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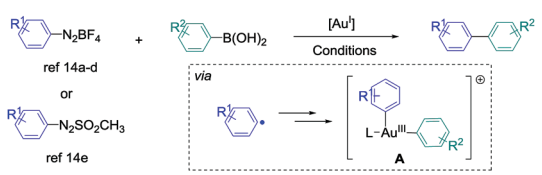
Mechanistic and asymmetric investigations of the Au-catalysed cross-coupling between aryldiazonium salts and arylboronic acids using (P,N) gold complexes†

Alexis Tabey, Murielle Berlande, Philippe Hermange * and Eric Fouquet*

In order to explore the different mechanisms possibly occurring in the Au-catalysed cross-coupling of ArN_2BF_4 and $ArB(OH)_2$ in the presence of CsF, various stoichiometric experiments were performed on gold complexes with (P,N) ligands. Employing 2-pyridylphenylphosphine allowed us to suggest three different mechanistic pathways, starting either with a transmetallation step, *via* two consecutive single electron transfers, or by implying a transmetallation between Au(I) and Au(III) species. Moreover, when using commercially available chiral (P,N) ligands, the asymmetric formation of atropoisomeric biaryls from suitable aryldiazonium salts and arylboronic acids could be achieved with e.e. up to 26%.

The synthesis of biaryl compounds by transition metal catalysed reactions has been the subject of numerous research studies these last few decades, and various elements in the d-block were explored.[1] Among them, Pd-based catalysts were undoubtedly the most successful species to enable the coupling of suitable aryl electrophiles and aryl nucleophiles with high efficiency and wide functional-group tolerance. Indeed, the palladium atom is easily able to undergo changes of its oxidation state, and its catalytic activity can be finely tuned by coordination to specifically designed monodentate/bidentate ligands.[2] In contrast, the use of gold catalysts for the synthesis of aryl–aryl cross-coupling products has remained extremely challenging for a long time.[3,4] Indeed, their reluctance to engage in Au(I)/Au(III) catalytic cycles has been seen as a barrier for such reactions,[5] and most of the research studies in homogeneous gold catalysis were focused on employing its carbophilic Lewis acid properties for pi-activation and cascade reactions.[6] However, new strategies appeared recently to overcome this issue, for example using a strong external oxidant to ensure the access to the Au(III) intermediates,[7] or designing specific (P,P), (P,N) and (N,N) ligands to enable the oxidative addition onto aryl halide.[8] On the other hand, employing aryldiazonium salts as electrophiles[9] also led to extremely fruitful results in gold-catalysed arylation reactions. Indeed, upon thermal, light-induced, base-induced or photoredox-induced[10] activation, the aryl radical generated *in situ* from the diazonium salt can produce the desired Au(III)-aryl species after two single electron transfers (SET).[11] These complexes, obtained under extremely mild conditions from simple Au(I) precursors, are able to engage in a wide variety of transformations,[12,13] including the synthesis of biaryl compounds from the cross-coupling of aryldiazonium salts (or derivatives) and arylboronic acids. Interestingly, this reaction could be catalysed by either coordinatively saturated or cationic Au species, and various conditions were reported (Scheme 1).[14]

However, contrary to the well-established catalytic cycle for palladium catalysed cross-couplings involving successive oxidative addition, transmetallation and reductive elimination steps,[1,2] mechanistic pathways leading to intermediate A, which undergoes the reductive elimination,[15] are still unclear in these gold-catalysed aryl–aryl cross-couplings. Based on stoichiometric ^{1}H and ^{31}P NMR studies, transmetallation was proposed to be the first step in ref. 14*a* and *b* (catalytic cycle I). In contrast, ref. 14*d* and *e* suggested that the double SET occurred first (catalytic cycle II), taking into account the modelling experiments on related gold-catalysed transformations involving aryldiazonium salts[16] and literature reports on the stoichiometric synthesis of aryl–Au(III)



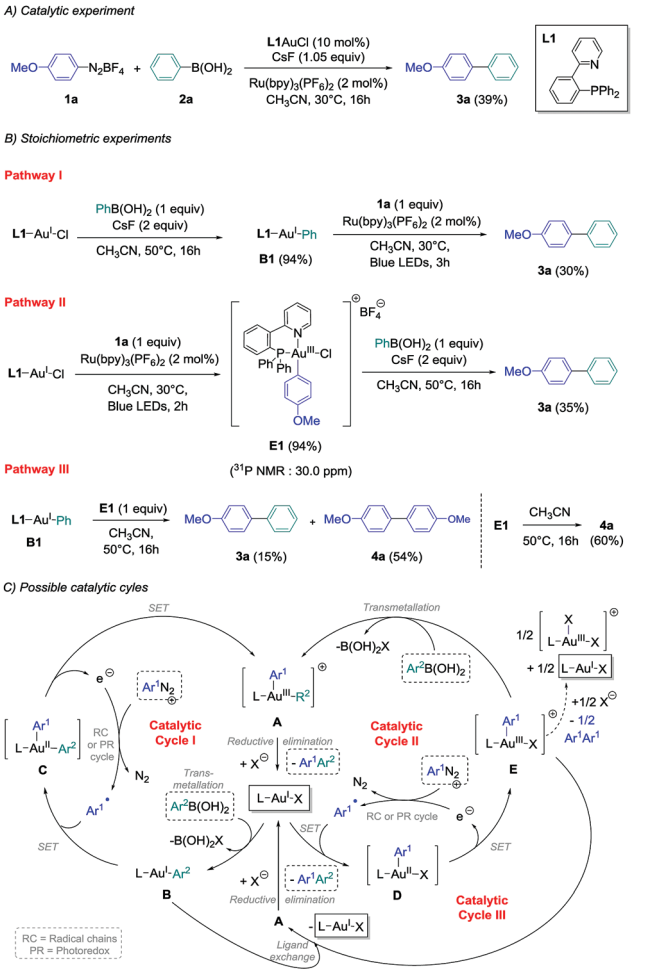
Scheme 1 Reported gold-catalysed cross-coupling between aryldiazonium salts (or arylazosulfones) with arylboronic acids. For the exact conditions, see ref. 14.

Univ. Bordeaux, Institut des Sciences Moléculaires, UMR-CNRS 5255, 351 Cours de la Libération, 33405 Talence Cedex, France.
E-mail: philippe.hermange@u-bordeaux.fr, eric.fouquet@u-bordeaux.fr

† Electronic supplementary information (ESI) available: General experimental procedures and analysis/spectroscopic data (^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HPLC chromatograms). CCDC 1843202. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc07530a

complexes.[11] An in-between situation was described by Lee *et al.*, whose NMR studies were in favour of either transmetallation first with PPh_3AuNTf_2 or oxidation first with PPh_3AuCl, thus showing the complexity of mechanism determination in this reaction. Finally, despite the evident analogy with the well-known [Pd]- or [Ni]-catalysed syntheses of atropoisomeric biaryls,[17] possible asymmetric induction with a gold-based system has not been described yet to our knowledge, but could open a new area of research in this field.

In view of these observations, we decided to perform stoichiometric experiments to investigate mechanistic and asymmetric possibilities of our conditions of gold-catalysed cross-coupling between aryldiazonium salts and arylboronic acids.[14b] Some of our preliminary experiments with PPh_3AuCl as a precursor were unsuccessful,[14b] and all the isolated aryl–Au(III) species reported in the literature contained a supplementary ligand, *i.e.* a chloride ion when starting from aryldiazonium chloride,[11b,e] or pyridine moieties present either on the aryldiazonium tetrafluoroborate[11d] or on the phosphine ligand.[11a,c] Thus, 2-pyridylphenyl-diphenylphosphine **L1** was chosen as the preferential ligand for stoichiometric studies, as the catalytic ability of **L1**-AuCl in the cross-coupling reaction could be confirmed (39% yield of product **3a**, Scheme 2(A)). Then, transmetallation of this model gold chloride complex with phenylboronic acid **2a** in the presence of two equivalents of CsF was explored following pathway I, and pleasingly it led to the desired **L1**AuPh (**B1**) with an excellent isolated yield of 94%.[18] Interestingly, adding one equivalent of diazonium **1a** to an acetonitrile solution of **B1** under photoredox conditions produced the cross-coupling biaryl compound **3a** in 30% yield (Scheme 2(B), pathway I), *i.e.* in a comparable yield to the one obtained employing catalytic amounts of the gold precursor (39%, Scheme 2(A)). Thus, as previously demonstrated with Ph_3AuCl,[14b] this would suggest that Cycle I could operate in the catalytic version of this reaction. Moreover, when **L1**AuCl was reacted directly with 4-methoxybenzenediazonium salt **1a** under blue light irradiation with $Ru(bpy)_3(PF_6)_2$ as the photocatalyst, the Au(III)-complex **E1** was also isolated with an excellent yield of 94% (Scheme 2(B), pathway II). Interestingly, the ^{31}P NMR signal at 30.0 ppm was in accordance to a *trans* configuration between the chloro ligand and the phosphorous atom as reported previously in the literature.[11b] Subsequently, **E1** was reacted with phenylboronic acid and cesium fluoride under the exact transmetallation conditions of pathway I, and **3a** could be isolated in 35% yield in this case,[19] therefore suggesting that Cycle II could also be a viable mechanism. Finally, we hypothesised that Au(I)–Au(III) ligand exchange might occur during the course of the reaction, and the reaction of **L1**AuPh (**B1**) with **E1** was investigated. Interestingly, along with the homo-coupling product **4a** resulting from the decomposition of **E1** under the reaction conditions, the desired cross-coupling product **3a** was obtained in 15% yield, confirming the possibility of a still undescribed third catalytic cycle (Cycle III). To gain further insight into the precise intermediates involved catalytically, we attempted to prepare the corresponding cationic and fluoride gold species for these three pathways,



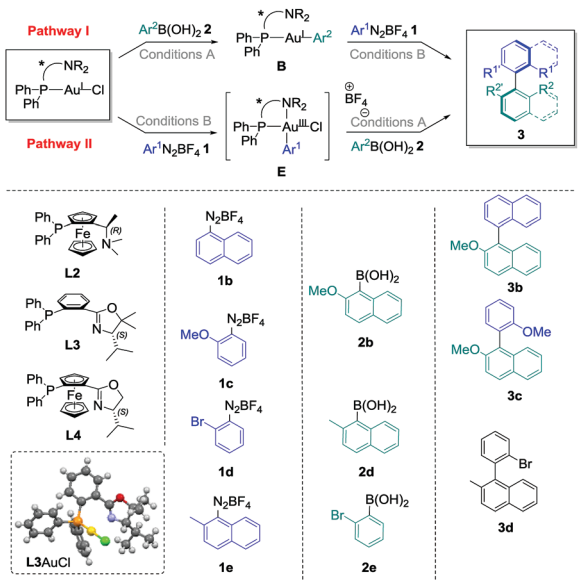
Scheme 2 Catalytic and stoichiometric experiments of the cross-coupling between 4-methoxybenzenediazonium tetrafluoroborate **1a** and phenylboronic acid **2a** using **L1**AuCl as the gold precursor, and possible catalytic cycles.

but unfortunately, it led only to unusable complex mixtures and/or degradation.

In a second part, the use of chiral catalysts was investigated in combination with more hindered starting materials to potentially produce enantioenriched atropoisomeric biaryl compounds.

The commercially available ligand (*R*)-(S_p)-(−)-PFNMe **L2** was firstly chosen for its established ability to produce good enantioselectivities in Pd-catalysed atropoisomeric biaryl couplings.[20] Pathway I was considered, and transmetallation of **2b** with **L2**AuCl was achieved smoothly. Indeed, the Au(I) complex **B2** was isolated in good crude yields (70–96%, see the ESI†) under the conditions previously developed, *i.e.* with two equivalents of cesium fluoride at 50 °C in acetonitrile for 16 h. Then, the reaction of this compound with one equivalent of the diazonium salt **1b** under photoredox conditions provided the desired biaryl product **3b** with isolated yields ranging from 28% to 41%, corresponding to a mean yield of 33% over the four experiments. Unfortunately, a very low asymmetric induction was measured for **3b** using chiral HPLC (mean enantiomeric

Table 1 Screening of ligands and substrates in the asymmetric gold-mediated cross-coupling of aryldiazonium salts and arylboronic acids[a]



Entry	Path	L	1	2	3	Yield[a] (%)	e.e.[b] (%)
1	I	**L2**	**1b**	**2b**	**3b**	33 ± 6[c] (n = 4)	+5 ± 2[c] (n = 4)
2	II	**L2**	**1b**	**2b**	**3b**	9 ± 13[c] (n = 6)	−8 ± 0[c] (n = 2[d])
3	I	**L3**	**1b**	**2b**	**3b**	42	+12
4	I	**L3**	**1c**	**2b**	**3c**	23	−3
5	I	**L3**	**1d**	**2d**	**3d**	<10[e]	nd[f]
6	I	**L3**	**1e**	**2e**	**3d**	5	+3
7	I	**L4**	**1b**	**2b**	**3b**	44	+26

Conditions A: arylboronic acid (1–1.5 equiv.), CsF (2 equiv.), CH_3CN, 50 °C, 2–72 h; conditions B: aryldiazonium tetrafluoroborate (1 equiv.), $Ru(bpy)_3PF_6$ (2 mol%), blue LED irradiation, 30 °C, 2–3 h. After step 1, the mixture was evaporated, filtered on celite, evaporated under reduced pressure and triturated in Et_2O or pentane to give the crude product, which was engaged without further purification in step 2 after NMR analyses. For the exact conditions, see the ESI. Mercury drawing of one of the structure of **L3**AuCl obtained by X-ray diffraction analysis (50% thermal ellipsoids).[a] Yield of product **3** over the two steps after isolation *via* preparative TLC on silica gel. [b] Determined by chiral HPLC (measurement error of ±2%). The plus sign was arbitrarily attributed if the major enantiomer of **3** corresponded to the HLPC pic with the lower retention time, and the minus sign in the opposite case. [c] Mean ± standard deviation of n experiments. [d] Calculated for the two successful reactions out of six performed. [e] Product **3d** was isolated in a mixture with multiple side-products, and a second purification by preparative TLC did not improved the purity of the sample. [f] nd: not determined.

excess of +5 ± 2%, n = 4, Table 1, entry 1). On the other hand, directly adding **1b** to **L2**AuCl in acetonitrile in the presence of 2 mol% of the $Ru(bpy)_3^{2+}$ as a photocatalyst under blue LED irradiation leads to the major formation of the gold complex **E2**, characterised by its signal at 20.6 ppm in ^{31}P NMR.‡ However, a lack of reproducibility was observed for step 2 in this case, as the desired product **3b** could only be isolated for two of the six experiments, despite a full conversion of the starting complex observed in all cases (Table 1, entry 2). A mean yield of only 9% was calculated (n = 6), and a low e.e. was again measured (−8 ± 0%, n = 2), which precluded compelling mechanistic conclusions. As this poor reproducibility might be due in these conditions to the competition between pathway I, catalytic cycle III and decomposition pathways of **E2**, we decided to focus solely on the fully reproducible pathway I for the other experiments. (P,N) Ligands with chiral oxazoline moieties were investigated and **L3**AuCl was prepared,[21] which produced single crystals suitable for X-ray diffraction analysis (Table 1).§ Interestingly, the crystal structure confirmed the expected absence of nitrogen coordination in this Au(I) complex. Then, the stoichiometric biaryl couplings were realised starting from this compound, and the yield of **3b** obtained was similar to the one with **L2**AuCl for pathway I (42%, entry 3), but led to a slightly higher enantiomeric excess of 12%. Ligand **L3** was selected to further investigate the substrate effects, which quickly appeared to be the determinant. Indeed, changing only the aryldiazonium salt to 2-methoxybenzenediazonium tetrafluoroborate **1c** resulted in an important decrease in both the yield and enantioselectivity. For instance, the desired biaryl **3c** was isolated in only 23% yield, as an almost racemic mixture (entry 4). The synthesis of **3d** mediated by **L3**AuCl was also explored, starting either from **1d**/**2d** or **1e**/**2e** reagent couples (Table 1, entry 5 and entry 6, respectively). Unfortunately, all isolated yields and measured e.e. of **3d** were relatively low (inferior to 10%). Finally, the best results were obtained when employing **1b**, **2b** and AuCl coordinated by (S_p)-1-(diphenylphosphino)-2-[(4*S*)-4-isopropyl-2-oxazolyl]-ferrocene **L3**[22] as starting materials, the desired biaryl product **3b** being isolated in a good 44% yield over two steps, and with an improved enantiomeric excess of +26% in this case (Table 1, entry 7).

To conclude, investigations on the gold-catalysed cross-coupling of aryldiazonium tetrafluoroborate salts and arylboronic acids in the presence of cesium fluoride were realised using (P,N) gold complexes. In a first part, stoichiometric experiments employing 2-pyridylphenyl-diphenylphosphine **L1** as a ligand for AuCl allowed us to propose three catalytic cycles from the same precatalyst, which demonstrated a mechanistic peculiarity of gold when compared to Pd-catalysed aryl–aryl cross couplings. In a second part, preliminary stoichiometric experiments proved that Au(I) catalysts could induce the asymmetric formation of atropoisomeric biaryl compounds from suitable aryldiazonium salts and arylboronic acids with e.e. up to 26% when coordinated to chiral (P,N) structures. Due to the high substrate dependence of the outcome of the reaction, thorough research studies will be probably needed to achieve a widely applicable method. However, we believe that this work could open the way for further applications of chiral (P,N) ligands in gold-catalysed reactions implying Au(III) intermediates in their catalytic cycles.[7,8,11–13,23] Such possibilities are currently being investigated by our team and will be reported in due time.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ A second minor peak was detected at 13.2 ppm by ^{31}P NMR (<10%). The exact structure of this side-product could not be clearly determined. See the ESI† for details.

§ Vapor diffusion method employing dichloromethane and diethyl ether as solvents. Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1843202.†

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