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Gold(I)-Catalyzed Cross-Coupling Reactions of Aryldiazonium Salts with Organostannanes

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Abstract. Gold(I)-catalyzed cross-coupling reactions of aryldiazonium salts with organostannanes is described. This redox neutral strategy offers an efficient approach to diverse biaryls, vinyl arenes and arylacetylenes. Monitoring the reaction with NMR and ESI-MS provided strong evidence for the *in situ* formation of Ph₃PAu^lR (R = aryl, vinyl and alkynyl) species which is crucial for the activation of aryldiazonium salts.

Oxidative gold catalysis is emerging as a powerful tool for a variety of C–C and C–X bond-forming reactions since last few years.¹ However, unlike the late transition metals, reports on analogues gold-catalyzed cross-coupling reactions are scarce.^{1e,2} The reason could be attributed to higher redox potential between Au(I) and Au(III) species.^{3,2b} Recent research revealed that the realization of Au(I)/Au(III) redox cycle is possible with two-electron redox processes; however, those reactions utilize sacrificial oxidants such as I³⁺ derivatives or F⁺ sources⁴ and often require harsh reaction conditions. To facilitate advancement in the field of oxidative gold catalysis, the development of new mode of reactivity is highly warranted.

Very recently, the research groups of Glorius,⁵ Toste,⁶ Hashmi⁷ and others⁸ have disclosed entirely new concept for gold-catalyzed cross-coupling reactions. Rather than involving external oxidants, the method employs aryl radicals (generated *in situ* via lightmediated decomposition of aryldiazonium salts, ArN₂X) which acts as both oxidant and coupling partner in an overall redox-neutral transformation (Scheme 1a). The research group of Shi achieved an alternative photo-free approach to trigger gold(I) oxidation via ligand/nucleophile-assisted activation of diazonium salts (Scheme 1b).⁹ We wondered whether it would be possible to develop a goldcatalyzed cross-coupling reaction that would eliminate the need of either light or nucleophile for diazonium activation.

We thought of generating organo-gold(I) species *in situ* which can be oxidized by ArN_2X leading to the cross-coupled product after

reductive elimination of gold(III) species. Unfortunately, the oxidation of LAu^{IX} to $[LAu^{III}ArX_2]$ by ArN₂X is reported to be achievable only under harsh reaction conditions.¹⁰ To circumvent this limitation, we mulled over organo-stannanes which reportedly have the ability to undergo transmetalation with various goldspecies¹¹ to form organo-gold precursors. Based on these reports^{10,11} and our interest in the field of oxidative gold catalysis,¹² we envisaged that aryltrialkylstannanes would generate catalytically active organo-gold(I) species A which would poised to undergo oxidation by aryldiazonium salts to generate [Au^{III}] intermediate **B** which after reductive elimination would give cross-coupled products (Scheme 1c). Be noted that the Sn/Au transmetalation has been well-documented in the Pd-catalyzed Stille cross-coupling reactions;¹³ however, to the best of our knowledge, it has never been employed in gold-catalyzed cross-coupling reactions. Herein, we report gold(I)-catalyzed cross-coupling reactions of aryldiazonium salts with organostannanes under redox neutral conditions to access diverse biaryls, vinyl arenes, and arylacetylenes at ambient conditions.

 a) Light-assisted decomposition of aryldiazonium salts (Glorius,⁵ Toste,⁶ Hashm⁷ and others⁸)

ArN₂X + ho
$$\stackrel{win or wintout}{\longrightarrow}$$
 [Ar[•]] $\stackrel{[AuII]}{\longrightarrow}$ Ar–[Au^{III}] $\stackrel{cross-coupled}{\longrightarrow}$ products

b) Ligand/nucleophile-assisted decomposition of aryldiazonium salts (Shi^p)

$$ArN_{2}X + R \rightarrow \left[Ar - N = N - R\right]^{\oplus} \underbrace{[Au']}_{Ar = [Au'']} \overset{K}{\longrightarrow} Ar - [Au'''] \overset{K}{\longrightarrow} cross-coupled products$$

c) Diazonium salt activation without needing light or ligand/nucleophiles (this work)

$$R'-SnBu_3 \xrightarrow{[Au^1]} R'-[Au^1] \xrightarrow{ArN_2X} R'-[Au^{II}] \xrightarrow{arN_2X} P'-[Au^{II}] \xrightarrow{arN_2X} P'-[Au^{II}]$$

Scheme 1. Mode of oxidation of gold(I)-precursors by aryldiazonium salts: known and present work

At the outset, we studied the coupling reaction of 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**1a**) and tributyl(phenyl)stannane (**2a**) in the presence of various Au(I)catalysts.¹⁴ The main challenge was the suppression of undesired homodimerization product which could results either from **1a** or **2a**. The optimum reaction conditions for obtaining the desired

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product **3a** in higher yield (69%) is treating **1a** with **2a** in the presence of 7 mol% Ph_3PAuCl in CH_3CN (Scheme 2).

Ar−N ₂ BF₂	ı + Ph−SnBu	7 mol% Ph ₃ PAuCl 0.1 (M) CH ₃ CN	Ar - Ph	+ Ph = Ph ·	+ Ar - Ar
1a	2a (1.3 equiv)	N ₂ , 16 h, rt Ar = (4-CO ₂ Et)C ₆ H ₄	3a , 69%	3a' , 13% (from 2a)	3a'' , ≤5%
Scheme 2. Optimized reaction conditions					

As shown in Table 1, the reaction is found to have worked well with a broad range of substituted aryldiazonium salts (1). For example, aryldiazonium salts containing -Br and -Ph substituents at the para-position, gave the corresponding cross-coupled products 3b and 3c in 48 and 46% yields, respectively. Interestingly, electronwithdrawing substituents such as -COMe, -CO2Me, -CN and -NO2 provided 3d-3g in slightly better yields (49-62% yields). However, in case of electron donating substituent such as 4-OMe and 3,4methylenedioxy, the products 3h and 3v were obtained in low yields (40 and 31% yields).^{6a,8h,j} Notably, aryldiazonium salts bearing 4-ethynyl group provided the product 3i in 37% yield. In the case of substituents at the ortho-position of the diazonium salts both electronic and steric factors seemed to play a crucial role. For example, -Br and -I substituent at the ortho-position of the diazonium salt led to the formation of 3j and 3k in 41% and 50% vields, respectively. Further, electron withdrawing substituent such as -COMe and -NO₂ provided coupling products (3I and 3m) in better yields (50 and 51%); whereas, electron donating substituents -OMe led to poor conversion (3n, 31%). The reaction of ArN₂BF₄ bearing o-Et, o-iPr and 2,4,6-trimethyl groups in the aryl ring gave 30, 3p and 3w in lower yields; probably because of the steric reasons.^{6a,8j} On the contrary, substituents at the meta-position of aryl ring in ArN₂BF₄ were tolerated affording 3q-3u in moderate yields (42-62%). Further, 1-phenylnaphthalene 3x was also accessed in 41% yield. The scope of the reaction was further extended to quinoline and indole based heteroaryls to obtain 3y and 3z in 19 and 56% yields, respectively.



^{*a*}Reaction conditions: 0.20 mmol **1**, 0.26 mmol **2a**, 7 mol% Ph₃PAuCl, degassed CH₃CN (0.1 M), N₂, rt, 16 h. ^{*b*}NMR yields using dibromomethane as an internal standard.

Next, the scope of the reaction with respect to various tributyl(aryl)stannanes $({\bf 2})$ and counteranions of the aryldiazonium

salts was examined. As can be judged from Table 2 that the substituent at the para-position of the aryl ring in tributyl(aryl)stannanes ($-^{t}Bu$, $-CF_{3}$ and -CN) were tolerated giving 3aa-3ac in 61-66% yields. However, lowering of yield was noticed in case of electron donating 4-OMe group (3ad, 39%). Changing substituents (-Cl, -OMe and -3,5-di-CF₃) at the meta-position didn't affect the outcome of the reaction (3ae-3ag, 59-71% yields). Orthosubstituted aryl stannanes, on the contrary, furnished the corresponding coupled products 3ah-3aj in poor yields (24-42%). Further, compounds 3ak and 3al were accessed in 74 and 56% yields. Heteroaromatic(aryl)stannanes also provided corresponding coupling products 3am-3ao in moderate yields (43-56%). Relatively bulky tributyl(3-methylbenzofuran-2-yl)stannane provided the desired product 3ap in 31% yield along with undesired 3ap' in 16% yield. The reaction also worked well with aryldiazonium salts with varying counter ions. For instance, cross coupled products 3a was accessed in 66% (X = PF₆), 70% (X = OCOCF₃) and 77% (X = OTs) yields.

Table 2. Scope with respect to tributyl(aryl)stannanes (2) and counteranions of the aryldiazonium salts^a



^{*a*}Reaction conditions: 0.20 mmol **1**, 0.26 mmol **2**, 7 mol% Ph₃PAuCl, degassed CH₃CN (0.1 M), N₂, rt, 16 h. ^{*b*}NMR yields using dibromomethane as an internal standard.

Very interestingly, vinyl-tributyltin was also found to be tolerated giving 3aq-3as; albeit, in poor yields (Table 3). However, electron deficient vinyl-stannnane-ethyl-(Z)-3-(tributylstannyl)acrylate provided better results (3at, 58%; 3au, 67%; 3av, 53% and 3aw, 55%). Notably, Z-selectivity is retained in all the cases. Next, C(sp²)-C(sp) coupling reactions employing tributyl(ethynyl)stannane were investigated. Reaction of aryldiazonium salts bearing electron withdrawing/donating groups (4-CO₂Et, 4-NO₂, 4-OMe and 3-CN) gave **3ax-3aaa** in 42-68% yields. However, aryldiazonium salts bearing substituents at the orthoposition afforded products with low yields (3aab, 47%; 3aac, 44%; 3aad, 35%; 3aae, 36%). Interestingly, diazonium salts bearing very labile TMS-acetylene group provided 3aaf in 29% yield. Further, 2ethynyl naphthalene (3aag) was accessed in 57% yield. Employing tributyl(phenylethynyl)stannane, unsymmetrical alkynes 3aah and **3aai** were also accessed in 41 and 33% vields, respectively. Unfortunately, alkyl-stannanes such as allyltributylstannane and benzyltributylstannane failed to provide $C(sp^2)-C(sp^3)$ coupled products **3aaj** and **3aak**.

Table 3. Cross-coupling reactions of aryldiazonium salts with vinyl, ethynyl and alkyl-stannanes^a



^{$^{0}}Reaction conditions: 0.20 mmol 1, 0.26 mmol 2, 7 mol% Ph₃PAuCl, degassed CH₃CN (0.1 M), N₂, rt, 16 h. ^{<math>^{b}}Reaction kept for 4 h. ^{<math>^{c}}No reaction$.</sup></sup></sup>

Next, the reaction of 1a and 2a under optimized reaction conditions was monitored with ³¹P NMR spectroscopy (Scheme 3a). We found the complete disappearance of $Ph_3PAu^{I}CI$ (δ 32.9 ppm) with the appearance of new signal at δ 44.2 ppm (after 5 min) and δ 22.9 ppm (after 16 h) which were assigned as $Ph_3PAu'Ph$ (II)^{8c} and X_1/X_2 , ^{6a,15} respectively. The presence of X_1 and X_2 was further confirmed by HRMS analysis.¹⁴ Notably, these species were not observed in appreciable amount in the ³¹P NMR spectrum as a large excess of stannane 2a (1.3 equiv) was employed. To gain further evidence on the plausible intermediates, 1aa was treated with 2a under standard reaction conditions (Scheme 3b). HRMS analysis of the reaction mixture taken after 10 min revealed the peak at m/z =690.1606 which corresponds to the X_3 .¹⁴ The detection of intermediates X_3 along with X_1 and X_2 clearly implies the involvement of Au(III)-intermediate via the oxidation of gold(I)precursors. Further, when 1a was reacted with 2a in the presence of preformed Ph₃PAu^lPh (II) as a catalyst, **3a** was obtained in 51% yield (Scheme 3c). This observation clearly indicates the intermediacy of Ph₃PAu¹Ph species (II) along with the fact that the reaction is proceeding via the transmetalation/oxidation sequence. A control experiment outlined in Scheme 3d clearly ruled out the intermediacy of azo-compound (3ap') as possible intermediate.^{9b}

Mechanistically,¹⁶ the catalyst Ph₃PAuCl would first undergo transmetalation with PhSnBu₃ (**2a**) to generate Ph₃PAu¹Ph (**II**). A process involving two-electron oxidative addition with diazonium salt would then convert Ph₃PAu¹Ph (**II**) into the transient gold(III)-species **III**.^{9a} The gold-species **III** then collapses to intermediate **V** via rapid transmetalation/N₂ extrusion sequence either in a concerted manner (path a) or in a stepwise manner (path b).^{15,17} Further, intermediate **V** would undergo fast reductive elimination¹⁷ to yield the desired **3a** (along with **3a'**).^{2d} However, at present, a

competitive radical chain mechanism (path c) cannot be ruled out completely. $^{\rm 5c,2d}_{\rm c}$

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Conclusions

In conclusion, we have developed a method for cross-coupling reactions of aryldiazonium salts with various oragnostannanes to access diverse array of biaryls, vinyl arenes, and arylacetylenes under gold(I) catalysis. This reaction proceeds under very mild conditions involving Au(I)/Au(III) redox cycle and showing excellent functional group tolerance which may be difficult to exhibit under conventional Pd-catalysis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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