



# A residue-free production of biaryls using supported gold nanoparticles



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## ABSTRACT

Small gold nanoparticles in the presence of O<sub>2</sub> are able to cleave C–H bonds of non-activated arenes and facilitate catalytic formation of biaryls under mild conditions. This procedure avoids the common requirement of iodine, acids, bases, and/or other stoichiometrical additives to accomplish multiple turnovers and results in a zero-waste synthetic process. A number of unactivated arenes such as benzene, toluene, p-xylene, nitrobenzene, chlorobenzene, or phenol are selectively converted to the corresponding biaryls, with accumulated turnover numbers greater than 600. Kinetic measurements, in combination with IR, HRTEM, and STEM-HAADF data, suggest that the reaction takes place on gold atoms that are metallic in character, with the highest C–C bond formation rate provided by gold nanoparticles of approximately 3 nm of diameter. A radical-free reaction mechanism is postulated on the basis of the kinetic measurements. The results represent a first stone for the waste-free preparation of biaryls using supported gold catalysis.

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## 1. Introduction

Biaryls are ubiquitous building blocks with application in agrochemistry, pharmacy, electronics, conductors, polymers, and liquid crystals, among others [1–4]. The industrial demand of biaryls is prominent, but the process to accomplish the formation of the C–C bond is, in general, costly. The high costs are in part derived from the difficulty of cleaving the Ar–H bond directly, which results in additional operations to pre-activate the arene prior to the coupling step. These processes typically involve aryl halides that are not ecofriendly to prepare (Friedel–Craft processes, [5] using metal-halide salts, and the Sandmeyer reaction, [6] starting from aniline, hydrochloric acid and sodium nitrite are some examples). The aryl halide is then coupled with a second activated arene in the presence of a metal catalyst (e.g., Suzuki [7] or Stille [8] couplings). Stoichiometric amounts of additives such as bases in solution [7] or metals such as Sn [8] are usually needed to facilitate the removal of the halide from the metal and enable multiple turnovers. The base/halide or metal/halide residues cause further increment of the costs in operations for purification of the downstream effluents. The atom efficiency of the coupling step is, in this scenario, often <30%, corresponding to approximately 2.3 kg of waste per kilogram of desired product. Aware of these problems, chemists have sought methods that limit the generation of residues, for example through reactions where only one of the

aromatic counterparts is functionalized [9,10], or upon substitution of iodine by lighter chlorine [11] or boronic acid group [12].

A major breakthrough would be brought by catalysts able to couple arenes that have not been activated in any manner before reaction and that operate without the necessity of other additives in the solution. In this sense, “unactivated arenes” react and yield biaryls in the presence of some metal catalysts and oxygen donors, although the number of examples is, up-to-date, scarce. For example, gold salts in acidic solutions used in tandem with iodine oxidants such as PhI(OAc)<sub>2</sub> or PhI(OH)OTs activate the Ar–H moiety and catalyze some coupling reactions [13,14]—but the use of iodine, and acids in solution is not yet avoided; Pd<sup>2+</sup> facilitates the coupling of unactivated arenes with O<sub>2</sub> as the oxidant and water as the residue—but then the biaryl formation occurs with reduction of Pd<sup>2+</sup> to Pd<sup>0</sup>, which is an inactive species [15]. To complete multiple turnovers, Pd must be re-oxidized before precipitation as palladium particles, usually in the presence of acids and/or a second metal that allow Pd to shuttle in between oxidation states [16–20]. Even then, the number of turnovers per active site is low, typically <100 [16,17], and often <10 [20,21], while significant amounts of hazardous wastes are generated.

To our knowledge, there is no precedent of a catalyst that affords multiple turnovers in the coupling of unactivated arenes without the generation of residues such as acids, bases, iodine derivatives, metals salts, or other stoichiometrical additives. In other words, we have not seen a catalyst that cleaves directly the Ar–H bond and subsequently forms a new C–C bond with O<sub>2</sub> as the only co-reagent and water as the only by-product.

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In the present investigation, we report such a catalyst, prompted by the realization that gold is active for a number of C–C bond formation reactions not only when is present in the form of a soluble metal salt, but also when arranged as small nanoparticles [22–26], and that the latter work notably better in processes that involve O<sub>2</sub> dissociation [27–32]. Our results demonstrate another remarkable feature of gold in heterogeneous catalysis [33–37].

## 2. Experimental methods

### 2.1. Catalysts preparation

1 wt% Au/TiO<sub>2</sub>, 1 wt% Au/Al<sub>2</sub>O<sub>3</sub>, and 1 wt% Au/ZnO catalysts were used as received from STREM (AUROLite™ catalysts). The catalysts can be prepared following a deposition–precipitation method from HAuCl<sub>4</sub>, as described elsewhere [32].

Pt/Al<sub>2</sub>O<sub>3</sub>, Rh/TiO<sub>2</sub>, Ni/TiO<sub>2</sub>, and Pd/TiO<sub>2</sub> samples were prepared by incipient wetness technique. H<sub>2</sub>PtCl<sub>6</sub> (hexahydrate, Aldrich, >37.5 as Pt), Ni(NO<sub>3</sub>)<sub>2</sub> (hexahydrate, Fluka, >98.5%), RhCl<sub>3</sub> (Aldrich, Rh content 40%) and PdCl<sub>2</sub> (Aldrich, 99%) were used to impregnate TiO<sub>2</sub> (Degussa P-25) in water. As an example, 20 mL of an aqueous solution containing 13.27 mg of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was contacted with 1 g of TiO<sub>2</sub> to prepare the 0.5 wt% Pt/TiO<sub>2</sub> catalyst. After a perfect mixing of the corresponding slurries, samples were dried at 373 K during 12 h. Some samples were reduced in flow of H<sub>2</sub> at 723 K for 3 h before reaction, as specified in Table 1.

To prepare Au/TiO<sub>2</sub> catalysts with variable particle sizes, HAuCl<sub>4</sub> was deposited on TiO<sub>2</sub> at a controlled pH. This method allows controlling the degree of metal aggregation by choice of the metal loading, the pH of the deposition, and the activation conditions, as reported [38]. Table S1 (below) provides details of the synthesis of Au/TiO<sub>2</sub> catalysts characterized by average particle sizes of 7.2 and 14.4 nm, respectively.

The bimetallic Au@Pd/TiO<sub>2</sub> catalyst was synthesized by impregnation of the Au/TiO<sub>2</sub> catalyst with a solution of PdCl<sub>2</sub> to have a final Au/Pd mol ratio of approximately 1. This catalyst was thoroughly washed with deionized water and dried at 373 K for 12 h before reaction.

The following information guides the identification of each of the samples in Fig. 2: (A) c, 1 wt% Au/TiO<sub>2</sub> sample supplied by

**Table 1**

Catalytic performance of several metal-based samples for the O<sub>2</sub>-assisted coupling of benzene at 413 K and 12 bar.

Entry	Catalyst	% Me <sup>d</sup> (mol)	TOF <sup>e</sup> (h <sup>-1</sup> )	TON <sup>f</sup> (mol/mol)
1	1%Au/TiO <sub>2</sub> <sup>a</sup>	0.022	382	230
2	1% Pd/TiO <sub>2</sub> <sup>b</sup>	0.041	0.21	<1
3	1% Pd/TiO <sub>2</sub> <sup>c</sup>	0.041	0	0
4	0.5% Pt/TiO <sub>2</sub> <sup>c</sup>	0.014	0	0
5	1% Ni/TiO <sub>2</sub> <sup>c</sup>	0.075	0	0
6	5% Rh/TiO <sub>2</sub> <sup>b</sup>	0.298	0	0
7	TiO <sub>2</sub> <sup>b</sup>	–	0	0
8	1% Au@0.5% Pd/TiO <sub>2</sub> <sup>b</sup>	0.043	0.02	<1
9	1% Au/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	0.022	244	164
10	1% Au/ZnO <sup>a</sup>	0.022	254	158
11	HAuCl <sub>4</sub>	0.01	0	0
12	(CH <sub>3</sub> )Au(PPh <sub>3</sub> )	0.01	0	0

Turnovers calculated per metal atom on the external surface of the nanoparticles [33]. Experimental details provided in SI.

<sup>a</sup> Supplied by STREM (AUROLite™ catalysts).

<sup>b</sup> Dried at 373 K before reaction.

<sup>c</sup> Preactivated in H<sub>2</sub> at 723 K before reaction.

<sup>d</sup> Mol of metal × mol of benzene<sup>-1</sup> × 100.

<sup>e</sup> Turnover frequency (mol of benzene converted × mol of metal<sup>-1</sup> × h<sup>-1</sup>).

<sup>f</sup> Turnover number (mol of benzene converted × mol of metal<sup>-1</sup>).

STREM (AUROLite™); d, the preceding catalyst after being used in the coupling of benzene at 413 K and 12 bar for 100 h; e, sample c after deposition of 0.5 wt% Pd by incipient wetness technique; f, 3 wt% Au/TiO<sub>2</sub> sample prepared by deposition–precipitation of HAuCl<sub>4</sub> at pH = 9 and calcined under static atmosphere of air at 673 K. (B) Particle size distributions, as determined from the corresponding HAADF-STEM and/or HRTEM images, of the preceding catalysts and the following: a, sample c treated in 50 mL/min of air at 1 bar and 673 K; b, sample d treated in 50 mL/min of air at 1 bar and 673 K; g, 3 wt% Au/TiO<sub>2</sub> sample prepared by deposition–precipitation of HAuCl<sub>4</sub> at pH = 6 and calcined under static atmosphere of air at 673 K. (C) Dependence of the TOF per external gold atom on the average particle size during the solvent-free coupling of benzene at 12 bar of O<sub>2</sub> and 413 K for the series of catalysts in (B). The selectivity to biphenyl was always >98%. Experimental details are provided in SI.

### 2.2. Oxidative coupling of arenes

Catalytic testing was performed in a reinforced glass reactor (2 mL volume) equipped with a temperature and pressure control and stirred magnetically. Catalytic testing was performed in a reinforced glass reactor (2 mL volume) equipped with a temperature and pressure control and stirred magnetically. The reactor vessel was bought to Supelco (Reference 2-7037) and modified to allow pressurization and/or extraction of liquids through a gas-tight needle. A 100 μL gas-tight syringe was used to get 15–20 μL aliquots at the various reaction times.

Before each experiment, all the material was washed with abundant acetone and dried at 383 K for >5 h. It is important to avoid acetone and other polar molecules in the reaction mixture to get optimal results. In a typical experiment, 891 mg of the aromatic compound was placed in the reactor together with 30–70 mg of catalyst and 9 mg of dodecane as an internal standard. Reactants were obtained from Sigma–Aldrich with purities above 99% and used as received. The reactor atmosphere was purged with O<sub>2</sub> at room temperature, pressurized with 12 bar of O<sub>2</sub> and placed into a silicon oil bath pre-heated at the desired reaction temperature. We systematically assigned time = 0 (start of the kinetic experiment) 30 s after the reactor had been immersed into the silicon oil bath. During the experiment, the pressure was kept at 12 bar, and the stirring rate was fixed at 700 r.p.m. Aliquots were taken at different times until the end of the experiment. The composition of these aliquots was determined with a gas chromatograph equipped with a FID detector and a 30 m HP-5 capillary column. Conversions and selectivities were calculated from the GC areas of the products corrected with the response factors determined experimentally. The products were identified by mass spectrometry using a GC/MS device (Agilent MDS-5973) equipped with a quadrupole electron-impact ionization detector (spectra provided in SI). Pure, commercially available compounds were used to compare the biaryls mass spectra and their GC retention times. We also performed HPLC analyses to evaluate the potential presence of heavier compounds. A Varian ProStar 240 device equipped with a column Mediterranean C18 (5 μm, 25 × 0.46 mm) was used; the mobile phase was acetonitrile/ethanol in a 30:70 ratio, and the flow was 0.5 mL/min; and detection was done using a PDA UV–Vis detector at a wavelength of 254 nm.

Some reactions were scaled-up (15 g of substrate) and the products purified by removal of the starting reactants in a rotatory evaporator at temperatures in the range 313–333 K. Isolated yields were calculated and are reported in the SI. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> with tetramethylsilane as the internal standard at 298 K on a Bruker Avance 300 (spectra provided in SI).

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