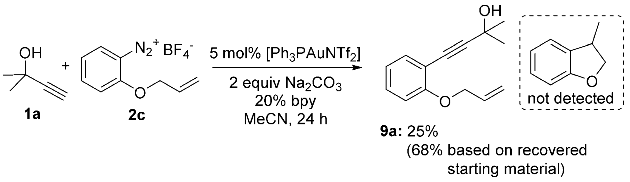


Figure 3. Radical-trapping experiment.

To further shed light on the reaction mechanism, we utilized the electrospray ionization mass spectrometry (ESI-MS) studies to detect possible intermediates.[21] As shown in Figure 4a, aryldiazenido gold complexes (**10**) were observed at the beginning of all tested reactions (see the Supporting Information).[22] To trap plausible intermediates, the compound **2d** (Figure 4b) was prepared. Under the standard reaction conditions, a small amount of the coupling product **9c** was detected by NMR spectroscopy and ESI-MS. After 10 minutes of reaction, ESI-MS analysis revealed the formation of a major ion: m/z 744.1. With the help from MS/MS fragment analysis (see the Supporting Information), the structure **11** was proposed. It was highly likely that the potential coordination of pyridyl with gold restricted the reductive elimination of **11**. However, without the presence of bpy, a dominant gold cation was detected with a peak at m/z 772.2, which was assigned as the aryldiazenido gold complex **10d** based on the MS/MS analysis. Although the exact reason is uncertain at this moment, the presence of bpy clearly assisted the nitrogen extrusion, which was crucial for the overall transformation. Based on these experimental results, a simplified mechanism was proposed as shown in Scheme 2.

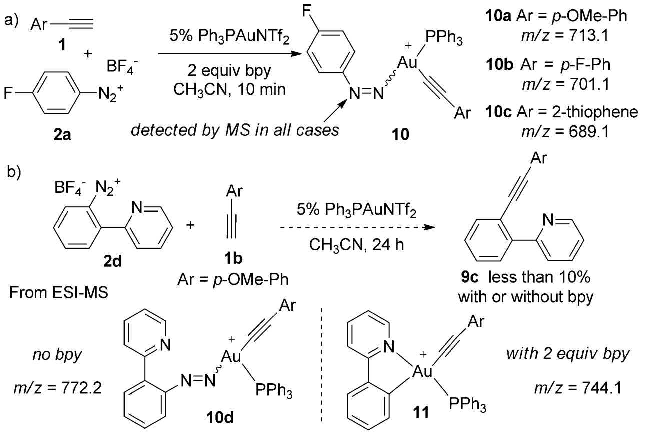
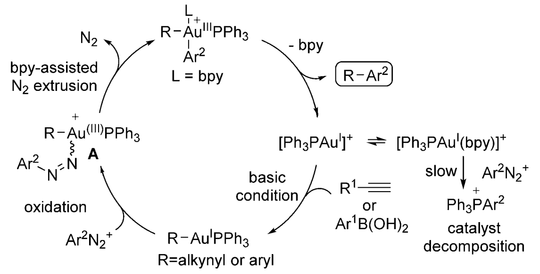


Figure 4. Exploring the reaction intermediates with ESI-MS.

Both ^{31}P NMR and ESI-MS confirmed the formation of [Ph$_3$PAu(bpy)]$^+$ by the addition of bpy. Based on current evidence, the diazonium oxidation occurred preferentially on either aryl gold or gold acetylide, thus forming the intermediate **A** (Scheme 2). The bpy-assisted nitrogen extrusion followed by rapid Au$^{\rm III}$ reductive elimination gave the desired coupling product and regenerated the Au$^{\rm I}$ catalyst. Certainly, it is interesting to uncover how L-Au-R reacts with the diazonium to form **A** and understand the exact function of bpy. Comprehensive mechanistic studies are currently ongoing in our lab and will be reported in due course.



Scheme 2. Proposed reaction mechanism.

In summary, we report a novel gold-catalyzed cross-coupling strategy using aryldiazonium salts as the oxidant. By forming an alkynyl or aryl gold complex in situ, oxidation of Au$^{\rm I}$ to Au$^{\rm III}$ was achieved without strong oxidants or photocatalysts. Preliminary mechanistic studies revealed the importance of the bpy ligand in assisting nitrogen extrusion, and appears to be a key step in this transformation. This strategy offers a new effective cross-coupling approach together with inspiring insight about gold redox catalysis.

Keywords: aryldiazonium salt · cross-coupling · gold · redox catalysis

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[9] The alkyne homocoupling product **4a** was observed when bpy was present (Table 1, entry 8), and it might be formed from transmetallation of the $\mathrm{Au^{III}}$ intermediate with the gold acetylide followed by reductive elimination. In most of the cases, fluorobenzene was also observed (generally < 10 %).

[10] The crystal structure of $[\mathrm{Ph_3PAu(bpy)}]^+$ has been reported previously: W. Clegg, *Acta Crystallogr. Sect. B* **1976**, *32*, 2712 – 2714. The bpy ligand possesses a pseudo-three-coordination with gold. For the coordination of bpy with $\mathrm{Au^{III}}$, see: A. P. Shaw, M. K. Ghosh, K. W. Törnroos, D. S. Wragg, M. Tilset, O. Swang, R. H. Heyn, S. Jakobsen, *Organometallics* **2012**, *31*, 7093 – 7100.

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[13] The high reactivity of *p*-methoxyphenyl acetylene (**3l**) resulted in a messy reaction with the desired product isolated in only 36 % yield (16 % alkyne homocoupling product detected by NMR spectroscopy).

[14] The $[\mathrm{Ph_3P\text{-}Ar}]^+$ was formed through reductive elimination of the corresponding $\mathrm{Au^{III}}$ complex: see Ref. [6b].

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[16] After the reaction was completed, $[\mathrm{Ph_3P\text{-}Ar}]^+$ (**M**) started to form because of the reaction between excess **2b** and $[\mathrm{Ph_3PAu(bpy)}]^+$.

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