Combinatorial Design of Copper-Based Mixed Nanoclusters: New Catalysts for Suzuki Cross-Coupling

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This paper is dedicated to the memory of Niraj B. Thathagar, who died at 23 years in a tragic accident in Mumbai, India.

Abstract: Quantum dots (2–5 nm) of copper and copper/palladium mixtures are found to be good catalysts for Suzuki cross-coupling. The catalysts are applicable to a wide range of iodo- and bromoaryl substrates, and give moderate yields using chloroaryl substrates. Cluster activity and stability is found to depend strongly on the preparation method and the reaction conditions. The mechanism of cluster deactivation and the sensitivity of the cluster-catalysed reaction to substituent effects are studied and discussed.

Keywords: aryl halides; biaryls; bimetallic catalysts; combinatorial catalysis; copper; cross-coupling; nanoclusters

Introduction

Catalysis is traditionally divided into 'heterogeneous', 'homogeneous' and 'enzymatic' subsections, each with its own methods and applications. Metal nanoclusters in the 2–5 nm range (also called 'quantum dots') are too big to be 'homogeneous catalysts', and too small to be considered 'bulk metals'.[1] These nanoclusters can display unique catalytic properties that differ from their homogeneous and/or heterogeneous analogues. A second important aspect of metal nanoclusters is their huge surface area. In small clusters most atoms are at the surface, which can lead to very high catalytic activity.[2,3] Transition metal nanoclusters, especially those of noble metals, have been reported as catalysts in olefin hydrogenation,[4–8] hydrosilation,[9] and C–C coupling reactions.[10–12]

Formation of carbon-carbon bonds *via* cross-coupling of aryl halides with arylboronic acids (the Suzuki–Miyaura reaction) is a key synthetic step in the production of agrochemicals, polymers, and pharmaceuticals.[13] This reaction benefits from low reagent toxicity and easy separation of by-products. Traditionally, C–C coupling is carried out using palladium(0), in the presence of ligands,[14,15] that are often laborious to synthesise.[16] During the reaction, and especially at high conversions, the palladium complexes deactivate and ultimately precipitate as micrometric aggregates (palladium black) or coat the vessel with a mirror. However, between the active Pd(0) atoms and the inactive bulk aggregates, the catalyst passes through an intermediate phase, forming small clusters. Such nanoclusters are themselves capable of catalysing Suzuki,[17] Heck,[12] and Ullmann-type coupling reactions[18] (see Figure 1). If aggregation is prevented, catalytic activity comparable with homogeneous systems can be achieved. Multimetallic cluster systems are important as incorporation of different metals can induce large changes in the structure and enhance the catalytic properties of the active component.[19–22]

The high activity reported for monometallic[23–27] and bimetallic[12] nanoclusters encouraged us to investigate further cluster catalysts for the Suzuki reaction. Copper-

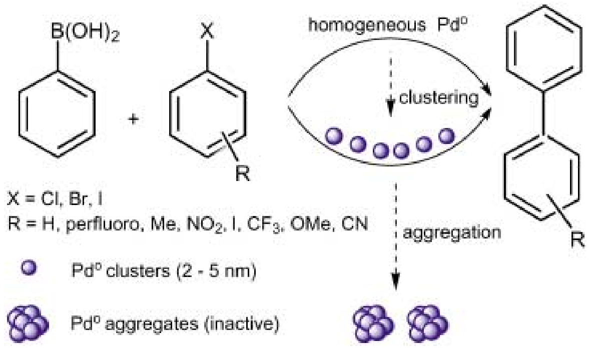

Figure 1. Cross-coupling of phenylboronic acid and halobenzene to give a biaryl derivative, showing clustering of the homogeneous palladium(0) catalysts followed by catalyst deactivation through aggregation.

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based alternatives are attractive because they are both cheaper and "greener" than any noble metals. Moreover, Cu(I) salts and Cu_2O have recently been reported as co-reagents[28–30] and co-catalysts[31] in C–C and C–N[32] coupling reactions. In a preliminary communication, we reported the first application of copper-based mixed nanoclusters as Suzuki cross-coupling catalysts.[33] Here we present a detailed investigation of the reaction scope and try to gain some insight into its mechanism.

Results and Discussion

Nanocluster Catalysts *via* $NaBH_4$ Reduction

We first synthesised nanoclusters by using sodium borohydride as reducing agent in the presence of tetraalkylammonium bromide (TOAB) as stabiliser. In a typical synthesis, 0.26 equivalents of aqueous borohydride were added dropwise to a toluene solution of palladium chloride containing 1.5 equivalents of tetra-*n*-octylammonium bromide (TOAB). A black colloidal suspension formed. This suspension, containing the Pd (or Ru or Pd/Ru) clusters, was tested as is in the cross-coupling of phenylboronic acid and iodobenzene to give biphenyl (Equation 1).

(1)

A mixture of iodobenzene, 1.5 equivalents of phenylboronic acid, 3 equivalents of K_2CO_3 and 1 mol % of metal clusters was stirred in toluene at 110 °C under N_2 for 3 h. Reaction progress was monitored by GC. The palladium clusters were most active, Ru gave 7% conversion after 3 h and no synergistic effect was observed for the bimetallic Pd/Ru clusters. The palladium clusters aggregated and precipitated after 90 min. We thought that the high initial concentration of Pd clusters led to more collisions between the particles and faster aggregation. To study the deactivation of Pd clusters, the same reaction was carried out using 1 mol % Pd in three portions (3×0.33 mol % Pd), added at intervals of 30 min. The initial activity of the clusters in the first two portions is high, but they also deactivate quickly (*cf.* data for ● and ○ in Figure 2). The third portion deactivates even faster than the first two and this may be due to aggregates already present in reaction mixture. Thus, it is *not* the high initial concentration that causes catalyst deactivation. Rather, the deactivation is more likely due to thermal instability and/or contamination by borides.

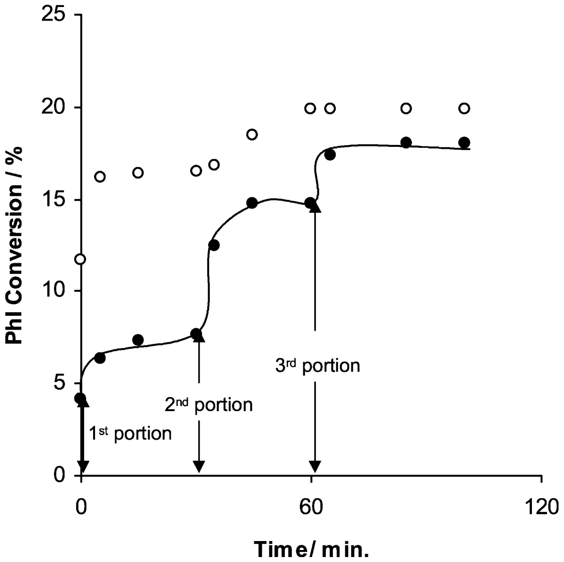

Figure 2. Suzuki coupling of $PhB(OH)_2$ with PhI catalysed by palladium nanoclusters (prepared *via* $NaBH_4$ reduction). Reaction conditions: 3.00 mmol PhI, 6.00 mmol $PhB(OH)_2$, 6.00 mmol K_2CO_3, 50 mL toluene, 110 °C. (○) 1 mol % catalyst, added in one portion at $t = 0$; (●) 1 mol % catalyst in total, added in three equal portions at intervals of 30 min.

The preparation of TOAB-protected Pd and Ru nanoclusters by borohydride reduction was straightforward, but our attempts to prepare Cu, Co, and Ni clusters by this method were unsuccessful. In all three cases metal aggregates formed in the aqueous phase, indicating that the interaction of these metals with the TOAB was insufficient. To avoid this biphasic system we switched to dimethylformamide (DMF), but here all clusters aggregated (including Pd and Ru) and precipitated out of the solution. The reason for this may be the strong reducing power of borohydride in the monophasic system.

Nanocluster Catalysts *via* Formate Reduction

To control the reduction rate we adopted the approach reported by Reetz and Maase, who used tetraalkylammonium carboxylates both as reducing and as stabilising agents.[34] The Pd clusters prepared in DMF were more active than those prepared in toluene, perhaps because the polar solvent itself acts as a stabiliser.[35] The results below all pertain to clusters prepared in DMF. A mixture design[36] assuming no prior knowledge was applied to test the singular and the combined catalytic effects of copper with three noble metals (palladium, platinum and ruthenium, see Figure 3). A library of 15 colloidal mixtures was prepared, by mixing the appropriate homogeneous stock solutions of the metal chloride precursors, followed by reduction with tetraoctylammonium formate (TOAF) in DMF at 65 °C. All

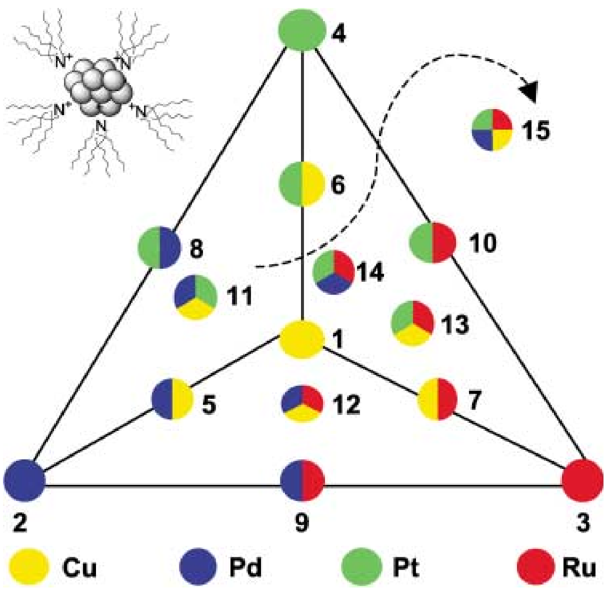

Figure 3. Cartoon of a metal cluster stabilised by tetraoctylammonium ions and experimental design for preparing cluster catalyst mixtures of copper, palladium, platinum and ruthenium.

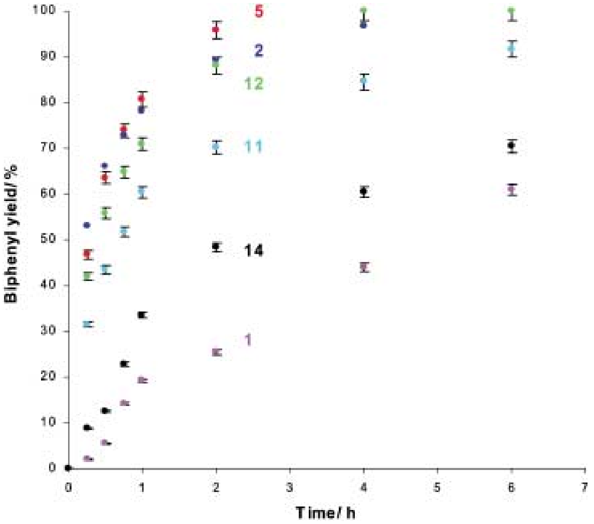

Figure 4. Time-resolved reaction profiles observed for Suzuki coupling of $PhB(OH)_2$ and PhI using various nanocluster catalysts. Duplicate experiments with catalysts **2**, **5**, and **12** were within ±3%. Reaction conditions are as in Table 1.

syntheses, reactions, and catalyst storage were performed under nitrogen. Cluster size was measured using XR diffraction. In all cases, the size of the metal core (excluding the stabilising tetraoctylammonium shell) varied between 1.6 and 2.5 nm in diameter, with a size distribution of ±0.1 nm.

This library was then screened for activity in the cross-coupling of phenylboronic acid with iodobenzene. The reactions were carried out using 2 mol % metal relative to PhI. The results are shown in Table 1. As expected, among the homometallic catalysts palladium **2** was most efficient, giving 100% yield after 4 h at 110 °C. No reaction was observed with the platinum clusters, but ruthenium and, surprisingly, copper clusters were found to be active and stable (see Figure 4). Cu/Pd **5** was the most active of the bimetallic combinations, comparable to pure Pd **2** (*cf.* Table 1, entries 4 and 2). Note that the amount of Pd in **5** is half of that in **2**. Apparently, there is a synergistic effect between Cu and Pd. However, the lower activity of the Pd/Pt catalyst **9** shows that no simple extrapolation can be made from one combination to another.

No reaction was observed with catalysts **6**, **7** and **10**. Activity trends continued with **12** > **11** > **14** for the trimetallic clusters. **15** was less active but stable, reaching 100% conversion after 24 h. Duplicate experiments carried out after 4 weeks using same stock solution of nanoclusters, confirmed that the results were reproducible, and that the catalysts retain their activity.

The bimetallic Cu/Pd clusters were active over a wide range of substrates (Table 2). In general, aryl iodides reacted faster then the corresponding bromides (entries 2–4). Aryl bromides containing electron-withdrawing groups (entries 8–11) gave quantitative yields after 1–6 h. 4-Bromoanisole, on the other hand, took 24 h to reach full conversion. The catalyst was also active towards aryl chlorides with electron-withdrawing groups, indicating that it is active enough to initiate the oxidative addition step of a strong C–Cl bond. In several experiments *ca.* 10% biphenyl was also observed. The amount of copper in these experiments is not enough to form biphenyl *via* the stoichiometric Ullmann reaction,[37] and in any case no 4,4′-dimethylbiphenyl was observed when *p*-iodotoluene was used as the substrate. It is more likely that some homocoupling of phenylboronic acid occurs in these cases when the cross-coupling is slow.[38,39] With hindsight, we see that the choice of model reaction was not ideal, as it is difficult to distinguish between the cross-coupling of iodobenzene and boronic acid and the homocoupling of the latter. Also, in contrast with earlier studies, no reduction of the nitro group was observed (Table 2 entries 12–16). We thought that this discrepancy was the result of solvent contamination by water but repeated control experiments using dried solvents in the presence and absence of 1 μL water showed that water does not effect the nitro group reduction. Further work to study the nitro group reduction is underway.

Mechanistic Studies

The accepted catalytic cycle for the homogeneous complex-catalysed Suzuki cross-coupling begins with oxidative addition of the aryl halide, followed by transmetallation and reductive elimination of the prod-

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Table 1. Biphenyl yields and rate constants using various nanoclusters catalysts.[a]

Entry	Catalyst[b]	Yield[c] [%]	k_{obs} [L/mol min^{-1}]	r^2 [5 obs.]
1	**1** (Cu)	62	3.2×10^{-3}	0.985
2	**2** (Pd)	100	5.9×10^{-2} [d]	0.990
3	**4** (Ru)	40	2.0×10^{-3}	0.938
4	**5** (Cu/Pd)	100	6.1×10^{-2} [d]	0.992
5	**8** (Pd/Pt)	94	9.7×10^{-3}	0.934
6	**9** (Pd/Ru)	100	2.9×10^{-2}	0.985
7	**11** (Cu/Pd/Pt)	92	2.5×10^{-2}	0.991
8	**12** (Cu/Pd/Ru)	100	3.8×10^{-2} [d]	0.996
9	**14** (Pd/Pt/Ru)	81	7.3×10^{-3}	0.923
10	**15** (Cu/Pd/Pt/Ru)	62[e]	2.8×10^{-3}	0.992

[a] Standard reaction conditions: 0.50 mmol iodobenzene, 0.75 mmol phenylboronic acid, 1.5 mmol K_2CO_3, 0.01 mmol catalyst (2 mol % total metal relative to PhI), 12.5 mL DMF, N_2 atmosphere, 110 °C.

[b] No conversion was observed with catalysts **3**, **6**, **7**, **10**, and **13**.

[c] GC yield after 6 h, corrected for the presence of internal standard.

[d] Value is the average of two repeated experiments.

[e] 100% yield obtained after 24 h.

uct.[40] Does this mechanism also apply to nanocluster catalysis? A partial answer to this question can be obtained by examining the influence of substituents on the reaction rate. For the substrates we studied, the reaction profile fits well to a second-order rate equation (see, e.g., the data for *p*-bromobenzotrifluoride in Figure 5). One may assume that the rate-determining step with nanocluster catalysts is, similar to the homogeneous reaction, the oxidative addition of ArX to the catalytic site. Indeed, a Hammett plot of the relative reactivity of various substituted bromobenzenes *vs.* σ_P gave $\rho = 1.48$ (Figure 6), in close comparison with the value obtained by Weissman et al. using homogeneous palladium complexes.[41] The positive ρ value indicates that the reaction is more sensitive to the electronic effects of electron-withdrawing substituents, which are expected to accelerate the oxidative addition step. It is likely that the two reactions involve similar transition states.

In principle, this similarity can also result from partial dissolution of the clusters in the reaction medium.[42, 43] Metal atoms could ‘leach out’ from the cluster and initiate a homogeneous catalytic cycle. We cannot disprove this hypothesis, but it seems to us less likely, especially considering the catalysis by copper nanoclusters. If atom leaching was the cause of the activity, we would expect Cu(0) complexes to be good cross-coupling catalysts.

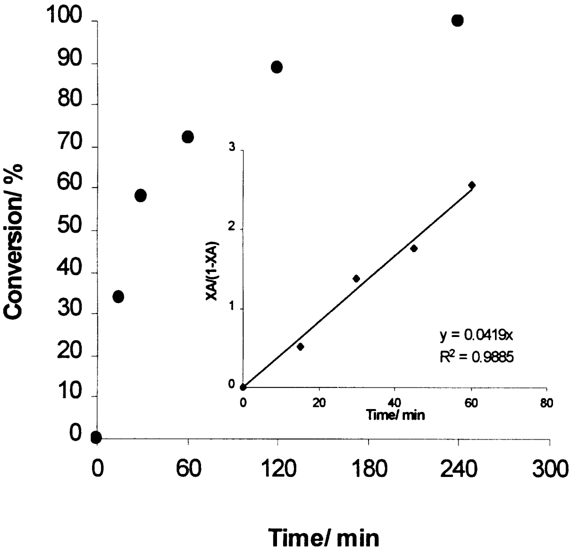


Figure 5. Suzuki coupling of $PhB(OH)_2$ with 4-bromobenzotriflouride using a mixed Cu/Pd nanocluster catalyst. Inset shows the fit of the initial reaction rate to a second-order rate equation. Reaction conditions are as in Table 1.

Conclusion

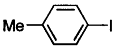
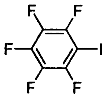
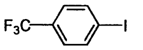
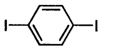
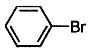
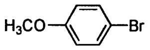
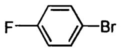
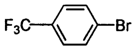
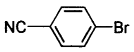
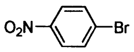
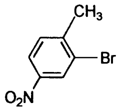
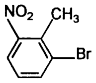
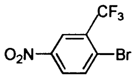
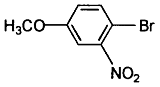
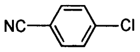
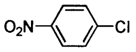
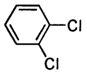
In the case of the Suzuki reaction, Cu nanoclusters are good catalysts, unlike Cu complexes or micrometric Cu particles. Furthermore, mixing two or more metal precursors can lead in this case to synergistic effects. The activity and stability of such clusters is strongly dependent on the reaction conditions and particularly on the stabilising shell. We anticipate that metal(0) nanclusters could have a high impact in catalysis of carbon-carbon coupling reactions, and perhaps provide new possibilities normally inaccessible with conventional homogeneous and heterogeneous catalysts.

Experimental Section

Materials and Instrumentation

^1H and ^{13}C NMR spectra were recorded in deuterated DMF on a 500 MHz Varian Inova instrument. GC analysis was per-

Table 2. Nanocluster-catalysed Suzuki cross-coupling with various substrates.[a]

Entry	Substrate	Catalyst [composition]	Time [h]	Conversion [%][b]
1		**1** (Cu)	8	100
2		**5** (Cu/Pd)	2	100
3		**5** (Cu/Pd)	2	100[c]
4		**5** (Cu/Pd)	2.5	100
5		**5** (Cu/Pd)	24	100[d]
6		**12** (Cu/Pd/Ru)	24	62
7		**5** (Cu/Pd)	24	100
8		**5** (Cu/Pd)	24	100[c]
9		**5** (Cu/Pd)	24	100[c]
10		**5** (Cu/Pd)	4	100
11		**5** (Cu/Pd)	1	100
12		**5** (Cu/Pd)	0.5	100[c]
13		**5** (Cu/Pd)	6	100[c]
14		**5** (Cu/Pd)	4	100
15		**5** (Cu/Pd)	4	100
16		**5** (Cu/Pd)	6	100[c]
17		**5** (Cu/Pd)	48	43
18		**5** (Cu/Pd)	48	54
19		**12** (Cu/Pd/Ru)	24	25[c]

[a] Standard reaction conditions: 0.50 mmol substrate, 0.75 mmol phenylboronic acid, 1.5 mmol K_2CO_3, 0.01 mmol catalyst (2 mol % total metal colloid relative to PhI), 12.5 mL DMF, N_2 atmosphere, 110 °C.

[b] GC conversion, corrected for the presence of an internal standard. Only the cross-coupling product was observed, unless otherwise noted.

[c] 8–10% biphenyl as by-product.

[d] 75% conversion to 1,4-diphenylbenzene (terphenyl).

formed using an Interscience Trace GC-8000 gas chromatograph with a 100% dimethylpolysiloxane capillary column (DB-1, 30 m × 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 × 0.25 mm). All products are known compounds and were identified by comparison of their spectral properties to those of authentic samples. Samples for GC were diluted with 1 mL DMF and filtered through an alumina plug prior to injection. GC conditions: isotherm at 105 °C (1 min); ramp at 20 °C min^{-1} to 260 °C; isotherm at 260 °C (5 min). All reactions were carried out under N_2 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 synthesised using the procedure reported by Maase.[44]

Synthesis of Colloids by Reduction with $NaBH_4$

Example – Pd colloids: A Schlenk-type vessel equipped with a rubber septum and a magnetic stirrer was evacuated and refilled with N_2. An aqueous solution of $NaBH_4$ (2.0 mL, 26.0 mM) was added dropwise over 1 h to the reaction mixture in the vessel containing $PdCl_2$ (0.20 mmol, 34.0 mg), TOAB (0.30 mmol, 164.0 mg) and toluene (50 mL) at 20 °C. The mixture was stirred further for 2 h after which the toluene layer was separated and used directly in the reaction.

Synthesis of Colloid Catalysts 1–15 using TOAF

Example – Cu/Pd 5: A Schlenk-type vessel equipped with a rubber septum and a magnetic stirrer was evacuated and refilled with N_2. The vessel was charged with CuCl and $PdCl_2$ 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 slight overpressure of N_2. The colour of the mixture changed from reddish brown to black. The resulting colloidal suspension (particle size ~2.5 nm) was then stored under N_2 and was used as a stock solution in the cross-coupling reactions. The other catalysts 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 rotating Cu-anode and a 2D image plate detector.

Cross-Coupling of Aryl Halides with Phenylboronic Acid

Sets of five reactions were performed in parallel, and in order to minimise errors and to test the reproducibility of the results, one reaction from each set was duplicated in the next set.

Example (1) – 4-Nitrobiphenyl: A Schlenk-type glass vessel equipped with a rubber septum and a magnetic stirrer was evacuated and refilled with N_2. The vessel was then charged with a Cu/Pd 5 colloidal suspension prepared in DMF (10.0 mL, 10.0 mM, 2.0 mol %), phenylboronic acid (0.914 g, 7.5 mmol), and K_2CO_3 (2.07 g, 15.0 mmol). 4-bromonitrobenzene (1.01 g, 5.0 mmol) was added and the mixture was stirred at 110 °C for 4 h under a slight overpressure of N_2. Reaction progress was monitored by GC and GC/MS. After 4 h the reaction mixture was poured into a separatory funnel, diluted with water (20 mL) and extracted with dichloromethane (2 × 20 mL). The organic layers were washed with 1M aqueous NaOH (20 mL), dried over anhydrous $MgSO_4$ and concentrated under vacuum at 40 °C to afford a yellow solid; yield: 1.0 g (> 99% yield based on 4-bromonitrobenzene). The crude product was recrystallised from hot ethanol to give light-yellow needles (0.955 g, 95.5% based on 4-bromonitrobenzene), mp 106 °C (lit. 103–104 °C [14]); ^{1}H NMR: $\delta = 8.371$ (d, 2H, $J =$ 8.7 Hz), 8.034 (d, 2H, $J = 5.5$ Hz), 7.854 (d, 2H, $J = 7.5$ Hz), 7.549 (t, 3H, $J = 7.2$ and 7.5 Hz); ^{13}C NMR: $\delta = 147.48$, 147.43, 138.69, 129.57, 129.37, 128.30, 127.72, 124.417. Good agreement was found with literature values.[14]

Example (2) – 4-Phenyltoluene: Reaction and work-up were performed as above, but using 4-bromotoluene (1.026 g, 6 mmol), to give 0.865 g (84.3%) of product. The crude material was recrystallised from hot ethanol to give a white solid, mp 46 °C (lit. 49–50 °C [45]); ^{1}H NMR: $\delta = 7.688$ (d, 2H, J = 8.4 Hz), 7.602 (d, 2H, $J = 8.1$ Hz), 7.478 (t, 2H, $J = 7.8$ Hz), 7.365 (t, 1H, $J = 7.248$ Hz), 7.309 (d, 2H, $J = 8.1$ Hz), 2.376 (s, 3H); ^{13}C NMR: $\delta = 141.0$, 138.1, 137.3, 129.8, 129.1, 127.4, 126.9, 126.7, 20.5. Good agreement was found with literature values.[45]

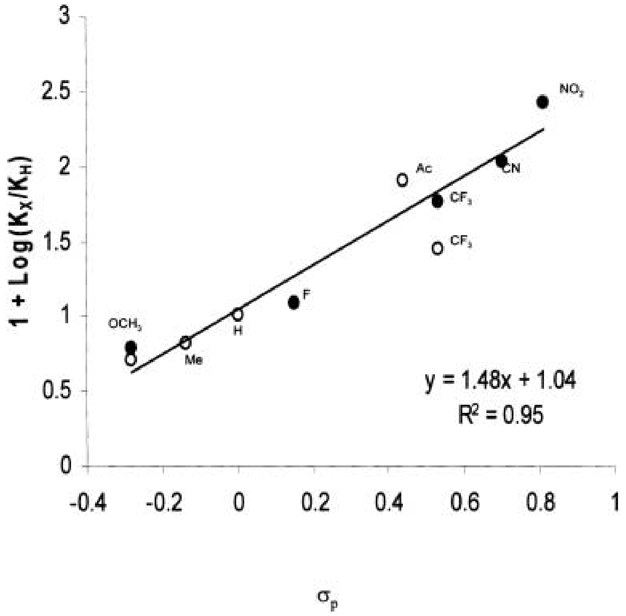


Figure 6. Plot of the relative rate constants *vs.* σ_p (Hammett plot); (○) results for cluster catalysts; (●) results reported for palladacycle catalyst in ref.[41]

Experimental Procedure for Kinetic Studies

Conditions and apparatus were similar to the cross-coupling procedure given above. The typical second-order rate constants observed for coupling of unsubstituted and various substituted bromobenzene with phenyl boronic acid were i) bromobenzene (k_{obs}=9.70×10^{-3} M^{-1} min^{-1}, $r^2 = 0.980$ for 5 observations), ii) 4-bromoanisole (k_{obs}=7.50×10^{-3} M^{-1} min^{-1}, $r^2 = 0.991$ for 5 observations), iii) 4-bromofluorobenzene (k_{obs}=1.18×10^{-2} M^{-1} min^{-1}, $r^2 = 0.992$ for 5 observations), iv) 4-bromonitrobenzene (k_{obs}=2.60×10^{-1} M^{-1} min^{-1}, $r^2 = 0.981$ for 5 observations), v) 4-bromobenzonitrile (k_{obs}=1.04×10^{-1} M^{-1} min^{-1}, $r^2 = 0.966$ for 5 observations), vi) 4-bromobenzotrifluoride (k_{obs}=4.19×10^{-2} M^{-1} min^{-1}, $r^2 = 0.988$ for 5 observations).

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