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A silver-free system for the direct C-H auration of arenes and heteroarenes from gold chloride complexes†

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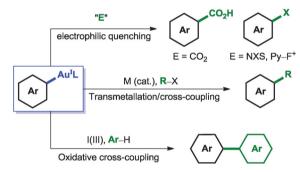
A new methodology for the direct C-H auration of electrondeficient arenes and heteroarenes with simple bases and readily available [Au(PR₃)CI] complexes is described. This system allows the preparation of a wide scope of aryl-Au(ı) compounds without the need for using Ag(ı) additives or preparing and isolating basic Au(ı) hydroxide complexes.

Introduction

Direct functionalisation of arenes by metal-catalysed C-H activation is among the most active topics in organic synthesis. Although dominated by Pd, other metals such as Cu, Rh, Ru, Ir or Co have been shown in recent years to mediate this type of reaction. Au(III) salts have also been used in C-H activation of electron-rich arenes under mild conditions. In contrast to Au(III), Au(I)-promoted C-H activation to afford (hetero)aryl-Au(I) compounds has been demonstrated only recently and is specific for electron-poor arenes.

Studies on the chemistry of (hetero)aryl–Au(1) compounds (Scheme 1) have shown them to be suitable organometallic partners for Pd- or Ni-catalysed cross-coupling reactions, although systems catalytic in Au are scarce. These species have also been shown to react with appropriate electrophiles such as CO₂, electrophilic halogen sources or strong acids. Finally, oxidation with I(III) reagents has allowed their use in the direct C–H arylation of electron-rich arenes exploiting the orthogonal selectivity of both Au oxidation states towards C–H activation, which opens a path for the development of Au(1/III)-catalysed double C–H activation cross-coupling reactions.

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Scheme 1 Transformations of aryl–Au(ı) compounds.

Aryl–Au(i) compounds are remarkably stable towards common decomposition pathways that affect related organometallic compounds.^{10,11} Thus, in addition to being air and moisture-stable, they do not participate in oxidative addition reactions,¹² undergo protodeauration only in the presence of relatively strong acids^{6a,8b,13} and, although one-electron reduction to Au(0) is possible with mild reductants such as Pd(0), this reaction is sufficiently slow to be outcompeted by other processes.^{6,14}

This combination of rich reactivity and stability towards undesired decomposition pathways makes aryl-Au(ı) compounds extremely interesting intermediates in the design of metal-catalysed transformations.

Two C-H auration systems have been reported to date by Nolan's group^{4b,c} (eqn (1)) and our group^{4a} (eqn (2)) based on the use of a [Au(IPr)(OH)] or a [Au(PR₃)Cl]-Ag₂O-K₂CO₃-PivOH reagent system, respectively.

$$[Au^{I}(IPr)CI] \xrightarrow{KOH} [Au^{I}(IPr)(OH)] \xrightarrow{H-C_6X_2F_3} X$$

$$= F \times 60^{\circ}C, 24 \text{ h}$$

$$X = F \times 86\%$$

$$X = H \times No \text{ reaction}$$

$$(1)$$

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[Au^I(P^tBu₃)Cl] + H-C₆X₂F₃
$$\xrightarrow{\text{PivOH, K}_2\text{CO}_3}$$
 X $\xrightarrow{\text{Au}^I\text{P}^t\text{Bu}_3}$ F \times X \times F \times Y \times F \times X \times F \times Y \times F \times Y \times F \times H 100%

It is worth noting that the second of these systems, despite working in an overall less basic medium, shows a higher activity, as exemplified by the direct auration of 1,3,5-trifluorobenzene $(pK_a = 31.5)^{15}$ which is not possible under the standard conditions reported for the [Au(IPr)(OH)] system. The exact origin of this difference in activity has been a matter of discussion, 4c,16 although no thorough mechanistic studies have been published to date.

We considered that the development of a system using a readily available [Au(PR₃)Cl] starting complex and a simple base, without other additives, would not only be synthetically useful but also help us determine which are the real differences between the reactivity of phosphine- and NHC-ligated gold complexes towards C-H activation of electron-deficient arenes.

Results and discussion

We took as a starting point for this investigation our previously reported conditions for the direct auration of electron-deficient arenes ([Au(P^tBu_3)Cl], PivOH, Ag₂O and K₂CO₃, eqn (2)) and studied the possibility of performing the reaction with only the base, in the absence of PivOH or Ag⁺ salts. Unsurprisingly, K₂CO₃ alone was not able to promote the reaction by itself when applied to [Au(P^tBu_3)Cl] (1a) and 1,3-dinitrobenzene (2a) in DMF (Table 1, entry 1). However, shifting to the stronger, but

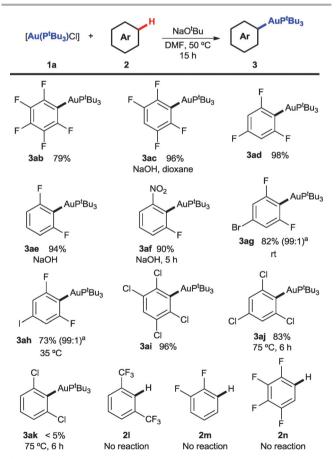
Table 1 Optimisation of the reaction conditions^a

Entry	Base	Solvent	Yield (%)
1	K ₂ CO ₃	DMF	0
2	KOH	DMF	47
3	$\mathrm{KO}^t\mathrm{Bu}$	\mathbf{DMF}	80
4	LiO ^t Bu	\mathbf{DMF}	57
5	NaO^tBu	\mathbf{DMF}	81
6	NaOH	DMF	64
7^b	NaO^tBu	\mathbf{DMF}	31
8	NaO^tBu	THF	45
9	NaO^tBu	$PhCH_3$	30
10	NaO^tBu	1,4-Dioxane	80
11	NaOH	1,4-Dioxane	74
12 ^c	NaO ^t Bu	DMF	90 $(82)^d$

 $[^]a$ Reactions carried out on the 0.03 mmol scale with 1a as the limiting reagent, 4 equiv. of 2a, 4 equiv. of base and 0.15 mL of solvent (0.2 M), at 50 °C for 18 h. Yields determined using 1 H NMR with an internal standard. b Reaction performed with 2 equiv. of 2a. c Reaction at the 0.1 mmol scale, at 75 °C for 5 h. d Isolated yield.

still simple, bases KOH (entry 2) or KO^tBu (entry 3) allowed us to obtain product 3aa in 47 and 80% yields, respectively. Interestingly, use of the more soluble LiO^tBu (entry 4) resulted in a decreased yield, while the less soluble NaO^tBu (entry 5) gave a result comparable to that obtained with KO^tBu. Consistently, NaOH (entry 6) afforded a somewhat higher yield than KOH, although still lower than the tert-butoxide salts. The use of 4 equiv. of 2a was necessary for optimal performance of the reaction, lower yields being obtained with smaller amounts of 2a (entry 7).17 Less polar solvents, shown to be effective in direct auration with [Au(IPr)(OH)], turned out to be detrimental in this case (entries 8 and 9), while dioxane (entries 10 and 11) afforded a yield very similar to that obtained in DMF. Finally, increasing the temperature to 75 °C in DMF with NaO^tBu (entry 12) allowed us to obtain the aurated product in 82% yield after purification (90% NMR yield).

With these optimised conditions, we set out to explore the scope of the reaction, aiming to determine the reactivity of this system towards electron-poor arenes (Scheme 2). A variety of polyfluorinated benzenes 2b-e, as well as 1-fluoro-3-nitrobenzene 2f, reacted smoothly to afford the corresponding aryl-Au(1) compounds 3ab-3af in excellent



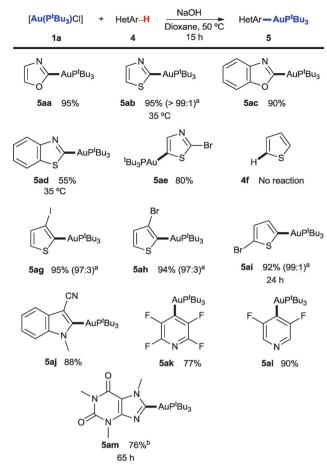
Scheme 2 Scope of the direct C–H auration of arenes. Reactions carried out between the 0.06 and 0.1 mmol scale with **1a** as the limiting reagent, 4 equiv. of **2** and 4 equiv. of NaO^fBu in DMF (0.2 M) at 50 °C for 15 h, unless stated otherwise. Yields are of the pure isolated product. ^a Regioisomer ratios determined using ¹H NMR of the crude mixture.

vields with only slight variations in the general procedure in some cases (use of NaOH as the base in 1,4-dioxane). Remarkably, even 2d reacted at 50 °C without any additive. This contrasts with previous observations where [Au(IPr)(OH)] was not able to activate this substrate under the standard conditions (eqn (1)), requiring the use of a silver salt as an additive. 16 A higher basicity of the active phosphine-Au(1) complex compared to that of [Au(IPr)(OH)] could explain this difference (vide infra). Benzene derivatives bearing two F atoms and another halogen such as Br or I (2g-h) reacted preferentially with the C-H bond ortho to the two F atoms, with virtually complete regioselectivity at nearly room temperature. These substrates are particularly interesting since, after functionalisation of the C-Au bond, they would give place to products bearing a useful functional group for further reactions via other metal-catalysed coupling processes.

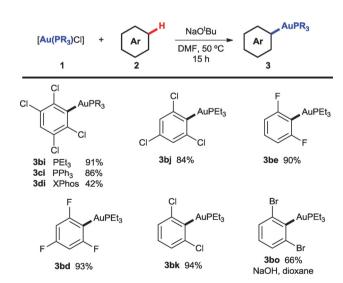
Polychlorinated benzenes 2i-k were also reactive, although in this case at least three chlorine atoms were necessary for good yields. 1,3-Di(trifluoromethyl)benzene 2l failed to afford any aurated product, as well as benzenes without a C-H bond ortho to two electron-withdrawing groups (2m-n).

A wide scope was also observed for electron-deficient heteroarenes (Scheme 3), with a clear dependence of reactivity on the acidity of the C-H bond to be activated. A brief reexamination of the reaction conditions showed that NaOH in 1,4-dioxane consistently afforded higher yields in the case of heteroarenes. Under these conditions, oxazole (4a), thiazole (4b), benzoxazole (4c) and benzothiazole (4d) all reacted to afford the corresponding auration products 5aa-5ad in good yields. In the case of thiazole, displaying two roughly equally acidic protons (p K_a = 29.5 for the C2 position and 29.6 for C4),15 selective C2-auration (>99:1) to give 5ab could be achieved at 35 °C. Additionally, blocking the C2 position with a Br substituent allowed preparation of the C4-aurated product 5ae, keeping the Br intact and available for further functionalisation. The less acidic thiophene (4f, $pK_a = 32.5$)¹⁵ was found not to be active in the reaction, thus determining an upper limit for the activity of our system. However, the presence of just one halogen substituent lowered the pK_a sufficiently for the corresponding aurated products 5ag-5ai to be obtained in excellent yields and regioselectivities, with auration occurring selectively α to the sulfur. Similarly, just one strong electron-withdrawing group allowed C2-auration of indole-type substrates $(pK_a \text{ of } N\text{-methylindole} = 37.3)^{15}$ to obtain 5aj, and two electron-withdrawing groups allowed preparation of pyridyl-Au(1) compounds 5ak-5al. Finally, a stable, electron-deficient imidazole-type substrate such as caffeine (4m) could be used, affording product 5am in good yield and using only 1.1 equiv. of the parent heteroarene.

Phosphine ligands other than P^tBu₃ were also explored (Scheme 4). For the highly electron-deficient tetrachlorobenzene, both alkyl and aryl phosphines (3ai-3ci) afforded high yields, and only with the very bulky XPhos (3di) was the yield significantly reduced. Reaction of 1,3,5-trichloro- and 1,3difluorobenzene with [Au(PEt₃)Cl] also led to excellent yields, comparable to those obtained with the P^tBu₃ ligand (compare



Scheme 3 Scope of the direct C-H auration of heteroarenes. Reactions carried out between the 0.06 and 0.1 mmol scale with 1a as the limiting reagent, 4 equiv. of the corresponding heteroarene 4 and 4 equiv. of NaOH in 1,4-dioxane (0.2 M) at 50 °C for 15 h, unless stated otherwise. Yields are of the pure isolated product. ^a Regioisomer ratios determined using ¹H NMR of the crude product. Reaction carried out with 1.1 equiv. of caffeine.



Scheme 4 Application of different phosphines. Reactions carried out between the 0.06 and 0.1 mmol scale with 1a as the limiting reagent, 4 equiv. of 2 and 4 equiv. of NaO^tBu in DMF (0.2 M) at 50 °C for 15 h, unless stated otherwise. Yields are of the pure isolated product.

Scheme 5 Direct auration with [Au(IPr)Cl].

3bj, 3be and 3bd in Scheme 4 with 3aj, 3ae and 3ad in Scheme 2). More interestingly, in some cases where $[Au(P^fBu_3)CI]$ had offered limited or no success, the use of a PEt₃ ligand allowed efficient preparation of the corresponding aryl-Au(1) compounds. This allowed efficient auration of the previously unreactive 1,3-dichlorobenzene (3bk), and even satisfactory reaction with 1,3-dibromobenzene (3bo).

In order to determine the origin of this system's ability to perform the auration of less acidic substrates, such as 1,3,5-trifluorobenzene, in contrast to the [Au(IPr)(OH)] complex, we tested the auration in our conditions with [Au(IPr)Cl] (6, Scheme 5). Treatment of 6 with 2b and NaOH or NaOfBu cleanly provided the aryl-Au(i) complex 7b in 95 and 93% yields, respectively, showing that the auration process with NHC ligands does not require isolation of the gold hydroxide complex. Reaction with 2d under the same conditions, however, did not afford the corresponding aryl-Au(i) compound. This shows that, at least under these reaction conditions, phosphine-ligated Au(i) complexes are intrinsically more active in the auration reaction than the corresponding NHC-ligated ones. 19

The exact nature of the species effecting the C-H activation proved elusive. Titration of 1a with NaO'Bu or NaOH, monitored by *in situ* ³¹P NMR, showed complete disappearance of the signal corresponding to the starting material (90.7 ppm), giving place to a new peak at 83.2 ppm with 1.0 equiv. of NaO'Bu or at 83.5 ppm with 1.5 equiv. of NaOH. Further addition of base did not give place to any other observable product. The product of reaction between 1a and NaO'Bu, unfortunately, resisted all attempts to isolate it, but it has been reported previously that treatment of [Au(PR₃)Cl] complexes with NaO'Bu in THF gives place to the corresponding [Au(P'Bu₃)O'Bu] complexes²⁰ (Scheme 6). Higher order complexes of the type {[Au(PR₃)]₂OR}⁺ have also been described,²¹ but their preparation usually involves the use of a "cationic" gold complex (such as [Au(PR₃)(BF₄)]), which makes

Scheme 6 Reactions of [Au(P^tBu₃)Cl] (**1a**) with NaO^tBu and NaOH.

Scheme 7 Previously reported products obtained from basic treatment of [Au(L)(NCMe)]BF₄ complex **10**. L = XPhos or JohnPhos.²³

it unlikely in our case. Thus, we hypothesise that the product of $1a + NaO^tBu$ could be 8. Regarding the reaction between 1a and NaOH, the NMR signals of the product matched those previously described for $\{[Au(P^tBu_3)]_3O\}BF_4$ (9'). Addition of NaBF₄ into the mixture of 1a + NaOH allowed isolation of 9' as a white solid in 92% yield, leading us to conclude that the product obtained is $\{[Au(P^tBu_3)]_3O\}Cl$ (9).

However, the reaction of 1a, 2a and either 1.0 equiv. of NaO^tBu or 1.5 equiv. of NaOH afforded the auration product 3aa in only 45 and 15% yield, respectively. These results seem to indicate different behaviour of compounds 8 and 9: in the case of 8 the yield obtained was moderate, still lower than that obtained under the standard conditions but indicative of some activity. On the other hand, 9 was less reactive and required the presence of a large excess of base (only 15% yield was obtained, despite the presence of 1.5 equiv. of base, more than theoretically needed for formation of 9).

Trinuclear μ^3 -oxo Au(i) species with biphenyl(dialkyl)-phosphines (12, Scheme 7) have recently been shown to be related to 10, 11 and 13 by an equilibrium which depends on the stoichiometry with respect to the base, as well as on the steric properties of the phosphine ligand.²³ The analogous compound 1d (PR₃ = XPhos) was effective in the auration process under the conditions reported here (product 3di in Scheme 4), leading us to hypothesise that a qualitatively similar situation could take place also with the other phosphines. Thus, *in situ* formation of a Au(i) hydroxide species, even as a minor component in the equilibrium mixture, can be hypothesised. Alternatively, direct deprotonation of the arene by the base followed by attack of the resulting aryl anion on an electrophilic gold(i) complex cannot be discarded either.²⁴

Conclusions

In summary, we have developed a simplified methodology for efficiently performing direct C–H auration of electron-deficient arenes and heteroarenes, combining readily available [Au(PR₃)Cl] complexes and simple bases. This system shows excellent activity for a wide range of substrates without requiring the use of silver salts as additives or the preparation and isolation of Au(1) hydroxide complexes.

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