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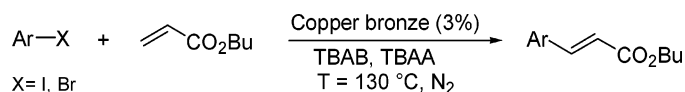
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ABSTRACT



Heck reaction of aryl iodides and activated aryl bromides catalyzed by copper bronze in tetrabutylammonium bromide as solvent and tetrabutylammonium acetate as base was developed. The effective catalysts are Cu nanoparticles deriving from the reaction of iodobenzene with copper bronze. These nanoparticles are very stable in tetraalkylammonium salts, are easily recycled, and can be stored for months without a loss of catalytic efficiency.

An important goal in catalysis research is the development of synthetic methods that provide atomic-level control over the nature of catalytic sites, with the formation of isolated single sites or homogeneously distributed and more complicated structures (clusters, nanoparticles, etc.) providing new and improved catalysts.¹ Among metal catalysts, palladium was largely utilized for carbon–carbon bond-forming reactions in allylic substitutions and Heck^{2–4} coupling of aryl halides with olefins. In view of the economy of these reactions, the recovery as well as recycling of the expensive Pd catalyst is mandatory. A solution for this problem could

be the use of cheaper metals as catalysts. Among these, copper has been used in numerous reaction types including nucleophilic substitution with alkyl halides, the Ullmann reaction, and Michael addition to enones and enoates.^{5,6} However, in these reactions, the copper reagent is utilized in stoichiometric amounts rendering this chemistry less economically and environmentally attractive. Whereas catalytic amounts of copper halides were utilized in the reaction of aryl halides with amines^{7a–d} and thiols,^{7e} few papers exist that treat the Heck reaction of aryl halides, mainly iodides, with acrylates and styrene, catalyzed by supported copper halides.⁸ Nevertheless, these catalysts, beside the requirement of high temperatures and toxic solvents, are fruitless in coupling aryl bromides and difficult to be recycled. In

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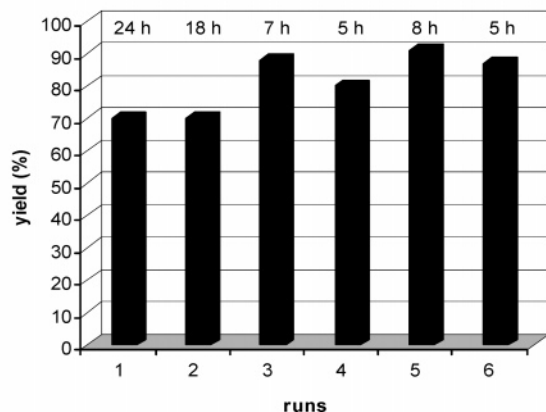
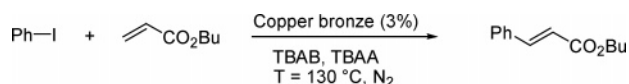


Figure 1. Reactions of iodobenzene with butyl acrylate catalyzed by copper bronze with TBAA as base in TBAB as solvent. First run: iodobenzene/butylacrylate/TBAA 1:1.2:1.5 mmol in 3 g of TBAB and 3 mol % of copper bronze; under nitrogen at 130 °C.

addition, the use of stoichiometric amounts of copper reagents, on scale-up, leads to problems of waste disposal and solvent recovery.

Recently, we reported that palladium nanoparticles suspended in tetrabutylammonium bromide (TBAB) as solvent and tetrabutylammonium acetate (TBAA) as base, did catalyze the regio- and stereoselective arylation of cinnamates⁹ and methacrylates.¹⁰ The efficiency of this system is due to the metal nanoparticles stabilized by an ionic liquid such as TBAB¹¹ and a fast neutralization of PdH by TBAA. Following these results, it would be interesting to test the catalytic performance of copper nanocolloids for the Heck reaction in this ionic liquid (IL). The advantages would be many since, under these conditions, together with the recycling of the catalyst and IL, the use of ligands, supports

and toxic or volatile solvents (VOCs) is avoided. While copper nanocolloids in DMF have been recently utilized for the Suzuki coupling of *p*-iodotoluene,¹² no Heck reaction, catalyzed by this type of copper catalyst in IL, was reported.¹³

We report that copper nanocolloids, derived from the reaction of iodobenzene with *copper bronze*, does catalyze the reactions of aryl iodides and activated bromides with acrylates in TBAB as solvent and TBAA as base.

The addition of iodobenzene (1 mmol), butyl acrylate (1.2 mmol), and TBAA (1.5 mmol) to a suspension of copper bronze 3 mol % (BDH flakes 99% or Aldrich powder 99%) in 3 g of TBAB at 130 °C and under inert atmosphere led to the dissolution of the metal and the formation of butyl cinnamate with a yield of 70% after 24 h (Figure 1, run 1). The reaction mixture was recycled a number of times showing an increment of both yields and reaction rates after the second cycle (Figure 1, runs 3–6).

These results suggest that the copper bronze (Figure 2a) undergoes, during the first two cycles, a slow dissolution as a consequence of the oxidative addition, affording more active copper nanoparticles with an average sizes of 4.2 nm (Figure 2d) homogeneously dispersed into TBAB, as revealed by the TEM image executed on the reaction mixture after the third cycle (Figure 2b,c).

p-Iodoanisole behaved similarly to iodobenzene (Figure 3, runs 1–11). After the eleventh cycle, the catalyst system Cu/TBAB, after the extraction of unreacted reagents and products, was charged with iodotoluene (Figure 3, runs 12 and 13). The same procedure was used in turn to catalyze the coupling of iodobenzoic acid (Figure 3, runs 14 and 15) and so on. The coupling of activated bromoaromatics also occurred albeit with lower yields (Figure 3, runs 17 and 20), while bromobenzene was much less reactive (Figure 3, run 16). Therefore, the catalytic system was recycled 20 times with an average total TON of ca. 490. Thus, contrary to different metal nanocolloids whose catalytic activity decreases with the time, these copper nanocolloids are extremely stable in TBAB and can be stored for months without a loss of activity.

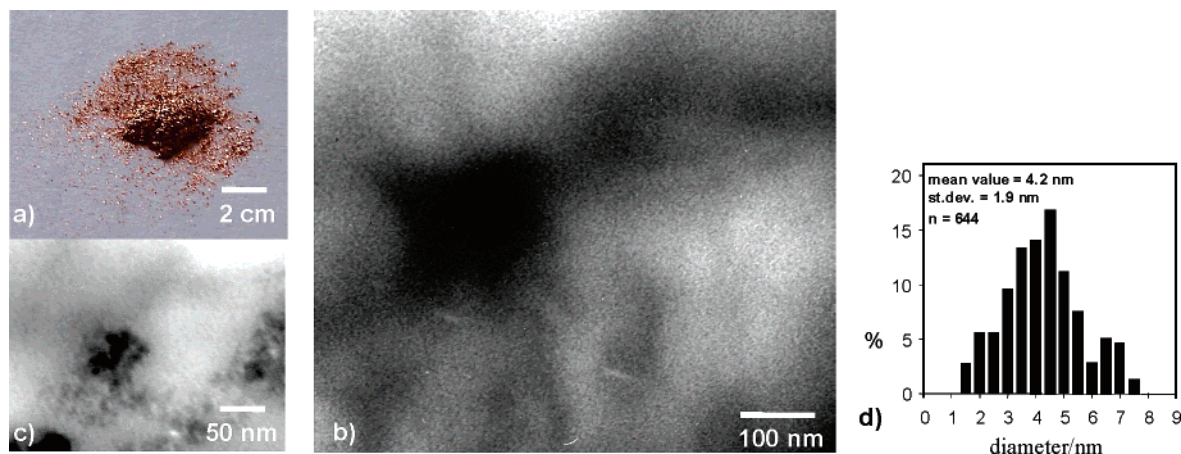


Figure 2. (a) Copper bronze flakes. (b, c) TEM pictures showing copper nanoparticles. (d) Histogram of the nanoparticles' size distribution.

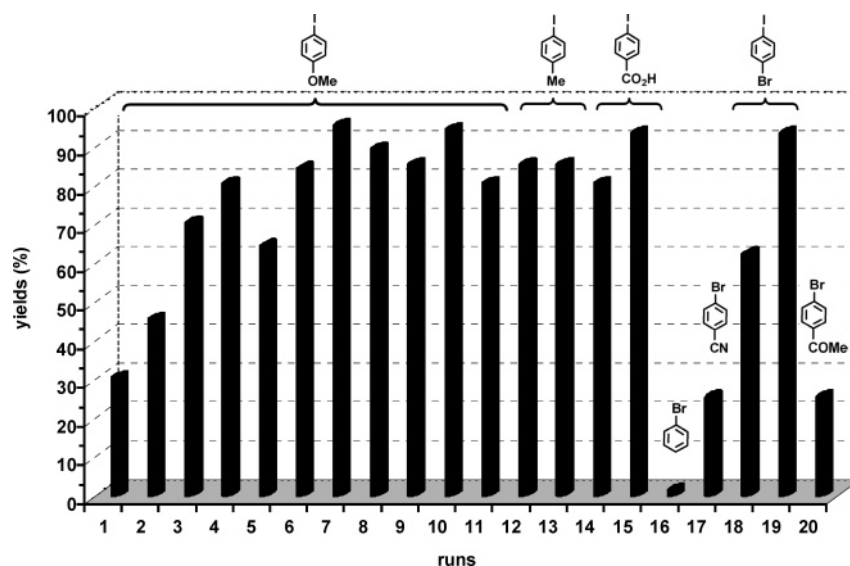
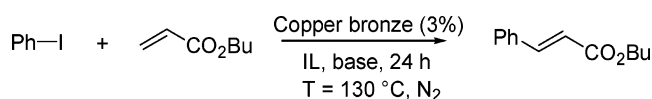


Figure 3. Recycling results for the coupling of several aryl halides with butyl acrylate catalyzed by TBAB/Cu nanoparticles. First run: *p*-iodoanisole/butylacrylate/TBAA 1:1.2:1.5 mmol in 3 g of TBAB and 3 mol % of copper bronze; under nitrogen at 130 °C for 16 h.¹⁴

The presence of both TBAB as solvent and TBAA as base was found to be essential to promote the coupling (Table 1,

Table 1. Screening of ILs and Bases^a



entry	solvent	base	yield (%)
1	TBAB	TBAA	70
2	TBAI ^b	TBAA	88
3	TBAB	^t Pr ₂ EtN	
4	TBAB	Na ₂ CO ₃	
5	[bmim] BF ₄ ^c	TBAA	
6	[bupy] BF ₄ ^d	TBAA	
7	[bmim] Br ^e	TBAA	
8	DMA	TBAA	10

^a Iodobenzene/butylacrylate/TBAA 1:1.2:1.5 mmol in 3 g of TBAB and 3 mol % of copper bronze; under nitrogen, at 130 °C. ^b TBAI = tetrabutylammonium iodide. ^c [bmim]BF₄ = 1-butyl-3-methylimidazolium tetrafluoroborate. ^d [bupy]BF₄ = *N*-butylpyridinium tetrafluoroborate. ^e [bmim]Br = 1-butyl-3-methylimidazolium bromide.

entry 1). Indeed, reaction did not occur in ILs as pyridinium and imidazolium salts (Table 1, entries 5–7) or with inorganic or organic bases (Table 1, entries 3 and 4), while in molecular solvents, such as, for example, dimethylacet-

amide (DMA), a very low yield was obtained (Table 1, entry 8). The replacement of TBAB with tetrabutylammonium iodide as solvent increases slightly the conversion rate (Table 1, entry 2).

From these results, the influence exerted by tetrabutylammonium salts on the reaction rates and catalyst stabilization emerges. This may be due to the formation of Cu nanoparticles surrounded by a large tetraalkylammonium salt that, by imposing a Coulombic barrier for collision, would impede the formation of clusters growing further into metal particles.¹⁵ As a consequence, TBAB would extend the catalyst life. Actually, we do not have a convincing explanation for the lack of reactions in imidazolium ionic liquids. A probable one is the failure of these liquids to stabilize the nanosized Cu particles.¹⁶

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(14) After each run, the reaction mixture containing the catalyst and TBAB, cooled at room temperature and after extraction of reagents and products with cyclohexane, was charged with fresh reagents. Yields were determined by GLC on extracted fractions by adding decane as standard. The reaction of *p*-iodobenzoic acid afforded (*E*)-4-(2-butoxycarbonylvinyl)-benzoic acid butyl ester.

(15) It was shown^{13b} that halide ions such as bromide and iodide influence the stabilization of Cu nanoparticles in water.

(16) Contrary to tetrahedral tetraalkylammonium salts, the imidazolium ones have planar structures which bind anions tightly. This would decrease the anion availability for the stabilization of Cu nanoparticles. See, for instance, ref 13b and: (a) Gannon, T. J.; Law, G.; Watson, P. R.; Carmichael, A. J.; Seddon, K. R. *Langmuir* **1999**, *15*, 8429–8434. (b) Fry, A. J. *J. Electroanal. Chem.* **2003**, *546*, 35–39. (c) Crosthwaite, J. M.; Aki, S. N. V. K.; Maginn, E. J. Brennecke, J. F. *J. Phys. Chem. B* **2004**, *108*, 5113–5119.

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We have shown here that these copper nanoparticles do catalyze the Heck reaction, and may eventually represent an inexpensive and eco-friendly alternative to noble metal catalysts. Further studies on the structure and activity of this catalyst are now in progress.

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Supporting Information Available: TEM morphological characterization of the catalyst, typical procedure for the copper bronze catalyzed Heck reaction, procedure for the catalyst recycling, and spectral data for reaction products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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