

Supporting information for the article
Copper-catalysed Suzuki Cross-coupling using Mixed Nanocluster Catalysts

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Experimental Procedures.

Materials and instrumentation. GC analysis was performed using a GC-8000 gas chromatograph with a 100% dimethylpolysiloxane capillary column (DB-1, 30 m \times 0.325 mm). GC/MS analysis was performed using a Hewlett-Packard 5890/5971- GC/MS equipped with a ZB-5 (zebron) column (15 m \times 0.25 mm). XR diffraction measurements were performed using a rotating Cu-anode (Rigaku UltraX 18S, Japan) as source and a 2D image plate detector (Marresearch, Germany) placed at a distance of 33 cm from the sample. All products are known compounds and were identified by comparison of their GC retention times to those of authentic samples and by MS analysis. Samples for GC were diluted with 1 mL dimethylformamide (DMF) and filtered through an alumina plug prior to injection. GC conditions: isotherm at 105 °C (1 min); ramp at 20 °Cmin⁻¹ to 260 °C; isotherm at 260 °C (5 min). All the reactions were carried out under N₂ atmosphere in Schlenk-type glassware that was oven dried prior to reaction. Solutions were dispensed using a micropipette. Unless noted otherwise, chemicals were purchased from commercial firms and were used as received. Tetra-*n*-octylammonium formate (TOAF) was prepared using a modification of the procedure published by Maase.¹

Preparation of terta-*n*-octylammonium formate (TOAF). 40 g of ion-exchange resin suspended in a 1.5 M NaOH solution were charged to a column that was subsequently flushed with 3 L of 1.5 M NaOH. A slight N₂ overpressure was applied. The elute was tested for Cl⁻ using AgNO₃. The color of the resin changed from yellow (Cl⁻ form) to orange (OH⁻ form). The column was then flushed with 3 L of distilled water followed by 500 mL of 0.2 M formic acid solution (without using N₂ overpressure), 3 L distilled water, and 1 L MeOH to switch to an organic medium. The resin was left to swell for 1 h and the column was subsequently flushed with an 18 mM solution of tetra-*n*-octylammonium bromide (TOAB) in MeOH, until the elute tested positive for Cl⁻ using AgNO₃. The appropriate MeOH fraction was evaporated on a rotavapor and the crude TOAF (light oil) was dried for 24 h under vacuum. A 0.2 M stock solution of TOAF in DMF was prepared and used without further treatment for the synthesis of colloids **1–15**.

Synthesis of nanocluster catalysts 1–15. Example: Cu/Pd/Ru/Pt (15). A Schlenk-type vessel equipped with a rubber septum and a magnetic stirrer was evacuated and refilled with N₂. The vessel was charged with CuCl, PdCl₂, PtCl₂ and RuCl₃ solutions in DMF (3 mL of each, 3.33 mM) using a syringe. 0.5 mL of a 0.2 M TOAF solution in DMF was added in one portion to the solution at 65 °C, and the mixture was stirred for 24 h under a

(1). Maase, M. *Ph.D. Thesis*, verlag Mainz, Aachen, 1999, ISBN 3-89653-463-7 (in German).

slight overpressure of N₂. The color of the mixture changed from reddish brown to black. The resulting colloidal suspension (particle size 2.1 ± 0.1 nm) was then stored under N₂ and was used as a stock solution in the Suzuki cross-coupling reactions.

Clusters **1–14** were prepared in a similar manner using stock solutions of the corresponding metal chlorides as starting materials. The size of the metal nanoclusters was determined by XR diffraction using a rotating Cu-anode and a 2D image plate detector. In all cases, the particle size of the metal core, excluding the stabilizing tetraoctyl ammonium shell, varied between 1.6 to 2.1 nm in diameter. The size distribution was ± 0.1 nm in each case.

Cross-coupling of aryl halides with phenylboronic acid. Sets of five reactions were performed in parallel in Schlenk-type glassware. In order to minimise errors and to test the reproducibility of the results, one reaction from each set was repeated in the next set. All reactions were performed in DMF. All reaction vessels were thoroughly cleaned to avoid the possibility of reaction due to remaining catalyst traces.²

A Schlenk-type glass vessel equipped with a rubber septum and a magnetic stirrer was evacuated and refilled with N₂. The vessel was then charged with above prepared colloidal suspension (3.00 mL, 0.01 mmol, 2 mol%), the phenyl boronic acid solution (3.12 mL, 240 mM, 0.75 mmol), K₂CO₃ (207 mg, 1.5 mmol) and the internal standard *n*-dodecane (3.00 mL, 100.6 mM, 0.30 mmol). The aryl halide solution (3.12 mL, 160 mM, 0.50 mmol) was added and the reaction mixture was stirred at 110 °C for 4 h. A slight overpressure of N₂ was maintained throughout the reaction. Reaction progress was monitored by GC and GC/MS.

Reaction profiles and kinetic analysis. The reaction profiles obtained for the monometallic, bimetallic, trimetallic and tetrametallic are shown in figures S1 – S4. The fit of the initial reaction rates to a second-order rate law is shown in figures S5–S8. In this analysis, the correlation coefficient, R^2 , gives a measure of the amount of variability in the data that is accounted for by a given model (in this case, the 2nd-order rate equation).

$R^2 = \sum (\hat{y}_i - \bar{y})^2 / \sum (y_i - \bar{y})^2$, where y is the set of results, \bar{y} is the mean of y , and \hat{y} is the model.³

(2). See Gruber, A. S.; Pozebon, D.; Monteiro, A. L.; Dupont, J. *Tetrahedron Lett.*, **2001**, 42, 7345, where trace amounts of palladium catalyst precursors were shown to catalyse the Heck coupling, albeit using extremely reactive substrates.

(3). For a discussion, see Tranter, R. L. in *Design and Analysis in Chemical Research*, Tranter, R. L., Ed., Sheffield Academic Press, Sheffield, England, 2000, pp. 430–431.

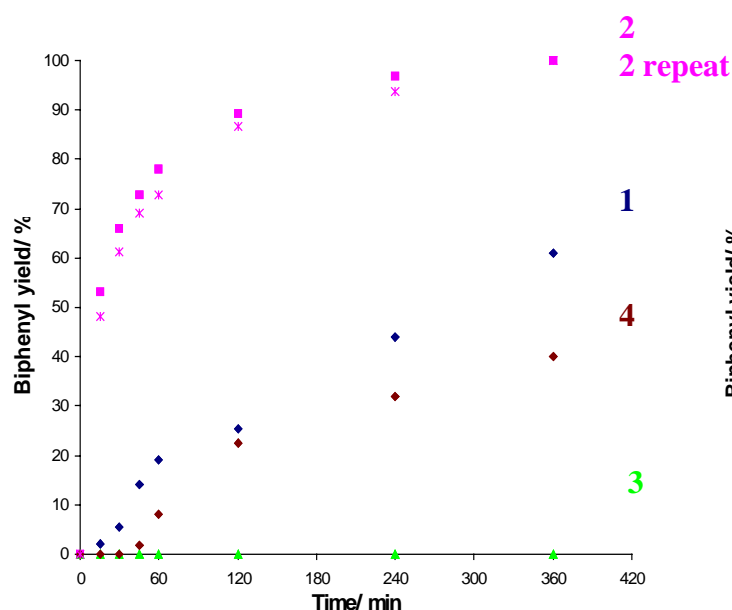


Figure S1. Suzuki coupling of phenylboronic acid with iodobenzene (PhI) using monometallic nanoclusters as catalysts. Reaction conditions: 0.50 mmol (102.0 mg) PhI, 0.75 mmol (91.44 mg) PB(OH)₂, 1.5 mmol (207.30 mg) K₂CO₃, 2 mol% catalyst (total metal nanoclusters relative to PhI), 12.50 mL DMF, 110 °C, N₂ atmosphere.

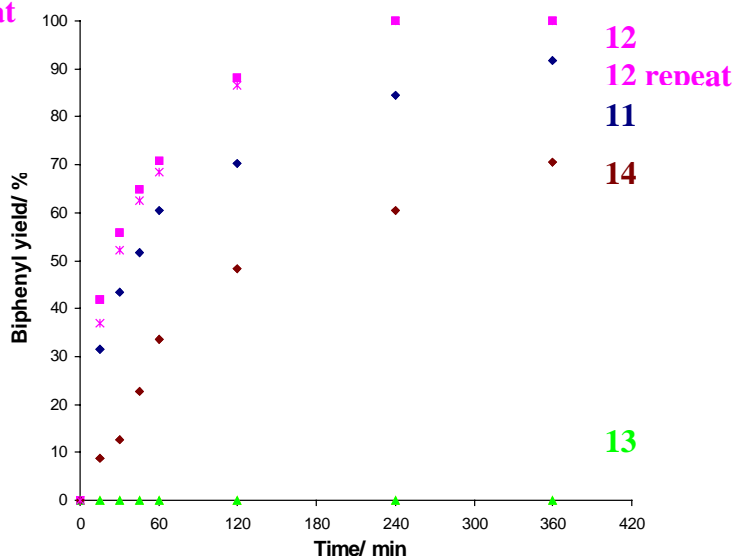


Figure S3. Suzuki coupling of phenylboronic acid with iodobenzene using trimetallic nanoclusters as catalysts. Reaction conditions are the same as figure S1.

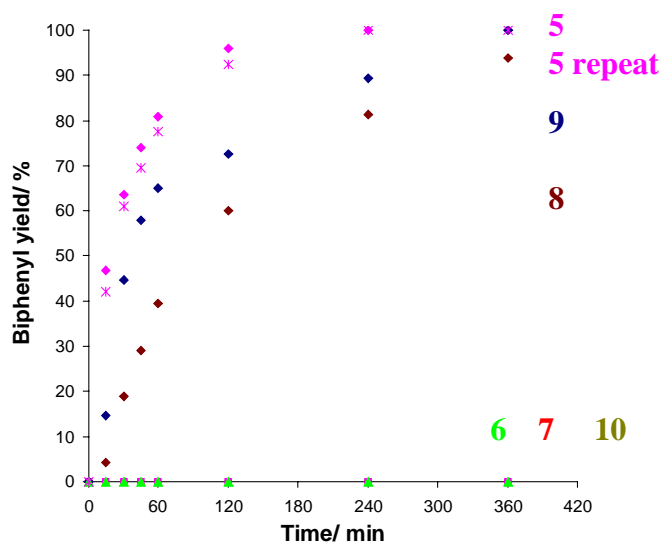


Figure S2. Suzuki coupling of phenylboronic acid with iodobenzene using bimetallic nanoclusters as catalysts. Reaction conditions are the same as figure S1.

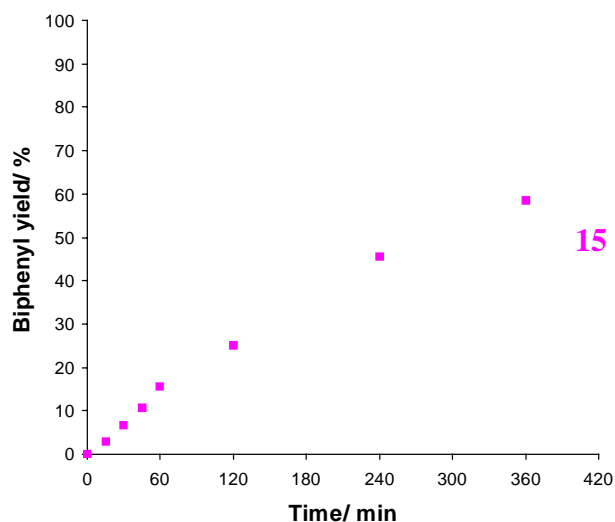


Figure S4. Suzuki coupling of phenylboronic acid with iodobenzene using tetrametallic nanoclusters as catalysts. Reaction conditions are the same as figure S1.

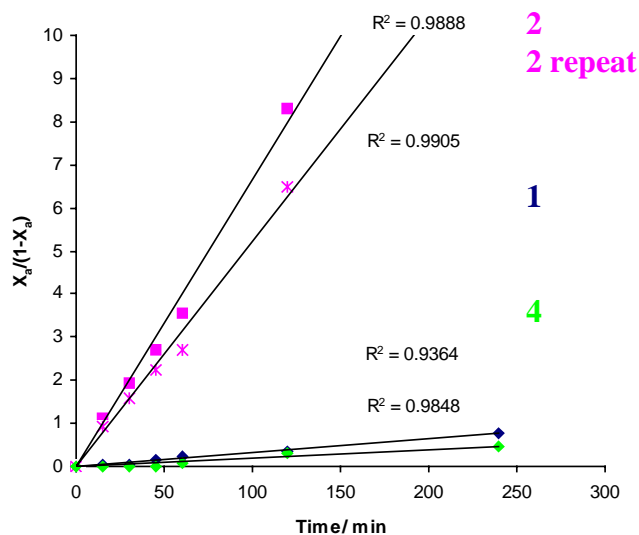


Figure S5. Second-order fit for Suzuki coupling of phenylboronic acid with iodobenzene using monometallic nanoclusters as catalysts. Reaction conditions are the same as figure S1.

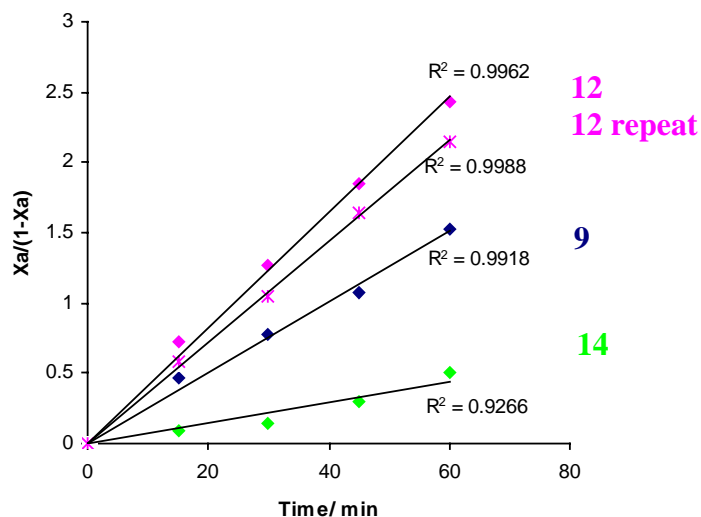


Figure S7. Second-order fit for Suzuki coupling of phenylboronic acid with iodobenzene using trimetallic nanoclusters as catalysts. Reaction conditions are the same as figure S1.

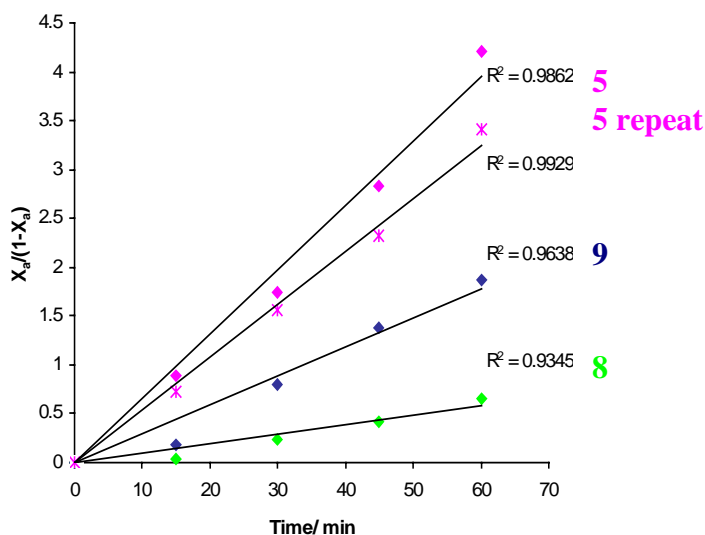


Figure S6. Second-order fit for Suzuki coupling of phenylboronic acid with iodobenzene using bimetallic nanoclusters as catalysts. Reaction conditions are the same as figure S1.

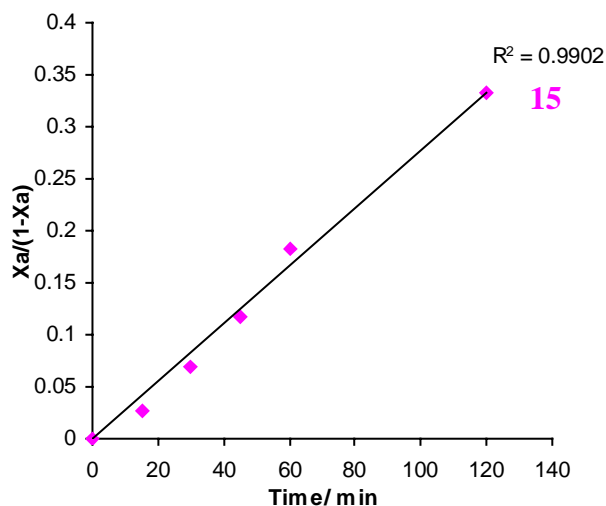


Figure S8. Second-order fit for Suzuki coupling of phenylboronic acid with iodobenzene using tetrametallic nanoclusters as catalyst. Reaction conditions are the same as figure S1.