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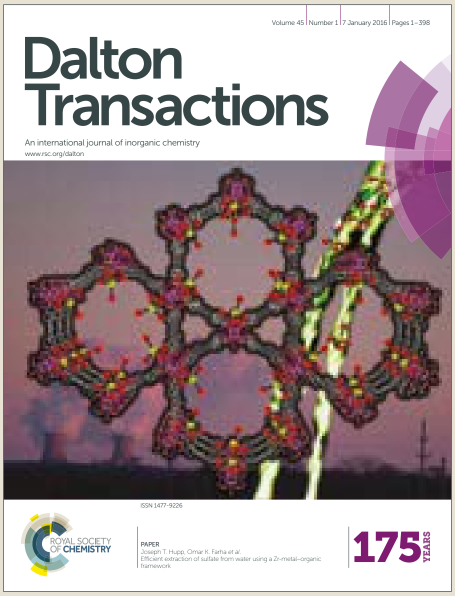

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Journal Name

COMMUNICATION

Synergistic effect of cobalt in a Pd/Co catalyzed Suzuki-Miyaura cross-coupling in water

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This work introduces the new trimetallic complex $CoPd_2(HBPDC)_2Cl_4\cdot(H_2O)_4$($H_2BPDC$ = 2,2'-bipyridine-4,4'-dicarboxylic acid) as a highly efficient and more cost-effective catalyst for a Suzuki-Miyaura reaction proceeding in water, without additives and under aerobic conditions. Catalytic studies revealed a synergistic Co-Pd cooperativity, fostered by ligation through H_2BPDC, and accounting for the superior performance of the heterobimetallic complex *vs.* its Co-free counterpart.

The Suzuki-Miyaura reaction[1] is likely the most versatile protocol for C-C cross-couplings used in production of pharmaceuticals, agrochemicals, fine chemicals, flavours and fragrances, advanced materials, etc. This chemical transformation has been extensively explored with a broad range of substrates in both homogeneous and heterogeneous phase employing highly active, chemoselective palladium and other transition metal catalysts.[2-4]

Combination of Pd with different transition metals in newest generations of heterobimetallic Pd complexes in order to induce synergistic interactions between the active metal sites has emerged as a fruitful approach in Suzuki-Miyaura cross-couplings.[4a,c,5]In heteronuclear systems the coordination environment of Pd can be finely manipulated *via* the additional transition metal.[4a] Depending on the electropositivity or electronegativity of the latter the rates of the distinct steps of the palladium catalytic cycle (e.g. reductive elimination or oxidative addition) will be affected. This interaction might be amplified by the organic linker which, by bridging the different metal centers, plays the role of a sensitive charge transfer vector. The anticipated outcome of this cooperation would be an enhancement of the overall reaction rate, hence an increase in activity of the heterobimetallic Pd catalysts. Moreover, the newtransition metal, the organic ligand and Pd may together confer attractive physical-chemical attributes to the complex like robustness, superior mechanical and thermal stability, and water and air tolerance.

Cooperativity between different transition metals and palladium has been clearly demonstrated in cross-couplings with phosphine-free Ni/Pd[4a,6a] and Ln/Pd[5a,6b,c] catalysts. For the Ln/Pd catalysts, namely, $[Ln_2Pd_3(BPDC)_2(HBPDC)_2(\mu_2\text{-}O)Cl_4(H_2O)_6]_n$(Ln=Pr,Gd,Tb)[6b] and $[LnPd(BPDC)_{5/2}(H_2O)\cdot 4H_2O]_n$ (Ln = Nd, Sm, Eu, Dy)[6c], our group has shown that interactions between the electropositive Ln ions and the Pd centres were facilitated by the 2,2'-bipyridine-4,4'-dicarboxylate ligand. As a result more robust, easily separable and recyclable heterobimetallic Pd catalysts were obtained, able to promote the reaction in aqueous systems (DMF-water), under mild conditions.[6b,c]

Herein, we report the convenient, one-pot hydrothermal synthesis[7-10]of a new, air-stable trimetallic Pd/Co complex, $Pd_2Co(HBPDC)_2Cl_4\bullet(H_2O)_4$ (**1**), (H_2BPDC = 2,2'-bipyridine-4,4'-dicarboxylic acid), its full structural characterization and superior catalytic performance in Suzuki-Miyaura C-C cross-coupling in water without any additive. Though cobalt, a non-precious metal, can save some of the noble metal, it has not been used, to our knowledge, in conjunction with Pd in phosphine-free heterobimetallic catalysts for Suzuki-Miyaura. Contrasting with the effect of electropositive Ln ions, we expect thatinteraction between Co and Pdwill benefit from the electronegative character of Co acting on the oxidation potential of Pd *via* the ligand. The latter, will considerably help charge transfer between Co and the two Pd atoms (Pd1 and Pd1A), since they all are connected by the heteroaromatic units and their para, conjugated COO^- groups (Fig. 1). We anticipate that this synergistic cooperativity will result in acceleration of the oxidative addition step, the rate determining step in the Pd catalytic cycle. In the layered structure of this Pd_2/Co complex, the trimetallic configuration in which two Pd centres are bridged by the cobaltoligand will increase the concentration and improve the dispersity of the

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Pd(II) catalytic sites, enhancing thus the catalyst activity and stability in water and air, as compared to conventional heterobimetallic Pd complexes. Ultimately, this approach will lead to cross-coupling with a high efficiency at lower catalyst loadings.

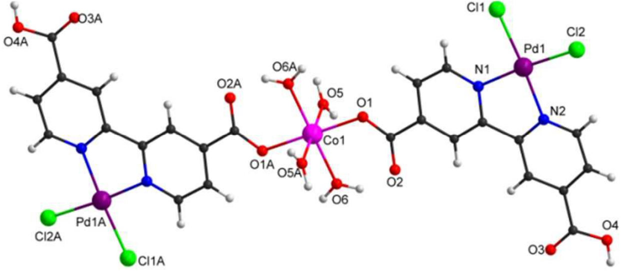


Fig. 1 View of the coordination environments of Pd(II) and Co(II) ions in **1**. Symmetry codes: A1-*x*, -*y*, 2-*z*

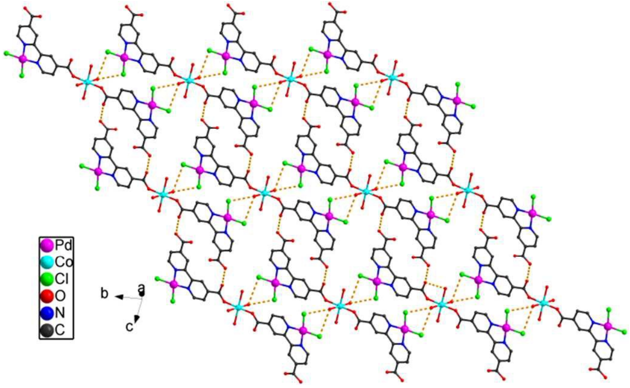


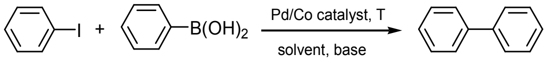
Fig.2 Two-dimensional layer formed by H-bond interactions of **1**

$Pd_2Co(HBPDC)_2Cl_4$•$(H_2O)_4$ complex (**1**) was prepared according to the well-established hydrothermal protocol for synthesis of the Pd coordination complexes, and structurally characterized by means of single-crystal X-ray diffraction, FT-IR, powder X-ray diffraction(PXRD), elemental analysis and thermogravimetric (TG) techniques (see ESI†).

Single crystal X-ray diffraction investigation revealed that complex**1**crystallizes in the triclinic space group *P*-1. As illustrated in Figure 1, the complex consists of two Pd(II) ions, one Co(II)ion, two $HBPDC^-$ ligands, four chlorine ions, and four coordinated water molecules. Pd1 constructs a square planar coordination mode connecting two nitrogen atoms from one $HBPDC^-$ ligand and two chlorine atoms in the remaining *cis*-positions. Co1 coordinates with six oxygen atoms, two carboxylate oxygen atoms from different H_2BPDC ligands, while the remaining four oxygen atoms are terminal water molecules. Within the complex, adjacent molecules are connected to a two-dimensional layer by H-bond interactions (Fig.2). Crystal and structural refinement data for **1** are displayed in Table S1 while important bond lengths and angles are listed in Table S2.

With the new Pd_2/Cocatalyst in hand, we next evaluated its catalytic activity in Suzuki–Miyaura coupling reactions. Initially, iodobenzene and phenylboronic acid were chosen as the model substrates to explore the optimal reaction conditions, and the selected results are shown in Table 1. Screening of solvents using K_2CO_3 as a base showed thatthe yield of cross-coupling product is greater when using neat water as solvent instead of toluene, DMF or EtOH (Entries 1-4). The base has previously been demonstrated to play a significant role in Suzuki-Miyaura cross-coupling reactions.[11]The K_2CO_3 resulted in much higher yield than Cs_2CO_3, NaOH and *t*-C_4H_9OK (Entries 4-7), and the reaction cannot be carried out in the absence of the base (Entry 9). In addition, the reaction temperature and time are essential reaction parameters. We found that the temperature of 70 °C and the reaction time of 5 h are the most effective reaction parameters in providing high yields of cross-coupling products (Entries 4, 10-13).

Table 1 Optimization of reaction conditions in the Suzuki-Miyaura cross-coupling.Table Caption.[a]



Entry	Solvent	Base	T/°C	Time/h	Yield[b](%)
1	Toluene	K_2CO3	70	5	16
2	EtOH	K_2CO_3	70	5	82
3	DMF	K_2CO_3	70	5	15
4	H_2O	K_2CO_3	70	5	95
5	H_2O	Cs_2CO_3	70	5	83
6	H_2O	NaOH	70	5	83
7	H_2O	*t*-C_4H_9OK	70	5	89
8	H_2O	K_2CO_3	70	5	82[c]
9	H_2O	None	70	5	0
10	H_2O	K_2CO_3	50	5	75
11	H_2O	K_2CO_3	90	5	85
12	H_2O	K_2CO_3	70	3	67
13	H_2O	K_2CO_3	70	9	92
14	H_2O	K_2CO_3	70	5	97[a]
15	H_2O	K_2CO_3	70	5	62[e]
16	H_2O	K_2CO_3	70	5	0[f]

[a]Reaction conditions:iodobenzene (1.0 mmol), phenylboronicacid (1.5 mmol), base(2.0 mmol), catalyst (10^{-3}mol%Pd),under air. [b]Yields were determined by GC and GC–MS analysis. [c]$Pd(H_2BPDC)Cl_2·H_2O$ (10^{-3}mol% Pd) was used to replace the Pd/Co catalyst. [d]Pd/Co catalyst ($1.5×10^{-3}$ mol% Pd). [e]Pd/Co catalyst ($5×10^{-4}$mol% Pd).[f]No catalyst

Studies on the influence of the catalyst amount on the product showed that the reaction affords a satisfactory yield (95-97%) with the amount of catalyst of $0.5\text{-}1.5\times10^{-3}$mol% (Entries 4,14). This relatively low catalyst loading is an important benefit of our methodology as compared to the frequently used palladium catalyst loadings (0.1-1 mol%) in Suzuki-Miyaura reactions.[5]Moreover, a high TON value of$1.24×10^5$ could be generated within 5 h with a TOF of

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2.48×10^4 $h^{-1}$when the Pd/Co catalyst loading was decreased to 5×10^{-4} mol% (Table S3).

It is noteworthy that there is an advantageous cooperation between palladium and cobalt, comparing the yields catalyzed by $Pd_2Co(HBPDC)_2Cl_4\cdot(H_2O)_4$ (**1**) and $Pd(H_2BPDC)Cl_2\cdot H_2O$ (**2**) (95% vs 82%, Entry 4 and 8, see also Figure 3). The increase in the yield of cross-coupling products when Co was incorporated into the Pd complex may be assigned to a substantial synergistic effect of Co, by its electronegativity pattern (1.84 on Allen scale), favoured by the organic linker (2,2'-bipyridine-4,4'-dicarboxylate), a very sensitive charge transfer agent. Noteworthy, Co will consequently affect the oxidation potential of Pd, facilitating thus the oxidative addition step, the rate determining step in the Pd catalytic cycle. That the unique trimetallic structure of our catalyst, consisting of two palladium active sites ligated through a Co/organic linker, improves the catalyst efficiency, is clearly demonstrated by the increase attained in the reaction yield (from 82% to 95%). Moreover, pure water as the solvent provides an ideal reaction medium for the mass transfer of all ionic species involved in the palladium catalytic cycle with a beneficial effect on the reaction yield. The general reaction conditions for the C-C coupling protocol have been optimized as follows: a mixture of iodobenzene (1.0 mmol), phenylboronic (1.5 mmol), K_2CO_3 (2.0 mmol), water (6.0 ml), 5 h reaction time and Pd/Co complex (**1**) (10^{-3} mol% Pd), was stirred at 70 °C in air, under normal conditions.

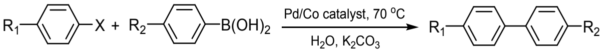
To further examine the scope of our trimetallic Pd_2/Co catalyst, the optimized conditions (Table 1, entry 4) were employed for reactions between various aryl halides and arylboronic acids in water under air. Selected results are given in Table 2 and illustrated in Fig.3. Higher yields are achieved for aryl halides endowed with electron-withdrawing substituents, as evidenced by the reactions of phenylboronic acid and substituted aryl iodides or bromides at the *para* position (Entries 1-2 and 3-5). Substituted arylboronic acids were also tested to furnish the corresponding biaryl products (Entries 6-7) and a better activity was observed for electron-rich arylboronic acid. As expected, aryl chlorides were less reactive than aryl bromides and iodides owing to the much higher C-Cl bond strength (*vs*. C-Br and C-I) (Entries 8-9).[12]

The proposed mechanism for the Pd/Co-catalyzed process, as shown in Scheme S1†, assumes that the palladium catalytic cycle involves, in a first step, the oxidative addition of Pd(0) to the aryl halide to form arylpalladium(II) species which, after complexation with base, undergoes transmetalation with aryl boronic acid. Finally, the reductive elimination step leading to the biaryl product and re-establishment of the Pd (0)/Co complex end the palladium catalytic cycle. The oxidative addition step, which is the rate determining step of the Pd catalytic cycle, appears to be substantially facilitated by charge transfer from Co to Pd, through the organic linker (2,2'-bipyridine-4,4'-dicarboxylate), thus enhancing the rate of the overall process.[13]

Studies effected by others[4a,6a,14] on cross-couplings with Pd/Ni catalysts revealed a similar influence of Ni, as we have observed for Co, due to the fact that Ni and Co have close electronegativity values. It was shown that within the Pd catalytic cycle the charge transfer from Ni to Pd has beneficial consequences on the oxidative addition step. Indeed, Pd/Ni catalysts were proved to have higher activities versus monometallic Pd counterparts as result of the synergism between Ni and Pd.[14a]

On the other hand, previous investigations carried out with bimetallic Pd/Ln catalysts in Suzuki-Miyaura, Heck and Sonogashira reactions pointed out to a distinct cooperative effect between these two metals, facilitated by the 2,2'-bipyridine-4,4'-dicarboxylate ligand. Contrasting with the electronegative Co and Ni, the electropositive Ln ions are supposed to affect the rate of the reductive elimination step from the palladium catalytic cycle, resulting in a positive effect on the overall reaction rate of the cross-coupling processes[6b,6c]

Table 2 Suzuki-Miyaura cross-coupling reaction of aryl halides and arylboronic acids.[a]



Entry	R_1	R_2	X	Yield[b](%)
1	CH_3	H	I	90
2	CH_3CO	H	I	98
3	H	H	Br	70
4	CH_3	H	Br	64
5	CH_3CO	H	Br	75
6	H	CH_3	Br	71
7	H	CH_3CO	Br	67
8	H	H	Cl	trace
9	CH_3CO	H	Cl	24

[a]Reaction conditions:iodobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), H_2O (6.0 mL), catalyst (10^{-3}mol% Pd), 70 °C, 5h. [b]Yields were determined by GC and GC–MS analysis.

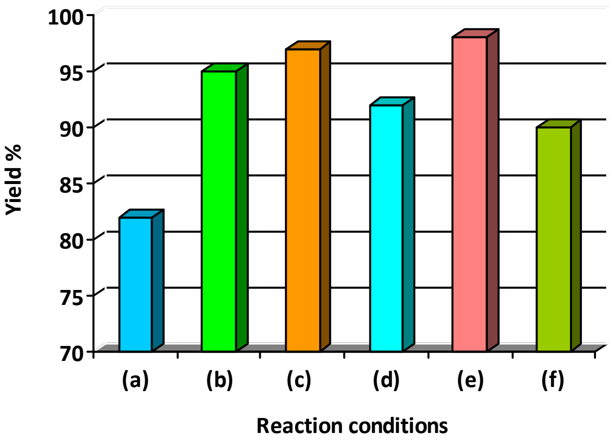


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Fig.3 Increase in catalyst activity in Suzuki-Miyaura of aryliodide with phenylboronic acid, in water and air, induced by $Pd_2Co(HBPDC)_2Cl_4{\cdot}(H_2O)_4$ (1) as compared to $Pd(H_2BPDC)Cl_2{\cdot}H_2O$ (2);(a) iodobenzene, catalyst 2 (10^{-3}mol% Pd) 5h;(b) iodobenzene, catalyst 1 (10^{-3}mol% Pd) 5h; (c) iodobenzene, catalyst 1 (1.5×10^{-3} mol% Pd); 5h (d) iodobenzene, catalyst 1 (10^{-3}mol% Pd), 9h; (e) Substrate CH_3COArI, catalyst 1 (10^{-3}mol% Pd) 5h; (f) Substrate CH_3ArI, catalyst 1 (10^{-3}mol% Pd) 5h.

In summary, a new trimetallic Pd_2/Co complex, involving the 2,2'-bipyridine-4,4'-dicarboxylate heteroleptic ligand, enabled high-yielding Suzuki-Miyaura cross-couplings in neat water and air and at low catalyst loadings. This robust and cost-effective catalyst led to environmentally friendly application with a variety of reagents. The synergistic cooperation between Co and Pd within this complex, mediated by the ligand acting as an effective charge transfer vector, has been for the first time clearly evidenced in a Suzuki-Miyaura process. Our results will be valuable for design of further potent Pd/Co catalysts suitable for diverse C-C cross-couplings.

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Notes and references

‡Synthesis of $Pd_2Co(HBPDC)_2Cl_4{\cdot}(H_2O)_4$ (**1**): A mixture containing K_2PdCl_4 (0.2 mmol), $Co(NO_3)_3{\cdot}6H_2O$ (0.1 mmol), H_2BPDC (0.2 mmol), water (8mL) and 0.01 $mol{\cdot}L^{-1}$ NaOH (1 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 95 °C for 96 hr and then cooled to room temperature. Yellow thin crystals of **1** were obtained and were picked out, washed with distilled water and dried in air (Yield: 40.6% based on Pd). Elemental analysis Calcd (%) for $C_{24}H_{22}Cl_4N_4O_{12}Pd_2Co$ (**1**): C 30.63; H 2.34; N 5.95. Found: C 31.01; H 2.51; N 6.23. IR(KBr,cm^{-1}): 3448w, 1719m, 1638s, 1550s, 1356s, 1258w, 1235w, 767m.

§Crystal data for **1** $Pd_2Co(HBPDC)_2Cl_4{\cdot}(H_2O)_4$: Triclinic, space group p-1, a= 5.301(11) Å, b= 12.470(3) Å, c=12.610(3) Å, α= 76.80(3)°, β= 79.55(3)°, γ= 81.30(3)°, V= 792.8(3) $Å^3$, Z= 1, T = 273 K, $\mu(MoK\alpha)$ =2.043 mm^{-1}, D_{calc} = 2.036mg cm^{-3}, 8006 reflections measured, 3591 unique (Rint = 0.0696) which were used in all calculations. The final R_1 was 0.0756 ($I > 2\sigma(I)$) and wR_2 was 0.2171 (all data)

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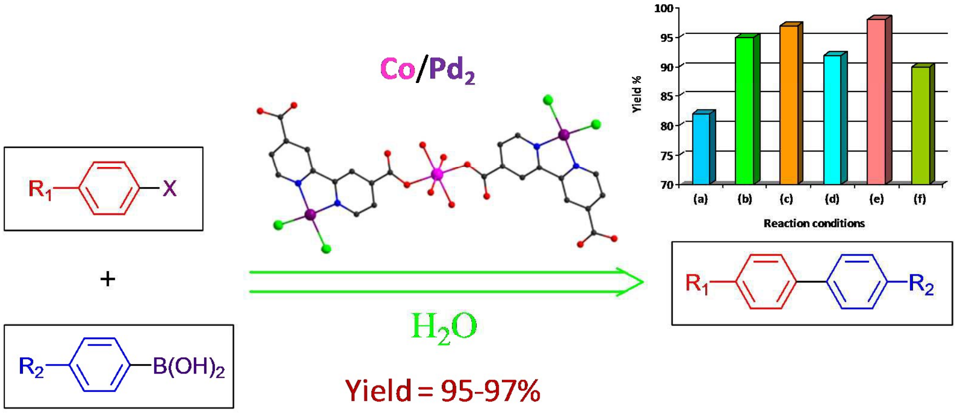

We report on the first Suzuki-Miyaura reaction promoted by a phosphine-free trimetallic Co/Pd$_2$ catalyst proceeding in water, under aerobic conditions. Results reveal a synergistic Co-Pd cooperation, fostered by the metals ligated through 2,2′-bipyridine-4,4′-dicarboxylate.