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Towards a Zero-Waste Oxidative Coupling of Nonactivated Aromatics by Supported Gold Nanoparticles

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We show that gold nanoparticles are able to perform the direct oxidative coupling of nonactivated aromatics with O_2 as the only co-reagent. In this reaction, the aromatic acts both as reactant and solvent. Biphenyl, for example, can be obtained from benzene with high selectivity and a turnover number (TON) of 230 per pass. Similarly, several substituted biaryls can be prepared. Pd performs only one TON and even when a second catalytic functionality is introduced, together with strong acidic conditions, TON is always lower than 100. Other catalysts require iodine for performing the reaction, leading to 2 kg of waste for 1 kg of biphenyl formed, whereas no waste is created by the oxidative coupling with gold nanoparticles.

Biaryls are involved in a variety of products such as agrochemicals, natural products, pharmaceuticals, and biologically active compounds.[1,2] The biaryl moiety is typically accomplished by the coupling of arenes that have been activated previously at a specific position within the aromatic ring. Aryl halides are often reacted with a transition metal, typically Pd, in the presence of a base to facilitate multiple turnovers.[3,4] A major drawback of this approach is the large amount of residues that arises upon the base-assisted removal of the halide group from the metal center.[5] A direct activation of the Ar–H moiety of arenes, although it is less favorable kinetically and energetically, would certainly be of interest.[6,7] In this regard, stoichiometric amounts of Pd^{II} in solution have been shown to yield biaryls by the aerobic coupling of nonactivated arenes, such as benzene, with water as the only byproduct.[8,9] However, after a stoichiometric reaction, Pd^{II} is converted into unreactive Pd^0.[10,11] To complete various turnovers (typically <100),[8,9,12] Pd must be reoxidized in situ before precipitation in the form of metallic Pd particles. This has been achieved by the introduction of a second catalytic function (molybdovanadophosphoric acids, or Zr^{IV}, Mn^{II}, or Co^{II} salts, for instance), and/or the use of strong acidic conditions at temperatures in the range 363–393 K.[8,9,12]

Recent reports have shown that soluble Au salts catalyze the oxidative coupling of aromatic compounds by a direct cleavage of Ar–H bonds,[13,14] which includes the arylation of nonactivated arenes with arylsilanes.[15] In these processes, $PhI(OAc)_2$ or PhI(OH)OTs (Koser reagent) are used as the oxidant,[13–15] and hypervalent iodine presumably plays a role in the reaction mechanism.[14] Au in the form of a salt or a complex is inferred to activate the arene and the iodine oxidant catalytically to form the new C–C bond.[14] As a result of the need for iodine and other additives such as acids, large amounts of byproducts are still generated per mole of desired product (e.g., the iodine residue leads to more than 2 kg of waste per kilogram of biphenyl). Alternatives that overcome this problem should be investigated for the sake of sustainability.

Other oxidative coupling reactions by Au have been reviewed recently.[16,17] These examples expand the idea of Au as a catalyst for a number of C–C bond formation processes.[18–22] Au is known to participate in coupling reactions such as the Sonogashira,[18] Ullmann,[23–25] and Suzuki couplings[19,20] and the homocoupling of phenylboronic acids.[21] Interestingly, the latter is also catalyzed by Au species in the form of small (supported or unsupported) nanoparticles.[18,22,26,27] A remarkable difference between soluble cationic Au species and small Au nanoparticles is that the barrier for the dissociation of O_2 is notably lower on the latter, which has opened the door to a number of oxidation processes.[28–32] With this in mind, we envisioned the possibility of using small Au nanoparticles, instead of cationic Au complexes, to accomplish the oxygen-assisted coupling of deactivated arenes. Our results here demonstrate the validity of this hypothesis and show the first catalytic formation of biaryls on a reusable supported Au catalyst in the absence of activating halide groups.

Our synthetic route together with other reported methods is displayed in Scheme 1. A first screening of solvents and reaction conditions revealed that Au nanoparticles of an average size of approximately 3 nm (high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images are provided in Figure S1) supported on TiO_2 catalyze the coupling of benzene to biphenyl provided that polar solvents such as ethanol, acetone, or acid acetic are avoided (Table S1). The turnover frequency (TOF, $[(\text{mol converted})\times(\text{mol of Au})^{-1}\times h^{-1}]$)[33] and turnover number (TON, $[(\text{mol converted})\times(\text{mol of Au})^{-1}]$)[33] in nonpolar solvents such as decane were low (39 and 13, respectively) at 413 K and 12 bar (Table S1), but they increased by two orders of magnitude when the aromatic compound was reacted alone in O_2. The initial TOF was then 382 h^{-1} and a TON of 230 could be reached in a single run (Table 1, entry 1). The selectivity to biphenyl was $>99\%$ with little formation of byproducts (aryl trimers, $<1\%$). Catalyst deactivation was observed after several catalytic cycles, but the active sites could be fully and easily regenerated by calcination

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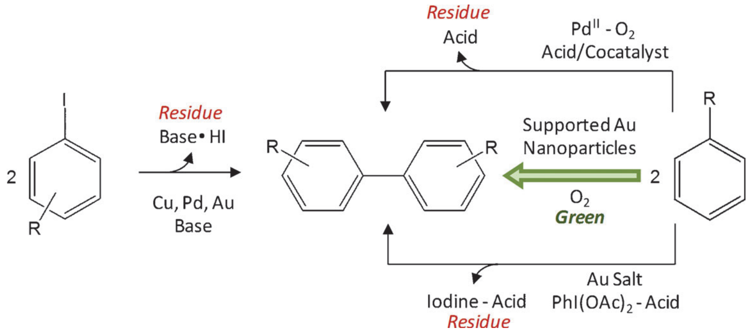

Scheme 1. Some relevant routes for the preparation of biaryls. Supported Au nanoparticles, as reported in this work, avoid the generation of residues.

Table 1. Catalytic performance of various supported metal catalysts for the O_2-assisted coupling of benzene at 413 K and 12 bar.

Entry	Catalyst	Metal/benzene [molar ratio × 100][a]	Conversion [%]	TOF[b,c] $[h^{-1}]$	TON[d]
1	1 %Au/TiO_2[e]	0.022	1.70	382	230
2	1 % Pd/TiO_2[f]	0.041	$<$0.02	0.21	$<$1
3	1 % Pd/TiO_2[g]	0.041	0.00	0	0
4	0.5 % Pt/TiO_2[g]	0.014	0.00	0	0
5	1 % Ni/TiO_2[g]	0.075	0.00	0	0
6	5 % Rh/TiO_2[f]	0.298	0.00	0	0
7	TiO_2[e]	–	0.00	0	0
8	1 % Au-0.5 % Pd/TiO_2[f,h]	0.043	$<$0.02	0.02	$<$1
9	1 % Au/Al_2O_3[e]	0.022	2.10	244	164
10	1 % Au/ZnO[e]	0.022	1.10	254	158
11	$HAuCl_4$	0.01	0.00	0	0
12	$(CH_3)Au(PPh_3)$	0.01	0.00	0	0

[a] Amount of catalyst as (mol of metal)/(mol of benzene) × 100. [b] Turnover frequency (mol of benzene converted)/[(mol of metal) × h]. [c] Typical relative standard deviations are 10–12 %. [d] Turnover number (mol of benzene converted)/(mol of metal). Turnovers calculated per metal atom on the external surface of the nanoparticles.[33] Experimental details are provided in the Supporting Information. [e] Supplied by STREM (AUROlite catalysts). [f] Dried at 373 K before reaction. [g] Preactivated in H_2 at 723 K before reaction. [h] Bimetallic Au-Pd catalyst formed by impregnation of the catalyst in Entry 1 with $PdCl_2$.

in air at 673 K. Each time the regenerated catalyst was contacted with fresh benzene, the original catalytic performance was essentially replicated (Figure 1). More than 600 turnovers were completed under these conditions. The catalyst allowed an accumulated conversion of ~4 % (~400 turnovers) in four consecutive short runs that used the same solution repeatedly (Figure S2). Although this conversion is low in comparison with that reported for tandem $HAuCl_4/PhI(OAc)_2/HOAc$ (60–80 % conversion),[14] a similar number of arene molecules are converted in both cases (~0.4 vs. ~0.7 mmol) as the Au/TiO_2 catalyst works under solvent-free conditions, whereas the conversion by $HAuCl_4$ is referred to the $PhI(OAc)_2$ oxidant in great excess of the arene (benzene/$PhI(OAc)_2$ molar ratio = 20) and requires large amounts of acetic acid [HOAc/$PhI(OAc)_2$ molar ratio = 17.5]. The number of turnovers with the supported Au catalyst is, moreover, several times greater than that reported previously with Au and Pd salts in solution,[8,9,12–14] even if all the metal in the solid sample in considered. Moreover, a better atom efficiency is achieved in our case because of the complete avoidance of iodine, solvent, acids/bases, or other metal salts. We believe that this unprecedented performance of Au nanoparticles, notwithstanding the observed deactivation phenomena and the need for regeneration of the active sites by calcination at 673 K, is relevant and could be the first step towards a more efficient "zero-waste" production of biaryls.

The performance of the Au/TiO_2 sample contrasts with that observed for other typical metal catalysts under identical reaction conditions, which include TiO_2-supported Pd, Pt, Ni, and Rh catalysts. Unlike the Au/TiO_2 catalyst, none of those metals nor the TiO_2 support showed catalytic activity for the benzene coupling (Table 1). Only the sample prepared by the deposition of $PdCl_2$ on TiO_2 used without any thermal treatment led to the formation of biphenyl as a reaction product, but the transformation is inferred to occur stoichiometrically (Table 1, entry 2), presumably with Pd^{II} as the reactive species, as reported previously.[8,9] Consistent with this inference, when this catalyst was reduced in H_2 at 673 K before reaction, no biphenyl was observed among the products (Table 1, entry 3). Moreover, the incorporation of Pd into the Au/TiO_2 catalyst (as $PdCl_2$; Table 1, entry 8) caused a practically complete cessation of the coupling activity (this sample was washed thoroughly with water to remove the excess chlorides). STEM imaging coupled with energy dispersive X-ray spectroscopy (EDS) evidenced the incorporation of Pd onto the Au nanoparticles (Figure S3). Evidently, Pd is not a catalytically active species in the aerobic coupling of arenes under our conditions, but rather an element that poisons Au. However, to check for the possibility that Au species are leached into solution during the reaction and are responsible for the C–C bond formation, we removed the Au/TiO_2 catalyst from the reaction solution after several turnovers,

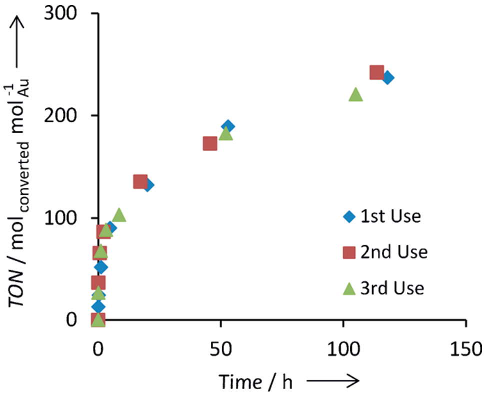

Figure 1. Evolution of TON (per external Au atom) with time on stream for the O_2-assisted coupling of benzene on Au/TiO_2 at 413 K and 12 bar for multiple runs. The catalyst was calcined at 673 K in air between runs. The selectivity to biphenyl was always ~99 %.

which resulted in the cessation of the catalytic activity (Figure S4). Catalyst removal was performed by filtration at the reaction temperature (413 K). In additional experiments, Au^{I} and Au^{III} species, introduced into the solution as $HAuCl_4$ or $(CH_3)(PPh)_3Au$, resulted inactive for the O_2-assisted coupling of benzene (Table 1). We infer, thus, that nanoparticulate Au in the Au/TiO_2 sample is responsible for the observed catalytic performance in the benzene coupling. In agreement with this postulation, Au nanoparticles on other supports such as Al_2O_3 or ZnO also showed high catalytic activity for the formation of biphenyl, although the resulting TOF and TON values were slightly lower than those provided by the Au/TiO_2 catalyst (compare entries 1, 9, and 10 in Table 1). Some reports have shown the unusual oxidation performance of Au if the size of the nanoparticles is <2 nm.[34] However, although the number of nanoparticles smaller than 2 nm is greater in Au/Al_2O_3 than in Au/TiO_2 (the fraction of these sites in our sample is rather low), the activity per exposed Au center is lower for the former, which suggests that highly dispersed Au sites are not particularly active for the O_2-assisted coupling of nonactivated arenes.

In a subsequent series of experiments, the Au/TiO_2 catalyst was evaluated for the coupling of various substituted arenes (Table 2). The biaryl formation took place selectively with aromatic compounds that incorporated alkyl, –Cl, –NO_2, and –OH groups, though at variable rates, which depended on steric factors, nature of the substituent, and reaction temperature. Recently, the aerobic coupling of electron-deficient arenes such as nitrobenzene was performed successfully with soluble Pd salts in the presence of trifluoroacetic acid,[12] but the number of turnovers achieved by this route is rather low (approximately 5). The Au/TiO_2 catalyst proposed here, in contrast, works under neutral conditions and allows the completion of at least 175 turnovers in the coupling of nitrobenzene, which opens the door for an environmentally friendly and highly atom-efficient route for the synthesis of biaryls. Other catalysts such as horseradish peroxidase are active for the coupling of aromatic alcohols through a rather benign approach (H_2O_2 as the oxidant) but selectivities to the dimeric alcohols are in general low.[35]

Table 2. Catalytic performance of Au/TiO_2 for the O_2-assisted coupling of various arenes at 12 bar.

Substrate	T[a] [K]	Au/arene[b] [mol ratio × 100]	TOF[c,d] [h^{-1}]	TON[e]	S_{Biaryl}[f] [%]
benzene	413	0.022	382	230	99
toluene	373	0.026	176	206	98
p-xylene	373	0.030	18	71	98
1,2,4-trimethylbenzene	373	0.034	6	8	98
chlorobenzene	413	0.032	368	88	99
nitrobenzene	413	0.035	176	175	99
phenol	373	0.027	85	336	80

[a] Reaction temperature. [b] Amount of catalyst as (mol of Au)/(mol of arene) × 100. [c] Turnover frequency (mol of benzene converted)/[(mol of metal) × h]. [d] Typical relative standard deviations are 10–12 %. [e] Turnover number (mol of benzene converted)/(mol of metal). [f] Selectivity to the substituted biaryl; some reactions produce a mixture of regioisomers (see the Supporting Information, Table S3). Turnovers calculated per metal atom on the external surface of the nanoparticles.[33] Experimental details are provided in the Supporting Information.

The observation that a mixture of all possible regioisomers is obtained with some reactants suggests the likelihood of a radical reaction mechanism, which is a common pattern in the C–H bond scission of arenes (e.g., by using stoichiometric amounts of $FeCl_3$).[36] As we do not observe any coupling activity if the experiments are performed under a pressure of N_2 rather than O_2, we postulate a homolytic sequestration of the H moiety by an Au–O adduct, as in other oxidative Au-catalyzed transformations.[37,38] The performance of Au is consistently striking in this type of reaction. The synthesis of asymmetric biaryls through Au-catalyzed aerobic cross-coupling reactions would certainly be of interest.[39]

In summary, our results demonstrate that catalytic amounts of Au in the form of small nanoparticles on TiO_2, Al_2O_3, or ZnO are able to activate Ar–H bonds directly in O_2 and yield a number of biaryls selectively at moderate temperatures without the need to use additives such as iodine, acids, or bases to facilitate multiple turnovers and in the total absence of a solvent. This synthetic protocol is en route towards a zero-waste production of biaryls.

Experimental Section

Catalyst preparation

The catalysts 1 wt % Au/TiO_2, 1 wt % Au/Al_2O_3, and 1 wt % Au/ZnO were used as received from STREM (AUROliteTM catalysts). The catalysts can also be prepared by following a deposition–precipitation method from $HAuCl_4$ as described elsewhere.[31] Pt/Al_2O_3, Rh/TiO_2, Ni/TiO_2, and Pd/TiO_2 samples were prepared by the incipient wetness technique. H_2PtCl_6 (hexahydrate, Aldrich, >37.5 % Pt), $Ni(NO_3)_2$ (hexahydrate, Fluka, >98.5 %), $RhCl_3$ (Aldrich, Rh content 40 %), and $PdCl_2$ (Aldrich, 99 %) were used to impregnate TiO_2 (Degussa P-25) in water. As an example, an aqueous solution (2 mL) that contained $H_2PtCl_6 \cdot 6H_2O$ (13.27 mg) was contacted with TiO_2 (1 g) to prepare the 0.5 wt % Pt/TiO_2 catalyst. After perfect mixing of the corresponding slurries, samples were dried at 373 K for 12 h. Some samples were reduced in a flow of H_2 at 723 K for 3 h before reaction as specified in Table 1. The bimetallic Au-Pd/TiO_2 catalyst was synthesized by impregnation of the Au/TiO_2 catalyst with a solution of $PdCl_2$ to have a final Au/Pd molar ratio of approximately 1. This catalyst was washed thoroughly with deionized water and dried at 373 K for 12 h before reaction.

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. Before each experiment, all the material was washed with abundant acetone and dried at 383 K for >5 h. The presence of acetone or other polar molecules such as ethanol in the reaction mixture must be avoided completely for good replication of the results. In a typical experiment, the aromatic compound (891 mg) was placed in the reactor together with catalyst (30–70 mg) and dodecane (9 mg) 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_2 at RT, pressurized with 12 bar of O_2, and placed into a silicon oil bath preheated to the desired reaction temperature. We assigned $t = 0$ (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 rpm. Aliquots were withdrawn at different times until the end of the experiment. A first aliquot was invariably taken 5 min after the beginning of each experiment. The composition of these aliquots was determined by using a gas chromatograph equipped with a flame ionization detector (FID) and a 30 m HP-5 capillary column. Conversions and selectivities were calculated from the corresponding GC areas corrected with the response factors determined experimentally. The products were identified by MS by using a GC–MS device (Agilent MDS-5973) equipped with a quadrupole electron-impact ionization detector. The retention times in the GC analysis and the MS spectra were compared with those of pure products obtained from commercial sources. For three substrates (benzene, toluene, and *p*-xylene), the experiments were scaled up, the products purified and characterized by ^1H and ^{13}C NMR spectroscopy, and the isolated yields calculated; details are provided in the Supporting Information.

Electron microscopy

Electron microscopy was performed by using a JEOL-JEM-2010F microscope with a LaB6 electron gun operated at 200 kV in scanning-transmission mode (STEM). This microscope has a structural resolution of 0.19 nm and allows the formation of, in STEM mode, electron probes with diameters down to 0.5 nm suitable for high-spatial resolution analytical investigation. STEM images were obtained by using HAADF detector, which allows Z-contrast imaging. Analytical electron microscopy was performed by using an ATW type EDS detector and the INCA Energy TEM platform. EDS spectra were collected at specific points of the samples and along electron-beam paths that go from vacuum through surface positions of the metal particles and the support. Particle size distributions were determined upon measurement of at least 200 particles per sample. Samples for electron microscopy studies were prepared by depositing small amounts of the powders directly onto holey-carbon coated Cu grids. Excess powder was removed from the grids by gentle blowing of air with a nozzle.

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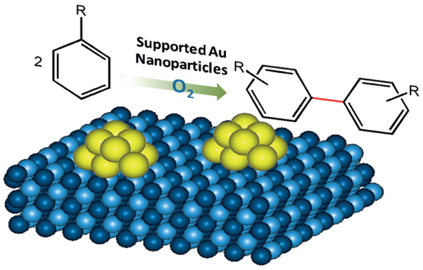
COMMUNICATIONS

No more waste: Supported gold nanoparticles catalyze the coupling of unactivated arenes in O_2 without the typical need of iodine oxidants, acids, bases, or additional metal salts in solution to result in a zero-waste synthetic process. This is in contrast to other catalysts that can perform for only a few turnovers and produce large quantities of waste.



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