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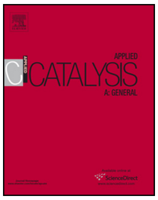

# Cooperative effects of lanthanides when associated with palladium in novel, 3D Pd/Ln coordination polymers. Sustainable applications as water-stable, heterogeneous catalysts in carbon–carbon cross-coupling reactions

Lixin You[a], Wenhui Zong[a], Gang Xiong[a], Fu Ding[a], Shuju Wang[a], Baoyi Ren[a], Ileana Dragutan[b], Valerian Dragutan[b,*], Yaguang Sun[a,*]

[a] *The Key Laboratory of Inorganic Molecule-Based Chemistry of Liaoning Province, Shenyang University of Chemical Technology, Shenyang, PR China*
[b] *Institute of Organic Chemistry, Romanian Academy, Bucharest, Romania*

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ABSTRACT

Three novel porous heterobimetallic coordination polymers, [Ln$_2$Pd$_3$(BPDC)$_2$(HBPDC)$_2$($\mu_2$-O)Cl$_4$(H$_2$O)$_6$·nH$_2$O]$_m$ (Ln = Pr, $n$ = 5 (**1**), Ln = Gd, $n$ = 4 (**2**), and Ln = Tb, $n$ = 4 (**3**)), were readily prepared by combining Pd(II) and Ln(III) with 2,2′-bipyridine-4,4′-dicarboxylic acid (H$_2$BPDC) as a heteroleptic ligand, under hydrothermal conditions, and structurally characterized by means of single-crystal X-ray diffraction, FT-IR, powder X-ray diffraction, elemental analysis and thermogravimetric (TG) techniques. Single-crystal X-ray diffraction examination showed that **1–3** have similar 3D frameworks, connected *via* hydrogen bonding interactions, and consisting of three distinct types of building blocks: Pd(BPDC)Cl$_2$, Pd(HBPDC)$_2$ and a Ln dimer (Ln$_2$O$_{15}$). The new isostructural, air and water stable coordination polymers, resulting from association of lanthanides with palladium, exhibited superior but distinct capabilities as eco-friendly heterogeneous catalysts in Suzuki-Miyaura, Heck and Sonogashira cross-couplings, under green reaction conditions. Supramolecular, solid catalysts **1–3** have been recovered quantitatively from the reaction mixtures by simple filtration. Also importantly, their sustainability, utility and cost-effectiveness have been demonstrated by recycling experiments with catalyst **1** in Suzuki-Miyaura, proceeding practically without loss of activity after four runs.

## 1. Introduction

The high interest in the rapid development of novel composite nanomaterials based on emerging generations of porous coordination polymers (PCPs) [1–3] is due to their valuable properties, suitable for appealing applications in many technologically important fields [4–6]. Such hybrid frameworks possess the unique feature that their crystalline structure, composition and functionality can be finely tuned by a proper variation of the inner metal clusters and adequate selection of the flexible organic ligands [7] as well as by advanced post-synthetic modification and functionalization [8]. By using a clever linker design and 'metalloligand' methodology to incorporate specific functional metallic sites, a broad range of transition and non-transition metals associated with various organic ligands have been thoroughly screened to obtain novel hybrid materials endowed with desired physical-chemical characteristics, *e.g.* crystal size and shape, inner porosity, surface area, catalytic activity, mechanical, optical, electrical and magnetic properties or chemical reactivity [9]. In some instances, an ingenious valorization of the assets of transition metals and lanthanides in functional organic-inorganic networks proved to be a convenient strategy for engineering the new materials designed for advanced applications [10].

A major utilization of porous coordination polymers regards the efficient heterogeneous catalysis of diverse chemical transformations leading to useful reaction products [11]. In addition to profitably modelling the catalyst activity and selectivity in these processes, this class of solid catalysts affords easy handling, facile separation and purification of products, good stability and recyclability while also working under mild conditions [12]. These attributes have not only great economical outcome but also key

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* Corresponding authors. Fax: +86 24 89389359.
*E-mail addresses:* vdragutan@yahoo.com (V. Dragutan), sunyaguang@yahoo.com (Y. Sun).

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significance in the rapid development of environmentally benign chemical processes [12e]. Of particular interest is their efficient application for constructing complex, bio-active organic molecules by versatile cross carbon–carbon couplings like Suzuki-Miyaura, Heck, Negishi and Sonogashira reactions [10a,13,14].

Palladium-catalyzed cross-couplings rank among most popular reactions for production of fine chemicals at ton-scale, especially in the pharmaceutical industry. As established powerful tools for creating C—C bonds, they have been widely investigated in both homogeneous and heterogeneous phase for the synthesis of a host of organic compounds [13,14]. A large platform of palladium catalysts bearing a diversity of ancillary ligands (phosphine, arene, bipyridine, pincer, N-heterocyclic carbene (NHC), acyclic diamino carbene (ADC), etc.) has been created and successfully applied for many synthetic purposes [15]. Nonetheless, certain cross-coupling reactions promoted by today palladium catalysts in homogeneous phase use uncommon, expensive ligands or occasionally suffer from significant waste of the costly palladium catalyst which can not be recovered and recycled [15]. On the other hand, although immobilization of homogeneous palladium complexes on solid supports facilitates catalyst separation, allows cross-coupling reactions in water and improves leaching resistance and recycling, some supported catalysts involve important disadvantages such as, tedious and expensive preparation of the immobilized catalyst, additional steric restraints imposed to the substrates, uneven distribution of the active sites, uncontrolled catalyst loading, all of which in many cases raise difficulties in developing large scale applications [16].

To overcome the above problematic issues, efforts have been recently devoted to create new functional hybrid materials by thoroughly tailoring the organic ligands coordinated at palladium [7,17] or by substituting purely organic linkers with designed metalloligands endowed with highly active and chemoselective sites. Further progress has been made in their functionalization by appropriate post-synthetic methods [8] and in elaborating innovative flow techniques [18a,b], microwave-assisted procedures [18c,d] as well as palladium nanoparticle or supported catalysts [19]. Combination of Pd with other metals to ensure synergistic interactions has been a promising option [10a,b]. However, examples of Pd-Ln systems are surprisingly scarce [10]. In their work on Suzuki-Miyaura and Heck reactions between substituted aryl halides and phenylboronic acid or olefins, in presence of heterobimetallic Pd-Ln systems (Ln = Sm, Eu, Gd, Tb; 2,2′-bipyridine-5,5′-dicarboxylic acid as organic linker), Jin et al. [10a] using specific conditions (0.5 mol% catalyst loading and temperatures of 90 and 100 °C) have successfully improved the reaction performance with respect to the catalyst activity. Whereas a high activity of the Pd-Ln initiator was recorded and the catalyst leaching was at a minimum, data on catalyst stability, recovery and recycling are still to be unveiled. Moreover, in spite of these remarkable advancements in palladium C—C cross-coupling catalysis, important environmental aspects related to the physical profile of the heterogeneous catalysts, chemical activity and stability, leaching or recovery and recycling are still of concern. With the aim of widening the scope and application area of coordination polymers in environmentally friendly catalytic C—C cross-coupling processes, here we report the facile construction of a new set of robust, air- and water-stable heterobimetallic coordination polymers *i. e.* $[Ln_2Pd_3(BPDC)_2(HBPDC)_2(\mu_2\text{-}O)Cl_4(H_2O)_6 \cdot nH_2O]_m$ (Ln = Pr, *n* = 5(**1**); Ln = Gd, *n* = 4(**2**); Ln = Tb, *n* = 4(**3**)), by a reticular synthesis approach, combining for the first time the nitrophilic Pd units and oxophilic Ln motifs through the heteroleptic ligand, 2,2′-bipyridine-4,4′-dicarboxylic acid, as suitable, bifunctional organic linker. It is anticipated that, by properly engineering the Pd network through inclusion of lanthanides by intermediacy of a totally different organic vector, the newly created hybrid materials will display a reasonably robust and stable structural pattern with enhanced physical and chemical features, dependent on the nature of the lanthanide incorporated. Such novel, porous heterobimetallic coordination polymers, endowed with unprecedented physical traits and versatile chemical reactivity and chemoselectivity, will allow access to quite active, water tolerant, easily separable and recyclable solid catalysts, suitable for superior applications in eco-friendly and cost-effective Suzuki-Miyaura, Heck and Sonogashira reactions.

## 2. Experimental

### 2.1. Materials and physical–chemical measurements

All chemicals were purchased commercially and used without further purification. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. The reaction vessels were filled to approximately 50% volume capacity. Water used in the synthesis was distilled before use. The C, H and N elemental analysis was performed on a PerkinElmer 240C elemental analyzer. FT-IR spectra using KBr pellets were recorded using a Nicolet IR-470 spectrometer. TG analysis was carried out on a SDT Q600 instrument with a heating rate of 10 °C min$^{-1}$. Powder X-ray diffraction (PXRD) patterns of the samples were collected on an X-ray diffractometer (BRUKER D8 ADVANCE) with Cu Kα radiation. GC analyses were performed on an Agilent Technologies 7890A gas chromatograph fitted with an HP-5 column (30 m × 320 μm × 0.25 μm). $^1H$ NMR spectra were recorded on a Bruker BioSpin GmbH AVANCE III 500 MHz spectrometer operating at 500 MHz. The amount of palladium was determined by Shimadzu AA-6300C atomic absorption spectrophotometer.

### 2.2. Synthesis of catalysts *1*–*3*

#### 2.2.1. Synthesis of $[Pr_2Pd_3(BPDC)_2(HBPDC)_2(\mu_2\text{-}O)Cl_4(H_2O)_6 \cdot 5H_2O]_m$ (*1*)

Synthesis of **1**–**3** proceeded under hydrothermal conditions currently applied in our group in both the Pd [20] and lanthanide series [1c,d]. For **1**, a mixture containing $K_2PdCl_4$ (0.145 mmol), $Pr(NO_3)_3 \cdot 6H_2O$ (0.09 mmol), $H_2BPDC$ (0.145 mmol), water (7 mL) and 0.01 mol L$^{-1}$ NaOH (4 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL) which was heated at 90 °C for 96 h and then cooled to room temperature in 48 h. Yellow rhombic crystals of **1** were obtained and picked out, washed with distilled water and dried in air (Yield: 44.6% based on Pr). Elemental analysis Calcd (%) for $C_{48}H_{48}Cl_4N_8O_{28}Pd_3Pr_2$: C 29.83; H 2.39; N 5.67. Found: C 29.91; H 2.51; N 5.81. IR (KBr, cm$^{-1}$): 3416s, 1625s, 1552s, 1385vs, 1291w, 1237w, 780m, 699m.

#### 2.2.2. Synthesis of $[Gd_2Pd_3(BPDC)_2(HBPDC)_2(\mu_2\text{-}O)Cl_4(H_2O)_6 \cdot 4H_2O]_m$ (*2*)

A mixture containing $K_2PdCl_4$ (0.145 mmol), $Gd(NO_3)_3 \cdot 5H_2O$ (0.09 mmol), $H_2BPDC$ (0.145 mmol), water (6 mL) and 0.01 mol L$^{-1}$ NaOH (6 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL) which was heated at 70 °C for 96 h and then cooled to room temperature in 48 h. Yellow rhombic crystals of **2** were obtained and collected, washed with distilled water and dried in air (Yield: 48.3% based on Gd). Elemental analysis Calcd (%) for $C_{48}H_{46}Cl_4N_8O_{27}Pd_3Gd_2$: C 29.37; H 2.20; N 5.59. Found: C 29.68; H 2.39; N 5.77. IR (KBr, cm$^{-1}$): 3422s, 1626s, 1552m, 1384vs, 1291w, 1245w, 778m, 670m.

#### 2.2.3. Synthesis of $[Tb_2Pd_3(BPDC)_2(HBPDC)_2(\mu_2\text{-}O)Cl_4(H_2O)_6 \cdot 4H_2O]_m$ (*3*)

A mixture containing $K_2PdCl_4$ (0.145mmol), $Tb(NO_3)_3 \cdot 6H_2O$ (0.09 mmol), $H_2BPDC$ (0.145 mmol), water (6 mL) and 0.01 mol L$^{-1}$

NaOH (6 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL) which was heated at 70 °C for 96 h and then cooled to room temperature in 48 h. Yellow rhombic crystals of **3** were obtained and collected, washed with distilled water and dried in air (Yield: 42.5% based on Tb). Elemental analysis Calcd (%) for $C_{48}H_{46}Cl_4N_8O_{27}Pd_3Tb_2$: C 29.34; H 2.15; N 5.95. Found: C 29.63; H 2.38; N 5.76. IR (KBr, $cm^{-1}$): 3418vs, 1623s, 1537m, 1374m, 1282w, 1236m, 764s, 688m.

### 2.3. X-ray crystallography

The collection of single-crystal crystallographic data was carried out on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation (0.71073 Å) at 293 K in the $\omega$-$2\theta$ scan mode. An empirical absorption correction was applied to the data using the SADABS program [21]. The structures were solved by direct methods and refined by full-matrix least squares on $F^2$ using the SHELXTL crystallographic software package [22]. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in calculated positions and refined using a riding mode. From the perspective of charge balance, both carboxyl groups should be deprotonated in one ligand and only one carboxyl group should be deprotonated in the other ligand of the asymmetric unit of compounds **1**–**3**. After carefully measuring all C-O bond lengths, we found that certain bond lengths (C12-O3A = 1.332 Å, C12-O3B = 1.307 Å in **1**, C12-O3 = 1.276 Å in **2**, and C24-O7 = 1.291 Å in **3**) in the respective carboxyl groups are far larger than those of the other C—O bonds without any distance restrained commands, indicating that the former carboxyl groups were not deprotonated. Therefore, the hydrogen atoms were added on these oxygen atoms except in **1** (O3 is disorder). The data completeness of 92.8% is a little low in the crystal data of **3** (as mentioned in alert A), but it cannot affect the structure confirmation. CCDC: 1020991(**1**); 1020990(**2**); 1020989(**3**).

### 2.4. Catalytic reactions

#### 2.4.1. General experimental procedure for the Suzuki coupling reaction

A mixture of aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), $K_2CO_3$ (2.0 mmol), DMF-$H_2O$ (1:1, 6 mL), and 0.4 mol% of catalyst was stirred at 70 °C in air for 3 h. Progress of the reaction was monitored by withdrawing samples periodically that were analyzed by GC–MS. Yields, calculated from GC, were based on the amount of aryl halide employed. At the end of the reaction, the catalyst was separated by simple filtration. The mixture was extracted with diethyl ether (20 mL), washed with water and dried over anhydrous $Na_2SO_4$. The solvent was completely removed from the extract with a rotary evaporator to obtain the product, which was further purified by column chromatography on silica gel. All reaction products were identified by gas chromatography-mass spectroscopy (GC–MS) and $^1H$ NMR spectra.

#### 2.4.2. General experimental procedure for the Heck reaction

A mixture of aryl halide (1.0 mmol), styrene (1.5 mmol), $K_2CO_3$ (2.0 mmol), DMF-$H_2O$ (1:1, 6 mL), and 0.4 mol% of catalyst was heated to 90 °C in air for 10 h. Progress of the reaction was monitored by periodically withdrawing samples from the reaction mixture and analyzing them by GC–MS. Yields, calculated from GC, were based on the amount of aryl halide employed. The resulting reaction mixture was filtered and washed with a saturated NaCl aqueous solution (10 mL) and extracted with ethyl acetate (20 mL). The organic phase was separated and dried over $Na_2SO_4$, and ethyl acetate was evaporated under reduced pressure. The final product was isolated by column chromatography. All reaction products were identified by GC–MS and $^1H$ NMR spectra.

#### 2.4.3. General experimental procedure for the Sonogashira reaction

A mixture of aryl halide (1.0 mmol), phenylacetylene (1.5 mmol), $K_2CO_3$ (1.5 mmol), 2,2′-bipyridine-4,4′-dicarboxylic acid (0.005 mmol), CuI (0.012 mmol), DMF-$H_2O$ (1:1, 6 mL), $Bu_4NCl$ (1.0 mmol) and 0.4 mol% of catalyst was stirred at 100 °C in argon. Progress of the reaction was monitored by GC–MS. Yields, calculated from GC, were based on the amount of aryl halide employed. At the end of the reaction, the mixture was poured into a saturated NaCl aqueous solution (10 mL) and extracted with ethyl acetate (20 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel. All reaction products were identified by GC–MS and $^1H$ NMR spectra.

#### 2.4.4. Hot-filtration test and catalyst recycling

The hot filtration test for the Suzuki-Miyaura reaction was carried out according to the standard procedure. After 0.5 h the reaction mixture was filtered at the reaction temperature to remove the solid catalyst, then the mother liquor was allowed to react for another 9 h under identical conditions and the conversion was monitored by GC at different time intervals (see Section 3.3.4). To quantitatively determine the amount of palladium in the final reaction solution atomic absorption spectrophotometry (AAS) was used; no traces of palladium could be detected in the filtrates from the reaction mixtures.

Reusability of the catalyst **1** was studied in the Suzuki-Miyaura cross-coupling reaction of 4-bromoacetophenone and phenylboronic acid. After completion of the reaction, the catalyst was recovered by simple filtration and washed with ethyl acetate, followed by an important amount of water to remove the base, then was dried under vacuum. The recovered catalyst was employed in the next run, with a new addition of substrates in appropriate amount, under the established optimum reaction conditions (see Section 3.3.4). After the catalytic reaction, the crystalline state of catalyst **1** was analyzed by powder X-ray diffraction.

## 3. Results and discussion

### 3.1. Crystallographic structure and characterization of compounds **1–3**

Crystal and structural refinement data for **1**–**3** are displayed in Table 1 while important bond lengths and angles are listed in Table S1. Compounds **1**–**3** are isomorphous, and crystallize in the monoclinic space group $P2/c$. Therefore, only the structure of **1** will be described in detail. The coordination environments around the Pd and Pr metal centers are illustrated in Fig. 1. The crystal structure of **1** contains two crystallographically independent Pd atoms. Pd1 constructs a square planar coordination mode connecting two nitrogen atoms in a $BPDC^{2-}$ ligand and two chlorine atoms in the remaining *cis*-positions with the average bond distances of $d(Pd-N) = 2.02$ Å and $d(Pd-Cl) = 2.28$ Å, respectively. The $N-Pd-N$ angle in **1** decreases from the normal 90° to around 81.0°. Correspondingly, the $Cl-Pd-N$ angle expands from the normal 90° to an average of 94.8°, indicating a typical mode of *cis*-chelating bipyridine. Pd2 has a similar coordination mode to Pd1, being coordinated by the four nitrogen atoms of two $HBPDC^{-1}$ ligands. Two crystallographically equivalent Pr atoms in **1** form Pr dimers with $d(Pr-Pr) = 4.48$ Å. Each Pr atom coordinates with eight oxygen atoms, a $\mu_2$-O atom bridges the two Pr atoms of the dimer, four are carboxylate oxygen atoms from different $H_2BPDC$ ligands

**Table 1**
Crystal data and structure refinement for **1**–**3**.

| | 1 | 2 | 3 |
|---|---|---|---|
| Formula | $C_{48}H_{48}Cl_4N_8O_{28}Pd_3Pr_2$ | $C_{48}H_{46}Cl_4N_8O_{27}Pd_3Gd_2$ | $C_{48}H_{46}Cl_4N_8O_{27}Pd_3Tb_2$ |
| Fw | 1927.76 | 1942.43 | 1945.77 |
| Temp (K) | 293(2) | 293(2) | 293(2) |
| Cryst system | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P2/c* | *P2/c* | *P2/c* |
| *a* (Å) | 17.756(4) | 17.560(3) | 17.683(3) |
| *b* (Å) | 7.052(14) | 6.973(14) | 6.991(14) |
| *c* (Å) | 25.693(5) | 25.330(5) | 25.531(5) |
| β(°) | 106.15(3) | 106.34(3) | 106.12(3) |
| $V$ (Å)$^3$ | 3090.2(11) | 2976.3(10) | 3032.2(10) |
| $Z$ | 2 | 2 | 2 |
| $\rho_{calc}$ (g cm$^{-3}$) | 2.072 | 2.167 | 2.131 |
| $\mu$/mm$^{-1}$ | 2.669 | 3.360 | 3.443 |
| $F(000)$ | 1880 | 1880 | 1884 |
| Reflns collected/unique | 30211/7118 | 18041/5141 | 18690/4965 |
| GOF | 1.108 | 1.050 | 1.010 |
| $R_1$[a] ($I > 2\sigma(I)$) | 0.0515 | 0.0816 | 0.0589 |
| w$R_2$[b] | 0.1214 | 0.1953 | 0.1273 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

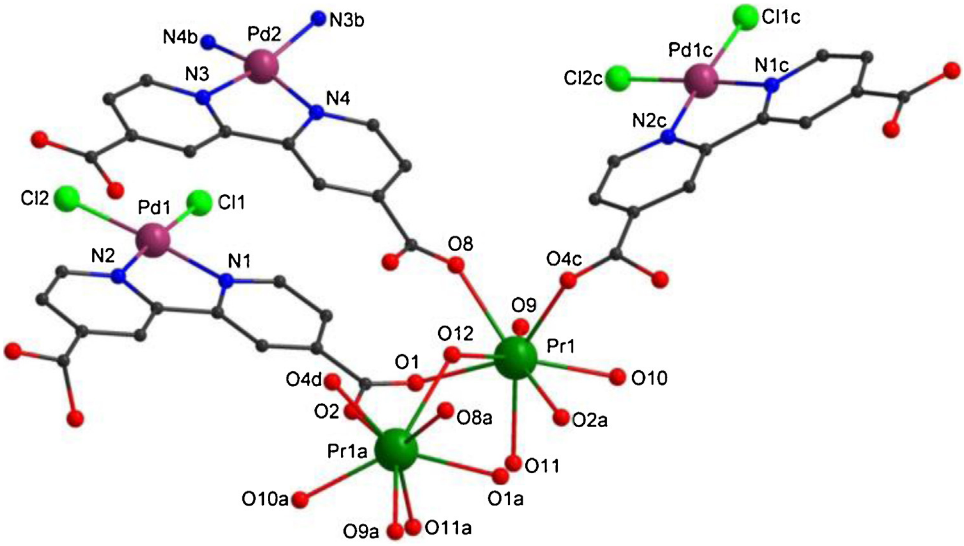


**Fig. 1.** View of the coordination environments of the Pr(III) and Pd(II) ions in catalyst 1. The free $H_2O$ molecules and hydrogen atoms were omitted for clarity. Symmetry codes: (a) -*x*, *y*, 1.5 – *z*; (b) 1 – *x*, *y*, 1.5 – *z*; (c) *x*, 1 – *y*, 0.5 + *z*; (d) –*x*, 1 – *y*, 1 – *z*.

with *d*(Pr – O) around 2.36–2.50 Å, while the remaining three oxygen atoms are terminal water molecules with the *d*(Pr – O) around 2.43–2.53 Å.

It is worth pointing out that the crystal structure of **1** is built up of three distinct types of building blocks: Pd(BPDC)$Cl_2$, Pd(HBPDC)$_2$, and the Pr dimer ($Pr_2O_{15}$). The Pr dimers are connected alternatively by the building blocks of Pd(BPDC)$Cl_2$ to form a 1D linear chain along the *c* axis (Fig. 2). The building blocks of Pd(HBPDC)$_2$ further connect the Pr dimers into infinite 1D chains to construct a 2D layer in the *ac* plane (Fig. 3). Moreover, the 2D layers are assembled into a 3D framework via hydrogen bonding interactions (Fig. S1).

### 3.2. *TG analysis and PXRD*

Thermogravimetric (TG) analysis was performed, in a nitrogen atmosphere, on polycrystalline samples of compounds **1**–**3,** and the TG curves are shown in Fig. S2. As the curves of the three compounds are similar, only that of catalyst **1** will be discussed in detail as a representative compound. The first weight loss of **1** occurring from 120 °C to 370 °C is about 10.17%, corresponding to the loss of the coordinated and free water molecules (calcd: 10.28%). The catalyst is stable up to 370 °C and decomposes above this temperature. The thermogravimetric study thus shows that the Pd(II) compounds degrade at considerably high temperatures.

Powder X-ray diffraction (PXRD) analysis of compounds **1–3** was performed at room temperature (Fig. S3). The patterns for **1–3** are in good agreement with the calculated ones obtained from the single-crystal structures, indicating that the single-crystal structure is really representative for the main constituent of the corresponding sample.

### 3.3. *Catalytic activities*

#### 3.3.1. *Suzuki-Miyaura cross-coupling reaction*

The performance of the Suzuki reaction is dependent on a variety of parameters such as the substrate nature, the catalyst type and its structure, the solvent, base, and temperature. To explore the catalytic activity of our new heterobimetallic catalysts, we based our investigation on the standard Suzuki-Miyaura cross-coupling reac-

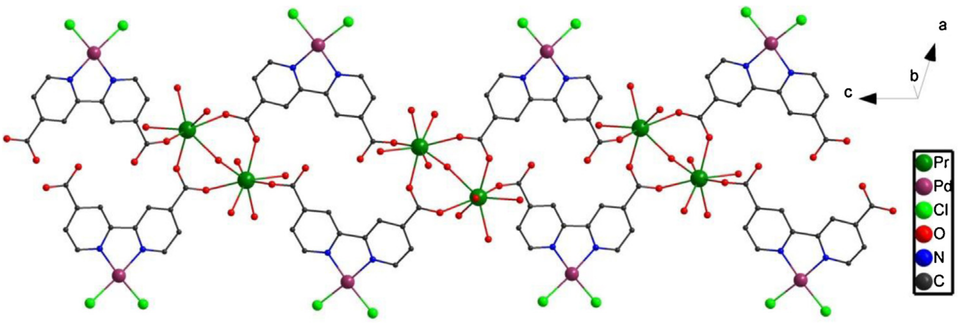


**Fig. 2.** One-dimensional chain of catalyst 1.

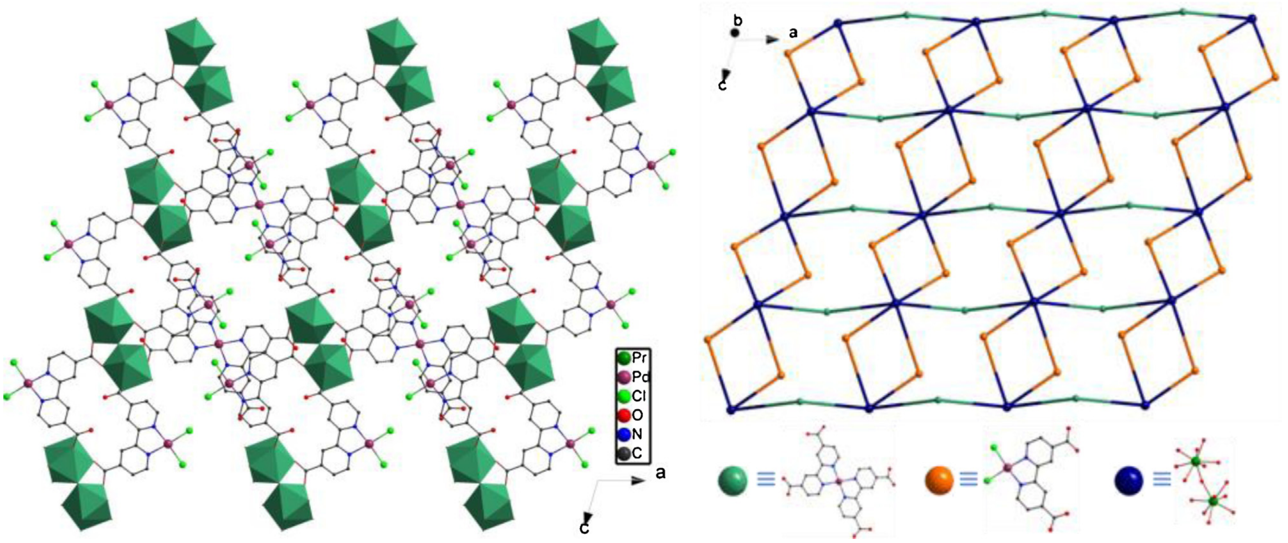
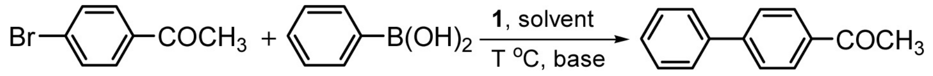


**Fig. 3.** Two-dimensional layer (left) and topology (right) of catalyst 1.

**Table 2**
Optimization of reaction conditions for the Suzuki-Miyaura coupling of 4-bromoacetophenone with phenylboronic acid, catalyzed by **1**.[a]



| Entry | Solvent | Base | T/°C | Time/h | Yield(%)[b] |
|---|---|---|---|---|---|
| 1 | Toluene | $K_2CO_3$ | 100 | 12 | 31 |
| 2 | $H_2O$ | $K_2CO_3$ | 90 | 12 | 59 |
| 3 | DMF | $K_2CO_3$ | 100 | 12 | 5 |
| 4 | DMF-$H_2O$ | $K_2CO_3$ | 70 | 3 | 91 |
| 5 | DMF-$H_2O$ | $t$-$C_4H_9ONa$ | 70 | 3 | 71 |
| 6 | DMF-$H_2O$ | $K_2CO_3$ | 50 | 7 | 87 |
| 7 | DMF-$H_2O$ | $K_2CO_3$ | 25 | 7 | 72 |
| 8 | DMF-$H_2O$ | $K_2CO_3$ | 70 | 1.5 | 83 |
| 9 | DMF-$H_2O$ | $K_2CO_3$ | 90 | 3 | 88 |
| 10 | DMF-$H_2O$ | $K_2CO_3$ | 70 | 12 | 0[c] |
| 11 | DMF-$H_2O$ | None | 70 | 12 | 0 |

[a] Reaction conditions: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst (0.4 mol%).

[b] Yields were determined by GC and GC–MS analyses.

[c] No catalyst.

tion of 4-bromoacetophenone and phenylboronic acid starting with catalyst **1**. The reaction conditions were systematically optimized, and the results are presented in Table 2. A control experiment indicated that, as expected, the coupling reaction did not occur in the absence of catalyst (entry 10). It was found that, among the tested solvents, unsatisfactory yields were obtained with single solvents like toluene, DMF or water, even at 100 °C and increased reaction times (Table 2, entries 1–3). However, a 1:1 mixture of DMF-$H_2O$ proved an efficient system for the cross-coupling making yields to improve significantly (Table 2, entries 4–9). The organic/aqueous co-solvent is conducive to solve the solubility problems of the organic reactants and the inorganic base thus accelerating the reaction. Moreover, it appears that water, in addition to better solving the inorganic base, has a beneficial kinetic effect on the transmetallation step of the catalytic cycle enhancing solvation of the inorganic and boronic salts involved in Suzuki-Miyaura reaction. This effect may not occur in conventional organic solvents like toluene [10a]. After selecting DMF-$H_2O$ (v/v = 1:1) as the optimal solvent combination, bases have been in turn screened. The base has previously been demonstrated to play a significant role in Suzuki-Miyaura cross-coupling reactions [23]. As shown in entry 11, Table 2, the reaction cannot be carried out in the absence of base. It became clear from the results that the inorganic base, $K_2CO_3$, was much more suitable than the organic one (Table 2, entry 4 *vs*. 5). Also, the temperature and time are essential reaction parameters (Table 2, entries 6 *vs*. 7 and entry 4 *vs*. 8). At room temperature, the yield dropped to 72% (Table 2, entry 7). We found that using $K_2CO_3$ as the base, in DMF-$H_2O$ (1:1) at 70 °C and 3hr reaction time, gave the coupled product in the best yield.

Having established the optimal reaction conditions, we then investigated the reaction using various aryl halides bearing electron-donating and electron-withdrawing groups in the *para* position which were coupled with arylboronic acids. As shown in Table 3, catalysts **1**–**3** displayed approximately the same catalytic activities leading to similar yields. Therefore, catalyst **1** was chosen as a model and further applied in other types of cross-coupling reactions. It is commonly believed that higher yields are achieved for aryl halides endowed with electron-withdrawing rather than electron-donating substituents. In our case this could be evidenced by the parallel reactions of aryl iodides bearing electron-releasing or electron-accepting substituents and phenylboronic acid (Table 3, entries 6–8). Substituted arylboronic acids were also tested to furnish the corresponding biaryl products (Table 3, entries 9–13). In contrast to the effects of substituents on the aryl halides, a better activity with the catalyst **1** containing Pr was observed for electron-rich relative to electron-poor arylboronic acids (Table 3, entry 10 *vs*. 13). As expected, aryl chlorides were less reactive than aryl bromides and iodides. A rationale for these outcomes is the much higher C—Cl bond strength (*vs*. C—Br and C—I) [24] accounting for the lower yields obtained (Table 3, entries 14–15). It is worth mentioning that the obtained yields for the catalyst loadings and eco-friendly reaction conditions used in our studies are in good agreement with previous reports [10a] on Suzuki-Miyaura cross-coupling with Pd-Ln systems where similar substrates but toluene as a solvent, higher temperatures and slightly longer times have been employed. Only in special cases (for highly hindered substrates or much elaborated, expensive Pd catalysts [13a]) the reported performance can significantly differ from ours.

### 3.3.2. *Heck cross-coupling reaction*

Stimulated by the above results obtained with catalysts **1**–**3** in the Suzuki-Miyaura reaction, our attention next turned to the palladium-catalyzed Heck cross-coupling reaction of aryl halides with styrene, an extremely valuable method for carbon—carbon bond formation. In activity studies with our catalysts in the Heck contextHeckhh, an excess of styrene with respect to the aryl halide (molar ratio = 1.5) was customarily employed to avoid the formation of homocoupling by-products. A series of experiments, run to optimize the reaction parameters, indicated that best results can be attained with tetrabutylammonium chloride (TBAC) as phase transfer agent, $K_2CO_3$ as the base, in DMF-$H_2O$ as the solvent (Table 4). The coupling reactions of aryl iodides and substituted aryl bromides with styrene proceeded smoothly and all products showed *E* configuration. Moreover, substituents on the aromatic ring of the aryl halides had a significant effect on the yields, *para*-substituted aryl iodides with electron-withdrawing groups reacting faster than those with electron-donating groups (Table 4, entries 1 and 4), yet aryl chlorides gave no conversion (entries 8–9). Compared with substituted aryl bromides, the reaction of bromobenzene led to a much lower product yield (entries 6 *vs*. 7). Again the role of water as cosolvent was similar to that observed in many “solid–liquid” phase-transfer catalyzed organic processes in which the importance of water has been well evidenced [25].

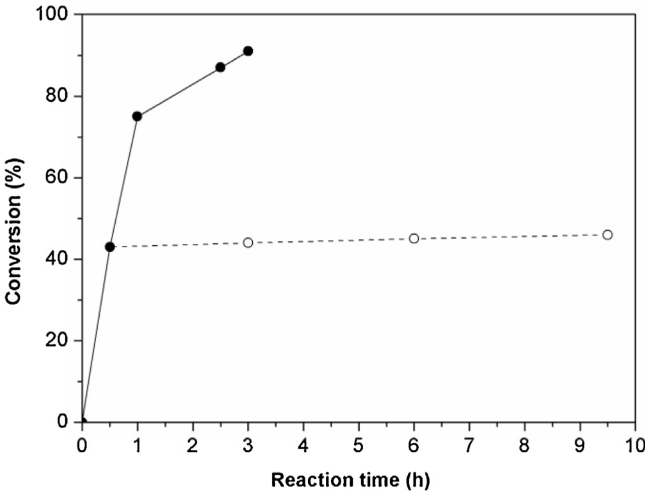


**Fig. 4.** Plots of conversion *versus* time for the Suzuki-Miyaura cross-coupling reaction of 4-bromoacetophenone with phenylboronic acid in the presence of 1 (solid line). Also shown is the conversion of the same reaction upon removal of 1 by filtration after only 0.5 h reaction time (dashed line).

### 3.3.3. *Sonogashira cross-coupling reaction*

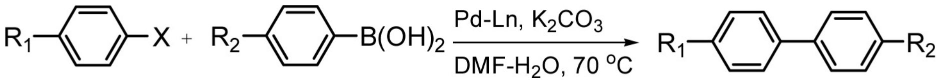
The encouraging results from the Suzuki and Heck reactions, led us to also examine the catalytic behaviour of **1**–**3** in the Sonogashira cross-coupling. To our delight, **1–3** were active enough to promote the Sonogashira reactions of various aryl halides and phenyl acetylene in good yields (Table 5). It was found that the reaction run in DMF-$H_2O$ using $K_2CO_3$ as the base, a small amount of $H_2$BPDC, CuI as co-catalyst and tetrabutylammonium chloride (TBAC) as phase transfer agent, at 100 °C under argon, displayed the best performance. Comparison of entries 1 and 4, entries 5 and 6, or entries 7 and 8 evidences that the yield improved slightly, not sharply, when CuI was added, what suggests that the activity of the catalyst itself is high. That, however, CuI plays a role in facilitating the transmetallation step of the catalytic cycle [26] is clearly evidenced in this work by the drop in yield in its absence (Table 5, entry 7). Aryl halides bearing electron-withdrawing or electron-donating groups showed obvious differences in reactivity with phenyl acetylene (entries 1, 6 and 8 in Table 5), indicating that under the tested conditions the reaction is sensitive to electronic effects of the substituents. As expected, aryl bromides and aryl chlorides were less reactive than aryl iodides (entries 9–12 in Table 5).

### 3.3.4. *Heterogeneity test and recyclability*

A hot-filtration test was carried out in the Suzuki-Miyaura cross-coupling reaction of 4-bromoacetophenone with phenylboronic acid to determine whether the reaction proceeds in a heterogeneous or a homogeneous phase. When catalyst **1** was removed by filtration after only half an hour, just a 40% conversion was recorded. Upon additional standing for 9.5 h of the filtrate, we found that no further conversion has taken place (Fig. 4), indicating the absence of catalyst in the filtrate. The important conclusions here are twofold: that a perfect separation and recovery of the solid catalyst can be achieved and plus that the catalytic system can be reused.

Recovery and reuse of the catalyst are important issues in environmentally benign coupling reactions [12d]. Easy catalyst separation and recycling in successive batch operations can greatly increase the economic outcome of the reaction. Tests were run on catalyst **1** in the Suzuki-Miyaura cross-coupling as a model reaction. In four consecutive runs high yields have been attained (over 85% yield in the fourth cycle, hence a loss of just 7% of the initial catalytic activity) (Fig. 5). Noteworthy also, the catalyst structure is preserved throughout the catalytic process. PXRD analysis shows

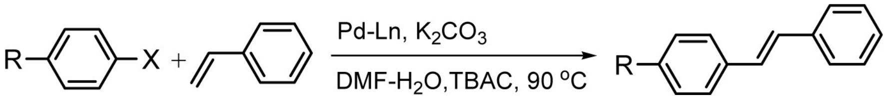
**Table 3**
Suzuki-Miyaura cross-coupling reaction of aryl halides and arylboronic acids using Pd – Ln catalysts **1–3**.[a]



| Entry | *R*$_1$ | *R*$_2$ | *X* | Catalyst[b] | Yield(%)[c] |
|---|---|---|---|---|---|
| 1 | $CH_3CO$ | H | Br | **1** | 91 |
| 2 | $CH_3CO$ | H | Br | **2** | 89 |
| 3 | $CH_3CO$ | H | Br | **3** | 92 |
| 4 | $NO_2$ | H | Br | **1** | 89 |
| 5 | H | H | Br | **1** | 86 |
| 6 | H | H | I | **1** | 80 |
| 7 | $CH_3$ | H | I | **1** | 90 |
| 8 | $CH_3CO$ | H | I | **1** | 93 |
| 9 | H | $CH_3$ | Br | **1** | 91 |
| 10 | $CH_3CO$ | $CH_3$ | Br | **1** | 92 |
| 11 | $NO_2$ | $CH_3$ | Br | **1** | 94 |
| 12 | H | $CH_3CO$ | Br | **1** | 89 |
| 13 | $CH_3CO$ | $CH_3CO$ | Br | **1** | 70 |
| 14 | $CH_3$ | H | Cl | **1** | Trace |
| 15 | $CH_3CO$ | H | Cl | **1** | 22 |

[a] Reaction conditions: aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), $K_2CO_3$ (2.0 mmol), DMF-$H_2O$ (1:1, 6.0 mL), catalyst (0.4 mol%), 3 h.
[b] **1** [Pd – Pr], **2** [Pd – Gd], **3** [Pd – Tb].
[c] Yields were determined by GC and GC–MS analyses.

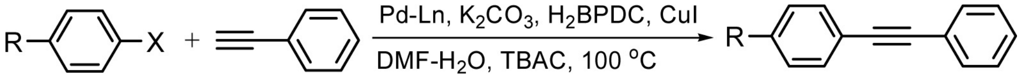
**Table 4**
Heck cross-coupling reaction of aryl halides and styrene using Pd – Ln catalysts.[a]



| Entry | R | X | Catalyst[b] | Yield(%)[c] |
|---|---|---|---|---|
| 1 | $CH_3CO$ | I | **1** | 83 |
| 2 | $CH_3CO$ | I | **2** | 83 |
| 3 | $CH_3CO$ | I | **3** | 85 |
| 4 | $CH_3$ | I | **1** | 77 |
| 5 | H | I | **1** | 80 |
| 6 | H | Br | **1** | 23 |
| 7 | $CH_3CO$ | Br | **1** | 63 |
| 8 | $CH_3$ | Cl | **1** | 0 |
| 9 | $CH_3CO$ | Cl | **1** | 0 |

[a] Reaction conditions: aryl halide (1.0 mmol), styrene (1.5 mmol), $K_2CO_3$ (2.0 mmol), DMF-$H_2O$ (1:1, 6.0 mL), TBAC (1.5 mmol), catalyst (0.4 mol%), 10 h.
[b] **1** [Pd – Pr], **2** [Pd – Gd], **3** [Pd – Tb].
[c] Yields were determined by GC and GC–MS analysis.

**Table 5**
Sonogashira cross-coupling reaction of aryl halides and phenylacetylene using Pd – Ln catalysts.[a]



| Entry | R | X | Catalyst[b] | Yield(%)[c] |
|---|---|---|---|---|
| 1 | $CH_3CO$ | I | **1** | 80 |
| 2 | $CH_3CO$ | I | **2** | 79 |
| 3 | $CH_3CO$ | I | **3** | 83 |
| 4 | $CH_3CO$ | I | **1** | 76[d] |
| 5 | $CH_3$ | I | **1** | 60[d] |
| 6 | $CH_3$ | I | **1** | 77 |
| 7 | H | I | **1** | 51[d] |
| 8 | H | I | **1** | 64 |
| 9 | H | Br | **1** | trace |
| 10 | $CH_3CO$ | Br | **1** | 12 |
| 11 | $CH_3$ | Cl | **1** | trace |
| 12 | $CH_3CO$ | Cl | **1** | trace |

[a] Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (1.5 mmol), $K_2CO_3$ (1.5 mmol), DMF-$H_2O$ (1:1, 6.0 mL), catalyst (0.4 mol%), $H_2BPDC$ (0.005 mmol), TBAC (1 mmol), CuI (0.012 mmol), 8 h.
[b] **1** [Pd – Pr], **2** [Pd – Gd], **3** [Pd – Tb].
[c] Yields were determined by GC and GC–MS analyses.
[d] No CuI.

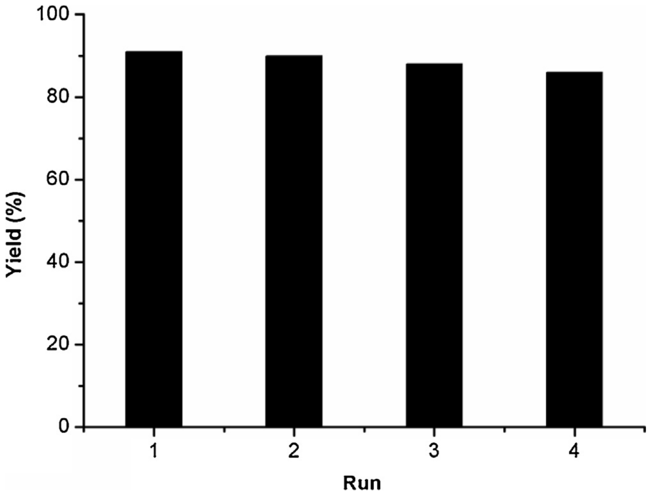


**Fig. 5.** Recyclability of catalyst 1 for the Suzuki-Miyaura cross-coupling reaction of 4-bromoacetophenone with phenylboronic acid.

that after the catalytic reaction, the crystalline state and structural integrity of catalyst **1** were maintained (Fig. S4). No deterioration of the recovered catalyst was observed and no palladium could be detected in the filtered liquid from the reaction mixture by atomic absorption spectrophotometry (AAS), confirming the high stability and robustness of this heterogeneous catalytic system and its great potential for reusability in several consecutive runs without a substantial loss of the initial activity. These findings are very important for the development of environmentally benign cross-coupling processes in compliance with the principles of green chemistry and sustainability.

## 4. Conclusions

A set of novel porous, heterobimetallic coordination polymers, containing clusters of Pd(II) and Ln(III) (Ln = Pr, Gd, Tb) interconnected by the heteroleptic ligand 2,2′-bipyridine-4,4′-dicarboxylate, have easily become accessible by hydrothermal synthesis. The new Pd-based nanostructures, resulting by association of two cooperative, distinct metal sites have been efficiently employed as heterogeneous catalysts in Suzuki-Miyaura, Heck and Sonogashira cross-coupling reactions. The catalysts used are stable in air and water, display substantial robustness and good tolerance towards functional groups, allowing remarkable versatility. Also important from environmental and green chemistry perspectives, these new heterogeneous promoters enable a safe and clean reaction profile by the facile separation and purification of the reaction products, outperforming previously reported palladium/lanthanide catalysts for carbon–carbon cross-coupling reactions. Further assets for a total cost reduction are the simplicity of the synthetic protocols, the advantageous recovery of the solid catalyst and its recyclability which proceeds without substantial catalyst deactivation. Sustainability has been demonstrated by four consecutive catalytic cycles without loss of catalyst activity. Moreover, being able to perform Suzuki-Miyaura, Heck and Sonogashira reactions in air and water systems as solvent makes such chemical transformations quite economical, eco-friendly and suitable for practical applications with a wide range of reagents.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.11.044.

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