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Au-Catalyzed Oxidative Arylation: Chelation-Induced Turnover of ortho-Substituted Arylsilanes

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ABSTRACT: Ortho-substituted aryl silanes have previously been found to undergo much slower Au-catalyzed intermolecular arylation than their m,p-substituted isomers, with many examples failing to undergo turnover at all. A method to indirectly quantify the rates of C–Si auration of o-substituted aryl silanes, under conditions of turnover, has been developed. All examples are found to undergo very efficient arylation, and comparison of conditions for arylation of ortho- versus para-ArSiMe3 (o/p-1).a

Introduction

Organosilanes are an attractive class of reagent for transition metal catalyzed couplings,1 with benefits of high stability, ease of preparation, and low toxicity.1,5 The gold-catalyzed2 direct arylation3 of aryltrimethylsilanes (1) with π-rich arenes (2) to afford biaryls (3) was first reported 2012.4 The reaction can be conducted under air, using laboratory grade solvent (CHCl3/MeOH), often at ambient temperature, and around 160 examples have been published to date.1,4-8 Mechanistic studies5-7 indicate that turnover proceeds via sequential electrophilic aromatic auration (SiAr) of the silane (kSi), then the arene (kAr), followed by reductive elimination (kRE) and Au(I)/I(III) redox (kSD) Scheme 1. For the vast majority of cases, the turnover-rate limiting event is intermolecular C-H arylation (kC,H), proceeding with a first-order kinetic dependence on 2 and a negative entropy of activation.5

Whilst the substrate scope for the coupling has proven to be reasonably broad,1,4-8 ortho-substituted arylsilanes (o-1) undergo slow intermolecular coupling, requiring prolonged reaction times or elevated temperatures, Scheme 1.4,5,9 Indeed, a number of examples of hindered ortho-substituted arylsilanes fail to couple at all. In contrast, substituted arenes (2) can be efficiently coupled, even though these must also generate a sterically-hindered diaryl-gold intermediate, 6. The slow rates of arylation of o-1 also contrast other SiAr processes, e.g. protodesilylation,9 and mercuridesilylation,10 where ortho-substituted arylsilanes react significantly faster than predicted based on the inductive effect of the substituents alone. Herein we analyze the reactivity of o-

1 in Au-catalyzed auration and show that efficient coupling can be induced by o-functionalization.

Discussion

We began by testing how steric hindrance affects the C–Si auration (kSi) of the arylsilane, comparing the relative rates of a small series of o-alkyl arylsilanes (o-1a-j) under catalytic conditions. Conventional competition experiments determine relative rates (kSi) for a pair of substrates by monitoring their ratio as a function of their conversion to product. However, this cannot be
employed with the many examples of o-1 that do not undergo turnover to product. We therefore developed an alternative approach that solely analyzes the effect of o-1 on the kinetics of another substrate that does undergo turnover. The intramolecular coupling of 1a to form fluorene (3a, Figure 1) proved ideal.

![Scheme 2](image)

**Scheme 2.** Relative rates of C-Si auration (k_{rel}) for o-1b-j.

The acceleration of aryl silane protodesilylation,3 and mercuridesilylation,18 by ortho-methyl substituents arises from alleviation of ground-state steric strain on approach to a pseudo-tetrahedral Wheland intermediate.9,10,12 An analogous effect in C-Si auration (k_{rel}), Figure 2A, may explain why o-1b reacts more than twenty-fold faster than p-1b (Scheme 2). The similar rates of C-Si auration of the ortho-benzyl, -methyl, -ethyl, -isopropyl, and -cyclohexyl substrates (o-1a-e) will arise from a combination of effects, including access to Ar-CHR: conformations that minimize steric compression with the silane (such a conformation is absent in the fastest reacting substrate o-1f), steric interaction with the incoming Au-electrophile, Figure 2B, and steric shielding of the charge-polarized Wheland intermediate from solvation. Analogous steric interactions attenuate the rate of protodesilylation of ArSiR3 species with larger Si-substituents.13 The EtMeSi and EtSi substrates o-1h,i behave accordingly, Figure 2C.

![Figure 2](image)

**Figure 2.** A. steric decompression during electrophilic auration (k_{rel}) of o-1b. B. Similar reactivities of ortho methyl, ethyl, isopropyl and cyclohexyl substrates o-1b-e. C. Reduction in reactivity of ArSiMeEt and ArSiEt o-1h,i.

Since the rate attenuation analysis (Scheme 2) shows that all of the o-arylsilanes undergo efficient C-Si auration (k_{rel}), the inhibiting effect5 of the ortho-substituent on the overall coupling (1→6) is therefore not manifest until the subsequent step: the C-H auration of o-5 (k_{rel}). In our
previous mechanistic studies on the cyclization of $1\text{a}$ we found that, unusually, the turnover-rate limiting event is reductive elimination from the corresponding biaryl intermediate $6\text{a}$, leading to pseudo zero-order kinetics (Figure 1).\textsuperscript{6} Consideration of the conformational equilibrium around the Ar-Au bond in the mono-aryl precursor $5\text{a}$ suggests that a perpendicular arrangement of the benzyl group to the square-plane of ligands at gold ($5\text{a}_{\text{per}}$) will be favored, on sterically ground, over a coplanar arrangement ($5\text{a}_{\text{co}}$), Figure 3.

![Figure 3. Conformations of Ar-Au intermediates ($o\text{-5}_{\text{co}}$ / $o\text{-5}_{\text{per}}$) leading to arylation ($k_{\text{5a}}$) and the impact of chelation.](image)

Arrangement $5\text{a}_{\text{per}}$ allows the benzyl group to undergo associative $\pi$-complexation then C-H auration ($k_{\text{5a}}$) to access the resting state ($6\text{a}$). In contrast to $5\text{a}$, intermediates of the type $5\text{b-f,h-j}$\textsuperscript{14} must undergo turnover-rate limiting intermolecular associative $\pi$-complexation to effect arylation ($k_{\text{5b}}$).\textsuperscript{3,6} Conformer $o\text{-5}_{\text{per}}$ will be significantly less accessible\textsuperscript{15} to the incoming arene (2) than $o\text{-5}_{\text{co}}$. Thus, the more sterically imposing the ortho-substituent, the further the equilibrium ($K_{\text{5a}}$) will bias toward $o\text{-5}_{\text{per}}$ and the greater the suppression of the rate of turnover. We have previously shown that the electronic influence of m- and p-arylsilane substituents on the rate of turnover is negligible ($\rho = -0.2$).\textsuperscript{5} The conformational equilibrium ($K_{\text{5a}}$), and steric shielding effect ($o\text{-5}_{\text{per}}$) thus provides a simple explanation for the five-fold faster turnover of $p\text{-1b}$ by 2-bromothiophene compared to $o\text{-1b}$, Scheme 3. The rate is further suppressed by Et ($o\text{-1c}$), with complete inhibition of turnover by tBu ($o\text{-1f}$), despite the latter undergoing the fastest C-Si auration (Scheme 2).

The $o$-Au-Ar conformational model\textsuperscript{16} suggests that the rate of arylation ($k_{\text{5a}}$), and thus net rate of turnover,\textsuperscript{5,6} can be accelerated by using chelation to bias the equilibrium toward the reactive species, $5\text{a}$. Introduction of ortho-n-alkylhydroxy groups ($o\text{-1k-n}$) resulted in an increase in turnover rate for intermolecular coupling, reacting smoothly at ambient temperature at a similar rate to $p\text{-1b}$, Scheme 3.

![Scheme 3. Relative rates of intermolecular arylation ($k_{\text{5a}}$) of $o\text{-5}$ by 2-bromothiophene.](image)

Unsurprisingly, the nature of the tether, e.g. coordinating ability, chelate ring size, and substitution pattern (steric effects), strongly impacts the rate of turnover. Detailed analysis is complex as the overall effect will arise through changes in chelate equilibrium ($K_{\text{5a}}$) and the efficiency of coordination of the incoming arene ($k_{\text{5a}}$). For example, addition of methyl substituents ($o\text{-1o-q}$) does not reduce turnover as much as might be anticipated, possibly due to a gem-disubstituent\textsuperscript{16} effect biasing $K_{\text{5a}}$. In contrast, the o-alkoxymethyl series ($o\text{-1r-t}$) induce a significant increase in turnover rate, with $o\text{-1r}$ undergoing coupling $>20$-fold faster than $p\text{-1b}$. The marked difference in turnover rate between pairs of alcohols $o\text{-1k,n}$ and ethers $o\text{-1r,s}$ suggests that shorter tether neutral two-electron (L-type) ligation, rather than X-type, provides the greater overall activating effect ($K_{\text{5a}}$ and $k_{\text{5a}}$). The rates for the trimethylsilyl ($o\text{-1k}$) and triethylsilyl ($o\text{-1l}$) substrates were identical, despite $o\text{-1k}$ undergoing addition ($k_{\text{5a}}$) to Au approximately 5-fold faster than $o\text{-1l}$, Scheme 2. This result is consistent with turnover-rate limiting intermolecular arylation ($k_{\text{5a}}$), i.e. both substrates converge on the same aryl-Au intermediate ($5\text{a} = 5\text{l}$). A selection of the more-efficient substrates from Scheme 3 ($o\text{-1k}; o\text{-1mn}; o\text{-1irs}$) plus a small range of other functional groups\textsuperscript{17} were then explored for preparative arylation; isolated yields of the coupling products ($o\text{-3a-ai}; 1 \text{mmol scale}$) are shown in Scheme 4.
temperatures and prolonged reaction times, oxidative gold catalysis, usually requiring high silyl groups are present in the substrate (underwent slow protodesilylation, were temperature induced efficient intermolecular coupling, at ambient functional groups, substituents tested no products detected, other than initial bromodesilylation of carbanate, underwent competing solvolysis or oxidation under the arylation conditions, the potentially coordinating ethers (1-1u), esters (1-1a, 1-1ab), a carbamate (1-1z), various sulfur-containing functional groups (1-1v-x), and a phosphate oxide, (1-1y) induced efficient intermolecular coupling, at ambient temperature. A small number of ortho-substituents that were tested underwent competing solvolysis, protodesilylation, or oxidation under the arylation conditions; see the SI for details. Hindered arenes underwent slow (1-3ah) or no reaction (1-3ai). When two silyl groups are present in the substrate (1-1ac), coupling is selective for the more-reactive ortho-silyl group, yielding 1-3ac; the meta-arylated isomer could not be detected.

Conclusions
In prior studies, ortho-substituted arylsilanes have been found to undergo slow intermolecular arylation under oxidative gold catalysis, usually requiring high temperatures and prolonged reaction times, with some substrates failing to turn-over at all. Herein, we employed rate-attenuation analysis, Figure 1, to confirm that the C-Si auration step (k_A) is significantly accelerated by substitution at the ortho-position, even with sterically-demanding substituents, Scheme 2. The effect is analogous to other SeAr reactions of ortho-aryl silanes, where there is alleviation of steric strain upon formation of the Wheland intermediate.\textsuperscript{9,10,12,13} The marked reduction, or complete inhibition, of turnover by simple ortho substituents (e.g. 1-1f, Scheme 3) arises from the impact of the substituent on the subsequent C-H auration step (k_A). A model involving two conformations of the aryl-Au intermediate 5, with steric shielding arising in the dominant conformer 5_5f. Figure 3, accounts for the inhibiting effect of ortho-alkyl substituents.\textsuperscript{14} Based on the model, ortho-chelation should increase the population of the reactive co-planar conformer 5_5f. A diverse range of synthetically-useful functional groups allow the arylated products to be obtained in good yield (Scheme 4). Of the carefully selected range of functional groups tested, short-chained methyl ethers, e.g. 1-1r-u, induced the fastest rates of arylation.

The above observations regarding the importance of Ar-Au conformation in the Au-catalyzed oxidative arylation of aryl silanes (Scheme 1), and the ability to bias this by chelation (Scheme 3) can be applied in the analysis and development of the wide range of other catalyzed reactions involving aryl-gold intermediates.\textsuperscript{2,19}
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