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Arenediazonium salts as electrophiles for the oxidative addition of gold(I)†

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Arenediazonium salts generated *in situ* from anilines have been found for the first time to efficiently oxidize [AuCl(L)] (L = SMe$_2$, PPh$_3$) complexes in DMSO as a solvent, under thermal conditions. The structure of the [AuArCl$_2$(L)] complexes formed has been confirmed by X-ray diffraction analyses. These complexes have been used as intermediates, in a one pot cross-coupling reaction of anilines with silver acetylides.

In recent years the development of new processes involving the oxidative addition of Au(I) has attracted significant interest. Due to the high redox potential of the Au(I)/Au(III) couple (E_0 = +1.41 V),[1] the oxidation of Au(I) in most cases has been achieved by adding external oxidants such as fluorinating or hypervalent iodine reagents.[2] In this regard many efforts have been made in order to understand and circumvent the high energy associated with this process.[3] The group of Toste successfully achieved the oxidative addition of allylbromide to a bimetallic Au(I) complex, *via* the formation of a Au(II)–Au(II) species.[4] Fernández and Bickelhaupt studied theoretically the factors governing the oxidative addition of aryl halides to Au(I),[5] and in line with their conclusions, Amgoune and Bourissou described the first direct experimental evidence of the oxidative addition of a C_{sp^2}–X bond to a single gold center, by using haloarenes with pendant phosphines, and diphosphino–carborane Au(I) complexes.[6] Later on, independently Toste, Amgoune and Bourissou found that it is possible to perform the oxidative addition of a strained C–C bond to cationic Au(I) complexes bearing NHCs or diphosphino–carborane ligands.[7] More recently, Ribas and coworkers have provided the first examples of external oxidant-free Au(I) catalysed carbon–heteroatom cross-coupling reactions, employing aryl halide macrocycles or aryl halides with a nitrogen chelating site.[8]

As an alternative to the aforementioned methods, we got interested in studying the use of arenediazonium salts to perform the oxidative addition of Au(I) to Au(III).[9] To date some radical transformations involving diazonium salts and Au(I) complexes have been described in the bibliography. In these processes the gold complexes act in combination with a photosensitizer in a dual catalytic fashion.[10] On the other hand Chen and Shi reported gold catalyzed C_{sp}–C_{sp^2} and C_{sp^2}–C_{sp^2} cross coupling reactions using arenediazonium salts, which take place *via* initial gold(I) acetylide formation, and subsequent oxidative addition of the arenediazonium salt assisted by a bpy ligand.[11] By contrast, herein we report that [AuCl(L)] (L = SMe$_2$, PPh$_3$) complexes undergo the direct oxidative addition of arenediazonium salts, generated *in situ* from anilines, in DMSO as a solvent. In constrast to our results, the group of Hashmi has very recently reported that [AuCl(L)] complexes can also undergo the direct oxidative addition of arenediazonium salts under irradiation with a blue light LED.[12]

We began our study analyzing the reaction of 4-benzoylbenzenediazonium chloride (**1**) with [AuCl(SMe$_2$)] in DMSO as a model system, with the aim of stabilizing the desired arylAu(III) complex by electronic and steric factors. 4-Benzoyl-benzenediazonium chloride was synthesized *in situ* from 4-aminobenzophenone in THF,[13] after removal of the solvent and addition of [AuCl(SMe$_2$)] in DMSO-d_6, the reaction was monitored by ^{1}H NMR spectroscopy at r.t. It could be observed that after 4.5 h of reaction, along with the set of signals corresponding to 4-benzoyl-benzenediazonium chloride [8.92 (d, 2H), 8.21 (d, 2H), and 7.94–7.39 (m, 5H) ppm], two new signals appeared at a higher field [7.40 (d), and 7.26 (d) ppm], in a ratio 1 : 0.60. Upon increasing the temperature to 50 °C, the reaction became faster and 4-benzoyl-benzenediazonium chloride was totally consumed within 3 h (Scheme 1). The chemical shift of the new signals was congruent with additional electronic density coming from the coordination to a gold atom, nonetheless attempts to isolate the new compound were unsuccessful. Emulating the work of Parkin[14] we tried to stabilize and facilitate the isolation of **3a** by adding one equivalent of PPh$_3$. After the addition of the phosphine, a single signal at 32.7 ppm was detected by ^{31}P NMR, pointing a phosphorous–gold coordination and the formation of **3b**.

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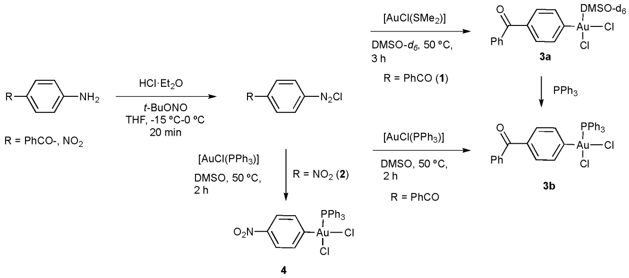


Scheme 1 Oxidative addition of [AuCl(SMe$_2$)] and [AuCl(PPh$_3$)] with ArN$_2$Cl (Ar = 4-PhCOC$_6$H$_5$, 4-NO$_2$C$_6$H$_5$).

Contrary to the reports where it is shown that phosphines decompose diazonium salts *via* single electron transfer,[15] **3b** could also be directly obtained from the reaction of 4-benzoylbenzenediazonium chloride with [AuCl(PPh$_3$)]. In this case the reaction time was reduced to 2 h, which is in accord with a more electron-rich Au(I) precursor. Fortunately, single crystals of **3b** could be obtained by slow diffusion of Et$_2$O into a solution of **3b** in DCM (37% yield), and its molecular structure was confirmed by X-ray diffraction analysis. Employing a similar strategy, we also succeeded in isolating (41% yield) and characterizing complex **4** obtained by the reaction of 4-nitro-benzenediazonium chloride (**2**) with [AuCl(PPh$_3$)]. Again, single crystals of **4** could be obtained by slow diffusion of Et$_2$O into a solution of **4** in DCM, and its structure was confirmed by X-ray diffraction analysis.

Both compounds are stable in air, but with time tend to decompose to [AuCl(PPh$_3$)] by reductive elimination. This was confirmed by the appearance of a second signal in the ^{31}P NMR spectrum at 33.7 ppm and by mass spectrometry. The solid-state molecular structures of **3b** and **4** are depicted in Fig. 1. The geometry around the gold center is essentially square-planar in both complexes, and the distance Au–Cl1 is longer than Au–Cl2 due to the higher *trans* influence of the aryl groups in both complexes: [Cl1–Au–C5 176.5(2) and Cl2–Au–P 175.73(8)° for **3b**, Cl1–Au–C1 176.4(5) and Cl2–Au–P 177.59(5)° for **3**], and [Au–Cl1 2.369(2) Å compared to Au–Cl2 2.323(2) Å for **3b**, Au–Cl1 2.365(1) Å compared to Au–Cl2 2.327(2) Å for **4**].

Once it was confirmed that it is possible to obtain arylAu(III) complexes by oxidative addition of [AuCl(SMe$_2$)] and [AuCl(PPh$_3$)] with arenediazonium salts, we turned our attention to study the possibility of performing a one-pot coupling reaction with nucleophiles. At first instance we examined the coupling between 4-aminobenzophenone and silver phenylacetylide,[16] hoping that the high affinity of silver for halogens would facilitate the transmetallation process.[17] Satisfactorily, when 1 equiv. of silver phenylacetylide was added at r.t. to the complex obtained by the oxidative addition of [AuCl(SMe$_2$)] with **1**, the expected coupling product 5 was formed in 58% yield (Table 1, entry 1). Upon employing [AuCl(PPh$_3$)] as a Au(I) source, **5** was obtained in a similar yield (56%, entry 2), hence to study the coupling reaction we preferred [AuCl(SMe$_2$)] over [AuCl(PPh$_3$)], since the former is a precursor of the latter. Increasing the amount of silver phenylacetylide up to 1.5 equiv. increased the yield to 75%. Comparatively, when 2 equiv. of silver phenylacetylide was added the yield did not increase significantly (entries 3 and 4). We also examined the feasibility of the coupling reaction in THF and CH$_3$CN instead of in DMSO. In the first case the yield decreased to 26% while in the second it was 66% (entries 5 and 6). Lastly, and in order to corroborate that the real intermediate of the coupling reaction is an arylAu(III) complex, we took isolated complex **3b** (1 equiv.) and subjected it to the reaction with silver phenylacetylide (1.5 equiv.). As expected, after stirring in DMSO for 1.5 h at rt, **5** was formed in 75% yield, thus confirming that the coupling is done *via* an arylAu(III) complex.[18]

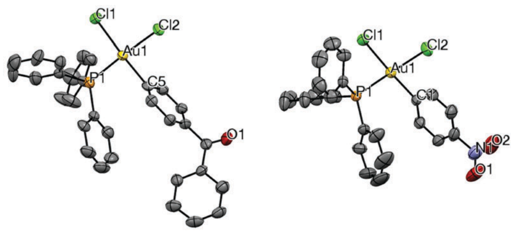
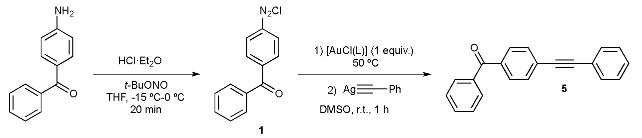


Fig. 1 ORTEP diagrams of **3b** (left) and **4** (right). Hydrogen atoms are omitted for clarity.

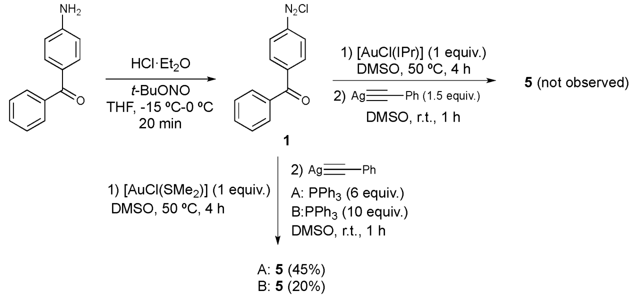
Table 1 Optimization of the coupling reaction of 4-aminobenzophenone with silver phenylacetylide



	Aniline[a] (equiv.)	[Au^I]	Oxid. addition conditions	$Ag\equiv Ph$ (equiv.)	Yield (%)
1	1	[Au(SMe$_2$)Cl]	DMSO, 4 h	1	58
2	1	[Au(PPh$_3$)Cl]	DMSO, 2 h	1	56
3	1	[Au(SMe$_2$)Cl]	DMSO, 4 h	1.5	75
4	1	[Au(SMe$_2$)Cl]	DMSO, 4 h	2	79
5	2	[Au(SMe$_2$)Cl]	DMSO, 4 h	1.5	59
6	1	[Au(SMe$_2$)Cl]	THF, 5 h	1	26
7	1	[Au(SMe$_2$)Cl]	CH$_3$CN, 4 h	1.5	66

[a] Aniline : *t*BuONO : HCl (1 : 1.2 : 2), [Au^I] = 0.034 mmol ml^{-1}.

Concerning the mechanism[19] of the coupling reaction, as far as we know, the reductive elimination step in Au(III) complexes to form a C_{sp}–C_{sp^2} bond has not been studied before. Nonetheless, there are reports dealing with reductive elimination from Au(III) complexes to form C_{sp^3}–C_{sp^3} and C_{sp^2}–C_{sp^2} bonds. In these studies it has been established that reductive elimination to form C_{sp^3}–C_{sp^3} bonds is slow and takes place directly from a tetrasubstituted Au(III) species, whereas reductive elimination to form C_{sp^2}–C_{sp^2} bonds is very fast and takes place from a three coordinated Au(III) species.[20] In order to gain more insights into the reductive elimination step, we examined the effect of adding an excess of phosphine. Thus, we observed that the addition of 6 and 10 equiv. of PPh$_3$ reduces the yield of **5** to 45% and 20% respectively (Scheme 2). On the other hand, upon employing [AuCl(IPr)] as the Au(I) source, the formation of **5** was not observed. Instead, upon analysing the crude mixture by mass spectrometry (DART, [M + H]*) two peaks were identified,

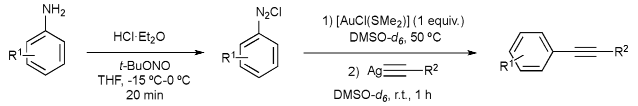


Scheme 2 Examination of the coupling step in the presence of an excess of phosphine and an IPr ligand.

one corresponding to benzophenone (*m*/*z* = 183) and the second one corresponding to 4-chlorobenzophenone (*m*/*z* = 217).[21] This result suggests that for the reductive coupling to take place, the dissociation of a ligand is necessary.

Aiming at extending the coupling reaction further, we studied its scope over a variety of anilines with different electronic properties, as well as with other silver acetylides containing alkyl substituents (Table 2). In all cases we used ^{1}H NMR to monitor the oxidative addition, and as soon as the arenediazonium salt was consumed,[22] the silver acetylide was added. Upon employing aniline and silver phenylacetylide as coupling partners, the oxidative addition proceeded cleanly in only 1.5 h, however the coupling product was obtained in 19% yield (entry 1). Anilines containing electron-withdrawing groups at the *para* position (*p*-CN, *p*-NO_2, *p*-Br) behaved similar to 4-aminobenzophenone with oxidative addition times of 4–5 h, and yields ranging from 49–70% for the coupling with silver phenylacetylide (entries 2–5). An exception was the *p*-CO_2Me substituent, which notably increased the reactivity of the corresponding arenediazonium salt. In this case the oxidative addition took 3 h at r.t., and the yield of the coupling with silver phenylacetylide decreased to 32% (entry 7). The presence of an *m*-Cl substituent also resulted in the acceleration of the oxidative addition step, so that the arenediazonium salt was consumed after 1.25 h. In this case, the yield of the coupling with silver phenylacetylide was also diminished (45%, entry 6). The decrease in the yield for anilines bearing *p*-CO_2Me and *m*-Cl substituents was attributed to a visible minor stability of the corresponding arenediazonium salts. Regarding anilines bearing electron-donating groups (*p*-Me, *m*-Me and *p*-OMe), the oxidative addition step was remarkably slow for 4-aminoanisole (36 h, entries 11 and 12). As a common feature, it was observed that for these substituents the coupling yields with silver phenylacetylide improved when the amount of aniline was increased up to 2 equiv. (entries 8–12). In addition, we got interested in examining the effect of adding alkyl substituents on the silver acetylide (entries 14–16, R^2 = $(CH_2)_3CH_3$, CH_2Ph, OCH_2Ph).[23] Using 4-aminobenzophenone as a model aniline for the coupling, a decrease in the yields as the size of the alkyl chain increased could be observed. Thus, a lower yield was obtained when R^2 = $(CH_2)_3CH_3$ (26%, entry 15). This effect can be attributed to the tendency of silver acetylide molecules to associate, forming supramolecular frameworks, which reduce their reactivity.[23b]

Table 2 Scope of the coupling reaction of anilines with silver acetylides



	R^1 aniline[a] (equiv.)	Oxid. addition conditions	R^2 acetyl. (equiv.)	Yield (%)
1	H (1)	50 °C, 1.5 h	Ph (1.5)	19
2	*p*-CN (1)	50 °C, 4 h	Ph (1.5)	49
3	*p*-NO_2 (1)	50 °C, 4 h	Ph (1.5)	61
4	*p*-Br (1)	50 °C, 4.5 h	Ph (1.5)	70
5	*p*-Cl (1)	50 °C, 5 h	Ph (1.5)	58
6	*m*-Cl (1)	50 °C, 1. 25 h	Ph (1.5)	45
7	*p*-CO_2Me (1)	r.t., 3 h	Ph (1.5)	32
8	*p*-Me (1)	50 °C, 4 h	Ph (1.5)	35
9	*p*-Me (2)	50 °C, 4 h	Ph (1.5)	55
10	*m*-Me (2)	50 °C, 4 h	Ph (1.5)	57
11	*p*-OMe (1)	50 °C, 36 h	Ph (1.5)	48
12	*p*-OMe (2)	50 °C, 36 h	Ph (1.5)	64
13	*p*-PhCO (1)	50 °C, 4 h	CH_2Ph (1.5)	47
14	*p*-PhCO (1)	50 °C, 4 h	CH_2OPh (1.5)	43
15	*p*-PhCO (1)	50 °C, 4 h	(CH2)3CH3 (1.5)	26

[a] Aniline : *t*BuONO : HCl (1 : 1.2 : 2), $[Au^I]$ = 0.034 mmol ml^{-1}.

Comparatively, the coupling with phenylacetylene as a nucleophile was less effective. Thus starting from 4-aminobenzophenone, and employing 2,6-lutidine as a base,[24] the coupling product was obtained in 38% when 1 equiv. of phenylacetylene was added and in 46% yield when 1.5 equiv. of phenylacetylene was added (Scheme 4).

Finally, and in order to study the effect of applying the optimal conditions found by Chen and Shi for the gold catalyzed cross coupling of arenediazonium salts with alkynes to our coupling,[11] we studied the coupling of **1′** with silver phenylacetylide (Scheme 3). However, using a $[AuCl(PPh_3)]$/$AgNTF_2$ mixture (1 : 1.1 equiv.) and Bipy (2 equiv.) as the Au(I) source, 5 was isolated in 12% when the oxidative addition was performed at r.t., and not observed when the temperature was increased to 50 °C. This result suggests that the Au(III) complex formed with a BF_4^- counteranion is not stable enough and decomposes before reacting with silver phenylacetylide. Similarly, when we applied our coupling conditions to **1′**, **5** was not observed confirming that **1′** with a noncoordinating anion is not an adequate precursor to form a stable arylAu(III) complex.

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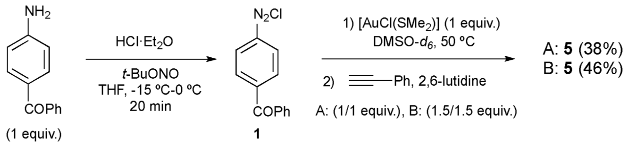
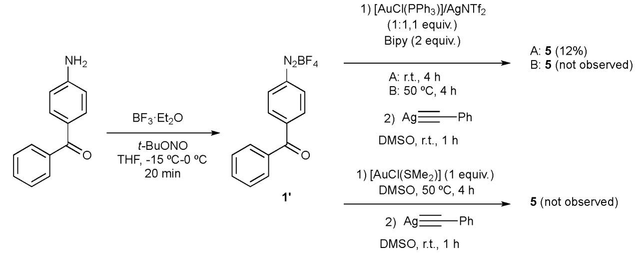


Scheme 3 Coupling with phenylacetylene.



Scheme 4 Examination of the coupling of 1′ with silver phenylacetylide.

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