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Gold(I)-catalyzed cross-coupling reactions of aryldiazonium salts with organostannanes†

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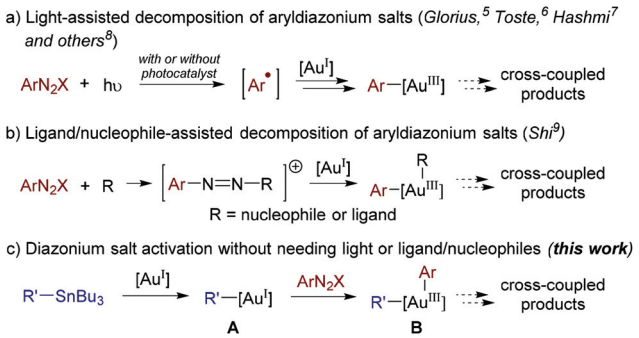
Gold(I)-catalyzed cross-coupling reactions of aryldiazonium salts with organostannanes are described. This redox neutral strategy offers an efficient approach to diverse biaryls, vinyl arenes and arylacetylenes. Monitoring the reaction with NMR and ESI-MS provided strong evidence for the *in situ* formation of Ph_3PAu^IR (R = aryl, vinyl and alkynyl) species which is crucial for the activation of aryldiazonium salts.

Oxidative gold catalysis has been emerging as a powerful tool for a variety of C–C and C–X bond-forming reactions over the last few years.[1] However, unlike the late transition metals, reports on analogue gold-catalyzed cross-coupling reactions are scarce.[1e,2] The reason could be attributed to a higher redox potential between Au(I) and Au(III) species.[2b,3] Recent research revealed that the realization of an Au(I)/Au(III) redox cycle is possible with two-electron redox processes; however, these reactions use sacrificial oxidants such as I^{3+} derivatives or F^+ sources[4] and often require harsh reaction conditions. To facilitate advancement in the field of oxidative gold catalysis, the development of a new mode of reactivity is highly warranted.

Very recently, the research groups of Glorius,[5] Toste,[6] Hashmi[7] and others[8] have disclosed an entirely new concept for gold-catalyzed cross-coupling reactions. Rather than using external oxidants, the method employs aryl radicals (generated *in situ via* the light-mediated decomposition of aryldiazonium salts, ArN_2X) which act as both oxidants and coupling partners 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* the ligand/nucleophile-assisted activation of diazonium salts (Scheme 1b).[9] We wondered whether it would be possible to develop a gold-catalyzed cross-coupling reaction that would eliminate the need for either light or nucleophiles for diazonium activation.



Scheme 1 Mode of oxidation of gold(I)-precursors using aryldiazonium salts: known studies and the present study.

We thought of generating organo-gold(I) species *in situ* which can be oxidized by ArN_2X leading to the cross-coupled product after the reductive elimination of gold(III) species. Unfortunately, the oxidation of LAu^IX to $[LAu^{III}ArX_2]$ by ArN_2X is reported to be achievable only under harsh reaction conditions.[10] To circumvent this limitation, we mulled over organostannanes which reportedly have the ability to undergo transmetalation with various gold-species[11] 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 the catalytically active organo-gold(I) species **A** which would be poised to undergo oxidation using the aryldiazonium salts to generate the [Au(III)] intermediate **B** which after reductive elimination would give cross-coupled products (Scheme 1c). Note that 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 under ambient conditions.

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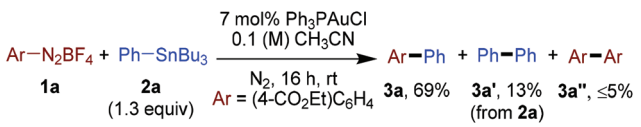
At the outset, we studied the coupling reaction of 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**1a**) and tributyl(phenyl)stannane (**2a**) in the presence of various Au(I)-catalysts.[14] The main challenge was the suppression of the undesired homodimerization product which could result either from **1a** or **2a**. The optimum reaction condition for obtaining the desired product **3a** in a higher yield (69%) is treating **1a** with **2a** in the presence of 7 mol% Ph_3PAuCl in CH_3CN (Scheme 2).

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, electron-withdrawing substituents such as –COMe, $–CO_2Me$, –CN and $–NO_2$ provided **3d–3g** in slightly better yields (49–62% yields). However, in the case of electron-donating substituents such as 4-OMe and 3,4-methylenedioxy, the products **3h** and **3v** were obtained in low yields, respectively (40 and 31% yields).[6a,8h,j] Notably, aryldiazonium salts bearing the 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 substituents at the *ortho*-position of the diazonium salt led to the formation of **3j** and **3k** in 41% and 50% yields, respectively. Furthermore, electron-withdrawing substituents such as –COMe and $–NO_2$ provided coupling products (**3l** and **3m**) in better yields (50 and 51%) whereas the electron-donating substituent –OMe led to a poor conversion (**3n**, 31%). The reaction of ArN_2BF_4 bearing *o*-Et, *o*-iPr and 2,4,6-trimethyl groups in the aryl ring gave **3o**, **3p** and **3w** in lower yields, probably because of the steric reasons.[6a,8j] In contrast, substituents at the *meta*-position of the aryl ring in ArN_2BF_4 were tolerated affording **3q–3u** in moderate yields (42–62%). Furthermore, 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.

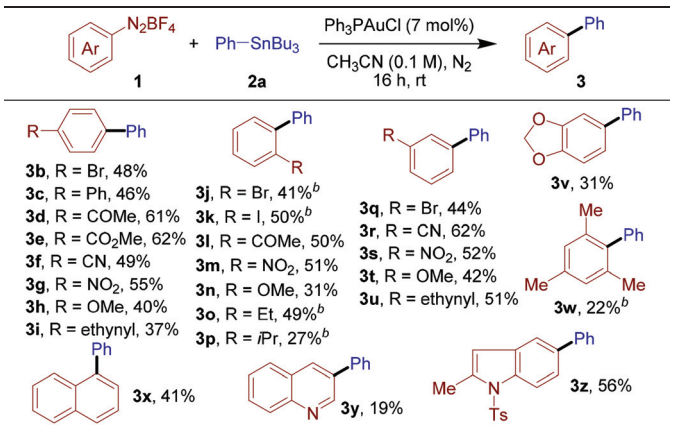
Next, the scope of the reaction with respect to various tributyl(aryl)stannanes (**2**) and counteranions of the aryldiazonium salts was examined. As can be seen from Table 2, the substituents at the *para*-position of the aryl ring in tributyl(aryl)stannanes ($–^tBu$, $–CF_3$ and –CN) were tolerated giving **3aa–3ac** in 61–66% yields. However, lowering of the yield was noted in the case of the electron-donating 4-OMe group (**3ad**, 39%). Changing substituents (–Cl, –OMe and -3,5-di-CF_3) at the *meta*-position didn't affect the outcome of the reaction (**3ae–3ag**, 59–71% yields). *ortho*-Substituted aryl stannanes, in contrast, furnished the corresponding coupled products **3ah–3aj** in poor yields (24–42%). Furthermore, compounds **3ak** and **3al** were accessed in 74 and 56% yields. Heteroaromatic(aryl)stannanes also provided the 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 the undesired **3ap′** in 16% yield. The reaction also worked well with the aryldiazonium salts with varying counter ions. For instance, the cross-coupled product **3a** was accessed in 66% (X = PF_6), 70% (X = $OCOCF_3$) and 77% (X = OTs) yields.

Very interestingly, vinyltributyltin was also found to be tolerated giving **3aq–3as**, albeit, in poor yields (Table 3). However, electron-deficient vinyl-stannane-ethyl-(*Z*)-3-(tributylstannyl) acrylate provided better results (**3at**, 58%; **3au**, 67%; **3av**, 53%



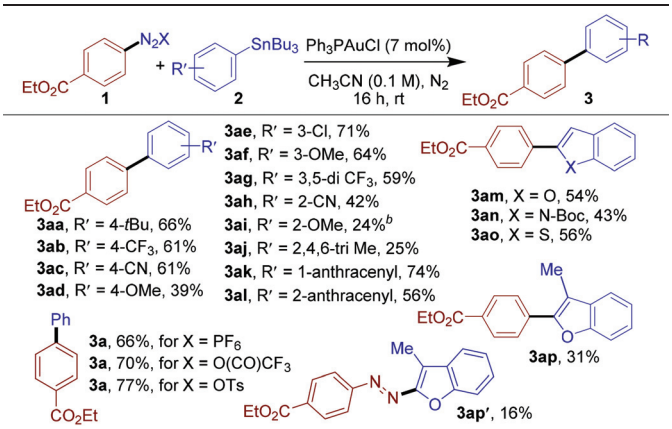
Scheme 2 Optimized reaction conditions.

Table 1 Cross-coupling reactions of ArN_2BF_4 (**1**) with $PhSnBu_3$ (**2a**)[a]



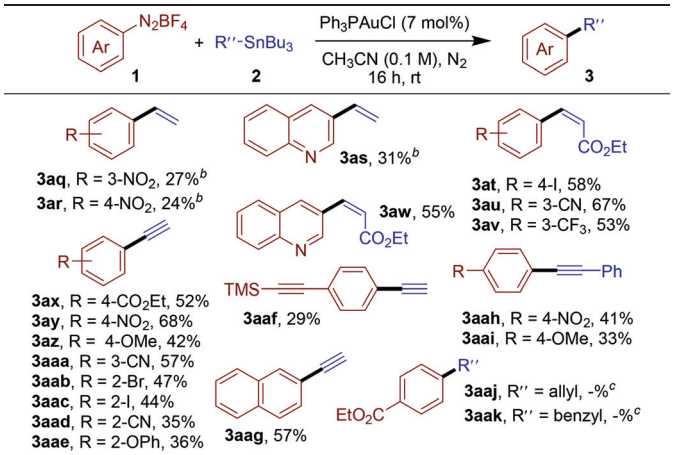
[a] Reaction conditions: 0.20 mmol **1**, 0.26 mmol **2a**, 7 mol% Ph_3PAuCl, degassed CH_3CN (0.1 M), N_2, rt, 16 h. [b] NMR yields using dibromomethane as an internal standard.

Table 2 Scope with respect to tributyl(aryl)stannanes (**2**) and counteranions of the aryldiazonium salts[a]

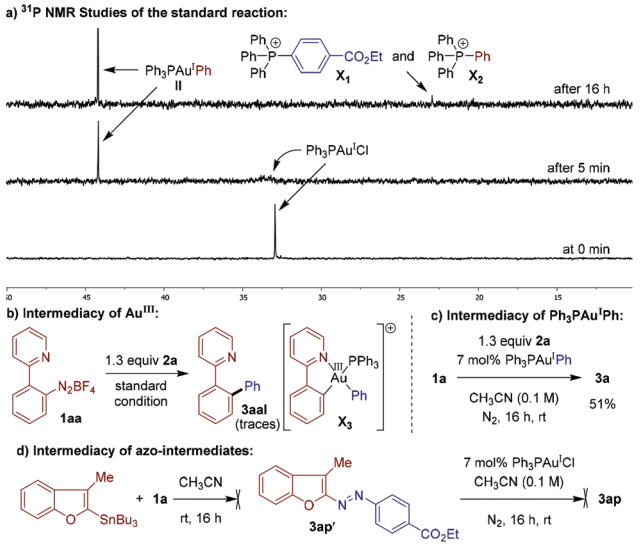


[a] Reaction conditions: 0.20 mmol **1**, 0.26 mmol **2**, 7 mol% Ph_3PAuCl, degassed CH_3CN (0.1 M), N_2, rt, 16 h. [b] NMR yields using dibromomethane as an internal standard.

Table 3 Cross-coupling reactions of the aryldiazonium salts with vinyl, ethynyl and alkyl-stannanes[a]



[a] Reaction conditions: 0.20 mmol **1**, 0.26 mmol **2**, 7 mol% Ph_3PAuCl, degassed CH_3CN (0.1 M), N_2, rt, 16 h. [b] Reaction kept for 4 h. [c] No reaction.

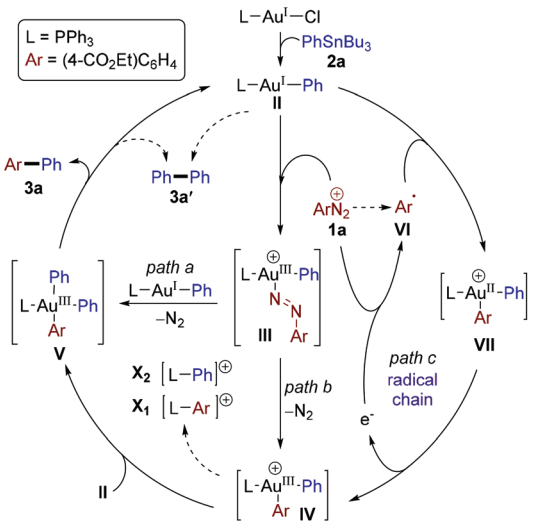


Scheme 3 Control experiments.

and **3aw**, 55%). Notably, *Z*-selectivity is retained in all the cases. Next, C(sp^2)–C(sp) coupling reactions employing tributyl(ethynyl)stannane were investigated. The reaction of the aryldiazonium salts bearing electron-withdrawing/donating groups (4-CO_2Et, 4-NO_2, 4-OMe and 3-CN) gave **3ax–3aaa** in 42–68% yields. However, the aryldiazonium salts bearing substituents at the *ortho*-position afforded products with low yields (**3aab**, 47%; **3aac**, 44%; **3aad**, 35%; **3aae**, 36%). Interestingly, the diazonium salts bearing a very labile TMS-acetylene group provided **3aaf** in 29% yield. Furthermore, 2-ethynyl naphthalene (**3aag**) was accessed in 57% yield. Employing tributyl(phenylethynyl)stannane, unsymmetrical alkynes **3aah** and **3aai** were also accessed in 41 and 33% yields, respectively. Unfortunately, alkyl-stannanes such as allyltributylstannane and benzyltributylstannane failed to provide C(sp^2)–C(sp^3) coupled products **3aaj** and **3aak**.

Next, the reaction of **1a** and **2a** under optimized reaction conditions was monitored by ^{31}P NMR spectroscopy (Scheme 3a). We observed the complete disappearance of Ph_3PAu^ICl (δ 32.9 ppm) with the appearance of new signals at δ 44.2 ppm (after 5 min) and δ 22.9 ppm (after 16 h) which were assigned Ph_3PAu^IPh (**II**)[8c] and $\mathbf{X_1}$/$\mathbf{X_2}$,[6a,15] respectively. The presence of $\mathbf{X_1}$ and $\mathbf{X_2}$ was further confirmed by HRMS analysis.[14] Notably, these species were not observed in an appreciable amount in the ^{31}P 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). The HRMS analysis of the reaction mixture taken after 10 min revealed the peak at *m*/*z* = 690.1606 which corresponds to $\mathbf{X_3}$.[14] The detection of intermediate $\mathbf{X_3}$ along with $\mathbf{X_1}$ and $\mathbf{X_2}$ clearly implies the involvement of the Au(III)-intermediate *via* the oxidation of gold(I)-precursors. Furthermore, when **1a** was reacted with **2a** in the presence of preformed Ph_3PAu^IPh (**II**) as a catalyst, **3a** was obtained in 51% yield (Scheme 3c). This observation clearly indicates the intermediacy of the Ph_3PAu^IPh species (**II**) along with the fact that the reaction proceeds *via* the transmetalation/oxidation sequence. A control experiment outlined in Scheme 3d clearly ruled out the possible intermediacy of azo-compound (**3ap′**).[9b]

Mechanistically,[16] the catalyst Ph_3PAuCl would first undergo transmetalation with $PhSnBu_3$ (**2a**) to generate Ph_3PAu^IPh (**II**). A process involving two-electron oxidative addition with the diazonium salt would then convert Ph_3PAu^IPh (**II**) into the transient gold(III)-species **III**.[9a] The gold-species **III** then collapses to form intermediate **V** *via* a rapid transmetalation/N_2 extrusion sequence either in a concerted manner (path a) or in a stepwise manner (path b).[15,17] Furthermore, intermediate **V** would undergo fast reductive



Scheme 4 The proposed catalytic cycle.

elimination[17] to yield the desired **3a** (along with **3a′**).[2d] However, at present, a competitive radical chain mechanism (path c) cannot be ruled out completely (Scheme 4).[5c,2d]

Conclusions

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

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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