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High catalytic activity in aqueous heck and Suzuki–Miyaura reactions catalyzed by novel Pd/Ln coordination polymers based on 2,2′-bipyridine-4,4′-dicarboxylic acid as a heteroleptic ligand

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ABSTRACT

Four novel heterobimetallic Pd/Ln coordination polymers, $[LnPd(BPDC)_{5/2}(H_2O)\cdot 4H_2O]_n$ (Ln = Nd (**1**), Sm (**2**), Eu (**3**) and Dy (**4**); H_2BPDC = 2,2′-bipyridine-4,4′-dicarboxylic acid), have been synthesized under hydrothermal conditions and characterized by X-ray crystallography, thermogravimetric (TG) analysis, powder X-ray diffraction (PXRD) spectroscopy, elemental analysis and infrared spectroscopy (IR). Single-crystal X-ray diffraction analysis revealed that compounds **1**–**4** are isomorphous, having a 2D layer structure with a triclinic crystal system. The new Pd/Ln coordination polymers displayed impressively high activity in Heck and Suzuki–Miyaura cross-coupling reactions under eco-friendly, aqueous conditions.

1. Introduction

Over the past few decades, research in the field of coordination polymers (CPs) has become one of the fastest growing areas of chemistry as these hybrid materials have intriguing structures and are endowed with unique properties, recommending them for multifarious applications [1]. Recent examples of such frameworks centre on the development of functional materials capable of inducing photocatalysis [2], photoluminescence [3], proton conduction [4] or which are suitable for chemical sensing [5], gas storage [6], adsorptive separation [7], drug delivery, etc. [8]. On the other hand, CPs have recently emerged as a versatile platform for creating heterogeneous catalysts, *e.g.* based on Pd(II), Ru(II) and Rh(II)-complexes [9,10], used in organic synthesis [11]. Palladium-containing coordination polymers (Pd-CPs) have been intensively investigated, owing to their powerful synthetic function and key role in industrial processes [12]. Pd-CPs and other metal-CPs catalysts have been used to trigger a range of reactions including alcohol oxidation [13,14], olefin hydrogenation [15], in photocatalysis [16] and carbon–carbon cross-couplings [17]. Of these, palladium-catalyzed cross-coupling reactions, the most popular method for forming C–C bonds, have become convenient tools in organic synthesis [18]. Improvements in C–C cross-couplings have been implemented using *green* solvents to reduce the generation of environmentally hazardous waste [19]. Water is especially attractive as a green solvent because it is largely available, non-toxic, non-flammable, inexpensive and can be easily separated from organic products [20]. Among the different approaches aimed at reaching environmentally-friendly reaction conditions, the most often used C–C coupling procedures are based on mixtures of organic solvents and water [21–23].

In the present work, we disclose the synthesis and full structural characterization of four novel heterobimetallic coordination polymers, namely $[LnPd(BPDC)_{5/2}(H_2O)_2\cdot 4H_2O]_n$ (Ln = Nd (**1**), Sm (**2**), Eu (**3**) and Dy (**4**)), which coordinate Pd(II) and Ln(III) ions with the heteroleptic ligand 2,2′-bipyridine-4,4′-dicarboxylic acid (H_2-BPDC). Moreover, we focus on the catalytic performance of the newly synthesized compounds **1**–**4** in Heck and Suzuki–Miyaura cross-couplings, proceeding in an environmentally benign reaction medium (DMF-H_2O).

2. Experimental

2.1. Materials and physical–chemical measurements

All chemicals were purchased commercially and used without further purification. The syntheses of **1**–**4** were carried out in

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20 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 analyses were performed on a Perkin-Elmer 240C elemental analyzer. FT-IR spectra, using KBr pellets, were recorded with 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 $K\alpha$ 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.

2.2. Synthesis of complexes **1**–**4**

The complexes **1**–**4** were synthesized under hydrothermal conditions. K_2PdCl_4 (0.145 mmol, 0.0473 g), 2,2′-bipyridine-4,4′-dicarboxylic acid (0.153 mmol, 0.0374 g) and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Nd (0.09 mmol, 0.0395 g), Sm (0.09 mmol, 0.0401 g), Eu (0.09 mmol, 0.0403 g) or Dy (0.09 mmol, 0.0402 g) were mixed in Teflon-lined vessels filled with a solution of 6 mL H_2O and 6 mL NaOH (0.1 mol L^{-1}); the mixture was placed in an oven and heated at 95 °C for 96 h, then cooled to room temperature. The resulting light yellow diamond crystals were filtered, washed thoroughly with distilled water and dried in air. The yields of the complexes, based on the rare earth nitrate, are: **1**, 37%; **2**, 41%; **3**, 38%; **4**, 37%. Elemental *Anal.* Calc. for **1** ($C_{30}H_{25}N_5O_{15}PdNd$): C, 38.08; H, 2.66; N, 7.40. Found: C, 38.05; H, 2.69; N 7.39%. *Anal.* Calc. for **2** ($C_{30}H_{25}N_5O_{15}PdSm$): C, 37.84; H, 2.65; N, 7.35. Found: C, 37.86; H, 2.59; N, 7.37%. *Anal.* Calc. for **3** ($C_{30}H_{25}N_5O_{15}PdEu$): C, 37.77; H, 2.64; N, 7.34. Found: C, 37.83; H, 2.69; N, 7.37%. *Anal.* Calc. for **4** ($C_{30}H_{25}N_5O_{15}PdDy$): C, 37.36; H, 2.61; N, 7.26. Found: C, 37.39; H, 2.69; N, 7.29%. IR (KBr, cm^{-1}) for **1**: 3422vs, 1638vs, 1541w, 1366vs, 1242w, 783w, 703 m; for **2**: 3414vs, 1638 s, 1555w, 1384.vs 1244w, 784 m, 704 m; for **3**: 3423vs, 1638vs, 1541w, 1384 s, 704 m; for **4**: 3400 s, 1615 s, 1551 m, 1408w, 1384vs, 1291w, 1244w, 1065w, 778 m, 702 m.

2.3. X-ray crystallography

Crystallographic data were collected on a Bruker Smart Apex CCD diffractometer applying graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). An empirical absorption correction was applied to the data using the SADABS program [24]. All the structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL crystallographic software package [25]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding mode. Crystal and structural refinement data for **1**–**4** are displayed in Table 1 while important bond lengths and angles are listed in Table S1.

2.4. Catalytic reactions

2.4.1. General experimental procedure for the Heck reaction

A mixture of aryl halide (1.0 mmol), styrene (1.5 mmol), t-C_4H_9OK (2.0 mmol), DMF-H_2O (1:1, 6 mL) and 0.4 mol% of catalyst (**1**–**4**) was heated at 90 °C in air for 9 h. The mixture was cooled to room temperature, filtered, 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. All coupling products were purified by column chromatography on silica gel and identified by Agilent 7890A-5975C GC–MS and ^1H NMR spectra. Yields calculated from GC were based on the amount of aryl halide employed.

2.4.2. 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 80 °C in air for 8 h. The mixture was extracted with diethyl ether (20 mL), washed with water and dried over anhydrous Na_2SO_4. All coupling products were purified by column chromatography on silica gel and identified by gas chromatography-mass spectrometry (Agilent 7890A-5975C GC–MS) and from ^1H NMR spectra. GC–calculated yields were based on the amount of aryl halide employed.

3. Results and discussion

3.1. Crystallographic structure and characterization of compounds **1**–**4**

X-ray crystal structure analysis revealed that compounds **1**–**4** are isomorphous and crystallize in the space group $P\bar{1}$. Therefore, only the structure of **2** will be described in detail. As illustrated in Fig. 1a, the unit cell of **2** contains one Sm(III) ion, one Pd(II)

Table 1
Crystal data and structure refinement for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{30}H_{25}N_5O_{15}NdPd$	$C_{30}H_{25}N_5O_{15}SmPd$	$C_{30}H_{25}N_5O_{15}EuPd$	$C_{30}H_{25}N_5O_{15}DyPd$
Fw	946.19	952.30	954.09	964.45
T (K)	293	293	293	293
Cryst. system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.677(5)	9.657(4)	9.652(4)	9.665(6)
b (Å)	13.760(6)	13.729(5)	13.716(4)	13.728(7)
c (Å)	13.946(8)	13.939(7)	13.913(5)	13.892(10)
α (°)	116.77(2)	116.537(14)	116.54(2)	116.31(2)
β (°)	94.29(4)	94.59(3)	94.69(3)	94.77(4)
γ (°)	106.85(3)	106.64(2)	106.526(19)	106.56(3)
V (Å)^3	1540.2(13)	1536.7(11)	1532.2(10)	1535.9(16)
Z	2	2	2	2
ρ_{calc} (g cm^{-3})	2.040	2.058	2.068	2.085
μ (mm^{-1})	2.338	2.565	2.703	3.087
F(000)	932.0	936.0	938.0	944.0
Reflns collected/unique	15874/7005	15925/7033	15852/7030	15934/7027
Goodness-of-fit (GOF)	0.808	1.045	1.042	1.078
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0532	0.0420	0.0388	0.0628
wR_2^b	0.1077	0.0930	0.0920	0.1252

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

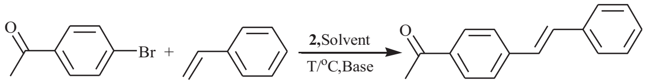
ion, 5/2 $BPDC^{2-}$ ligands, one coordinated water molecule and four lattice water molecules. The Pd(II) ion connects four N atoms from the bipyridine rings of two ligands in a square planar coordination mode to form a $Pd(BPDC)_2$ building block, with an average Pd–N bond distance of 2.046(4) Å. Each Sm(III) ion is coordinated by nine O atoms in a distorted monocapped square antiprismatic geometry, one being from the coordinated water and eight from the carboxyl groups of four different $BPDC^{2-}$ ligands, with Sm–O distances around 2.35–2.65 Å. Two neighbouring Sm(III) ions are bridged by two carboxyl oxygen atoms (from two ligands) to form a dimer (Sm_2O_{16}) with an Sm–Sm distance of 3.9809(13) Å. The Sm_2O_{16} dimers are connected alternatively by two $Pd(BPDC)_2$ and one $BPDC^{2-}$ ligand to form a 1D linear chain along the *c* axis (Fig. 1b). The 1D chains are further connected by the carboxyl groups of $Pd(BPDC)_2$ to construct a 2D layer (Fig. 1c). In addition, the 2D layers are assembled into a 3D framework *via* hydrogen bond interactions (Fig. S1).

3.2. Thermogravimetric (TG) analysis and powder X-ray diffraction (PXRD)

Thermogravimetric (TG) analysis was performed in a nitrogen atmosphere on polycrystalline samples of compounds **1**–**4**; the TG curves are shown in Fig. S2. As the curves of the four compounds are similar, only that of catalyst **2** will be discussed in detail as a representative example. The first weight loss of **2**, occurring from 50 to 180 °C, is about 9.37%, corresponding to the loss of coordinated and free water molecules (calcd: 9.45%). This demonstrates the high stability of **1**–**4**, degrading only at considerably high temperatures.

Powder X-ray diffraction (PXRD) analysis of compounds **1**–**4** was performed at room temperature, 50, 90, 180 and 250 °C (Figs. S3 and S4). The patterns obtained for **1**–**4** are in good agreement with the calculated ones resulting from the single crystal structures; this indicates that every single crystal structure is indeed representative for the main constituent of the corresponding sample and that **1**–**4** retain considerable stability up to 250 °C.

Table 2
Optimization of the reaction conditions for the Heck cross-coupling of 4-bromoacetophenone with styrene, catalyzed by 2.[a]



Entry	Solvent	Base	*T* (°C)	Time (h)	Yield (%)[b]
1	Toluene	*t*-C_4H_9OK	90	9	21
2	H_2O	*t*-C_4H_9OK	90	9	9
3	DMF	*t*-C_4H_9OK	90	9	32
4	DMF-H_2O	*t*-C_4H_9OK	90	9	92
5	DMF-H_2O	K_2CO_3	90	9	85
6	DMF-H_2O	Cs_2CO_3	90	9	78
7	DMF-H_2O	*t*-C_4H_9OK	90	12	93
8	DMF-H_2O	*t*-C_4H_9OK	90	6	72
9	DMF-H_2O	*t*-C_4H_9OK	90	3	51
10	DMF-H_2O	*t*-C_4H_9OK	100	9	87
11	DMF-H_2O	*t*-C_4H_9OK	50	9	21
12	DMF-H_2O	None	90	9	0
13	DMF-H_2O	*t*-C_4H_9OK	90	9	79[c]

[a] Reaction conditions: 4-bromoacetophenone (1.0 mmol), styrene (1.2 mmol), catalyst **2** (0.4 mol%).

[b] Yields were determined by GC analysis.

[c] $Pd(H_2BPDC)Cl_2{\cdot}H_2O$ (0.4 mol%) was used to replace **2**.

3.3. Catalytic activities

3.3.1. Heck cross-coupling reaction

The performance of the Heck cross-coupling reaction is dependent on a variety of parameters, such as the substrate nature, the catalyst type and its structure, the solvent, base, and temperature. Complex **2** was chosen as a model to investigate the catalytic activ-

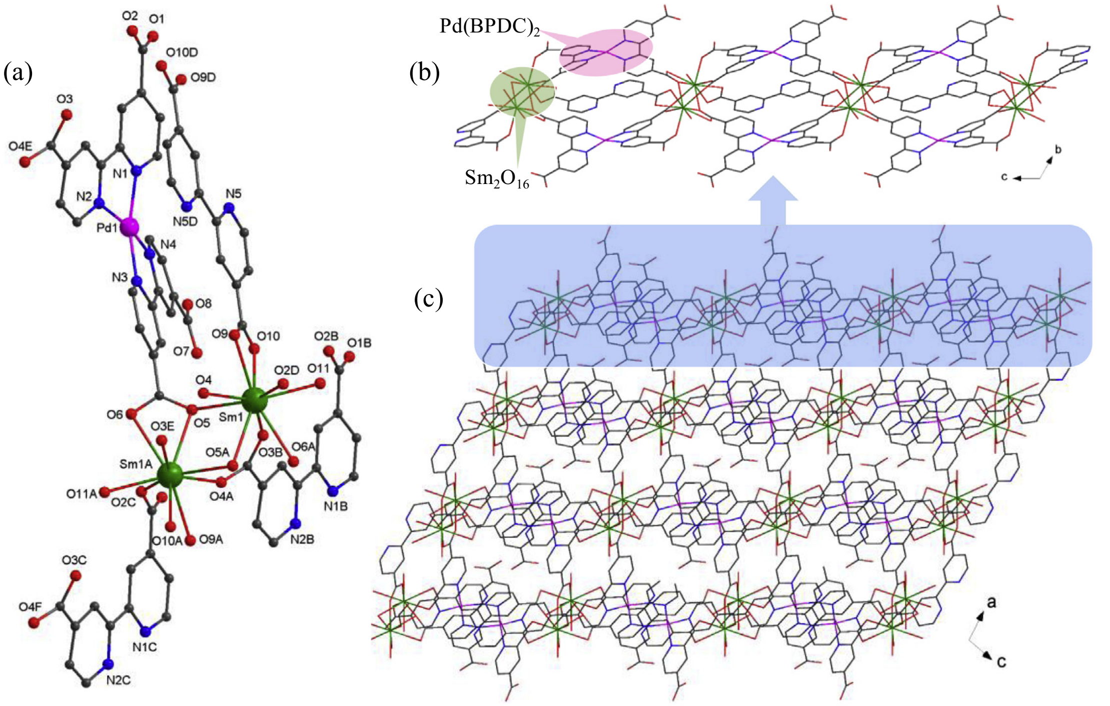


Fig. 1. (a) View of the coordination environments of the Sm(III) and Pd(II) ions in **2**. All hydrogen atoms and free lattice water molecules are omitted for clarity. Symmetry codes: (A) −*x*, −*y*, −1 − *z*; (B) *x*, *y*, −1 + *z*; (C) −1 + *x*, *y*, −1 + *z*; (D) 1 − *x*, −*y*, −*z*; (E) −*x*, −*y*, −*z*; (F) −1 − *x*, −*y*, −1 − *z*. (b) One-dimensional chain of **2**. (c) Two-dimensional layer of **2**.

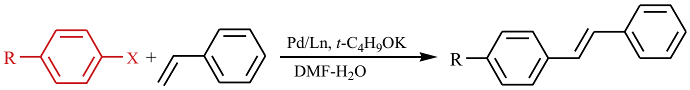
ity in the Heck cross-coupling reaction. The reaction conditions were systematically optimized in the standard reaction of 4-bromoacetophenone with styrene; the results are presented in Table 2. Optimization of the solvent was first performed using toluene, DMF and water under identical reaction conditions. It was found that among the tested solvents unsatisfactory yields were obtained with single solvents (entries 1–3). However, a 1:1 mixture of DMF-H_2O proved an efficient system for the cross-coupling, making the yields improve significantly (entry 4). We further investigated the effect of different bases (Cs_2CO_3, t-C_4H_9OK and K_2CO_3) using DMF-H_2O (1:1, vol.), which was found in this research to be the best solvent combination. The results indicated that t-C_4H_9OK was the most efficient base (entries 4–6), and that the reaction cannot be carried out in the absence of t-C_4H_9OK (entry 12). On the other hand, studies on the effects of reaction temperature and time, conducted using complex **2** under the optimal conditions, revealed that the yield was only 21% after 9 h of reaction at 50 °C (entry 11), as compared with a yield of 92% at 90 °C (entry 4). However, the yield was found to decrease to 87% when the temperature was raised to 100 °C (entry 10). The yields had a tendency to increase when the reaction time was prolonged from 3 to 9 h (entries 4, 8 and 9), but the yield improvement was almost negligible when the time was lengthened to 12 h (entry 7). An advantageous cooperation operating between palladium and the lanthanides is apparent when comparing the yields of the Heck reactions catalyzed by **2** and $Pd(H_2BPDC)Cl_2 \cdot H_2O$ (92 versus 79%; Table 2, Entries 4 and 13). The substantially better performance of catalyst **2** is still more evident if we take into account that **2** ($PdSm(BPDC)_{5/2}(H_2O) \cdot 4H_2O$) has less than half the Pd weight content of $Pd(H_2BPDC)Cl_2 \cdot H_2O$. That lanthanides play a significant role in C–C cross-couplings promoted by 3D Pd/Ln coordination polymers (Ln = Pr, Gd, Tb) has already been demonstrated in our recent study on Suzuki–Miyaura, Heck and Sonogashira reactions [17b].

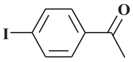
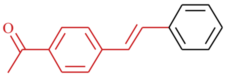
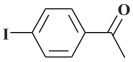
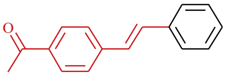
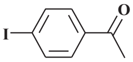
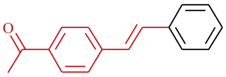
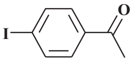
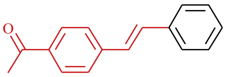
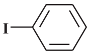
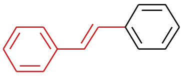
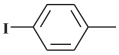
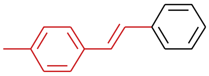
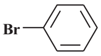
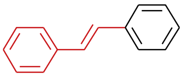
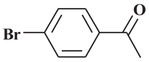
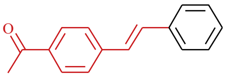
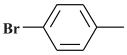
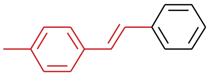
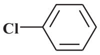
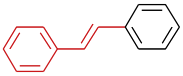
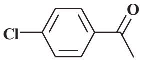
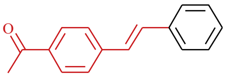
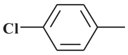
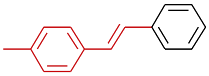
In summary, the optimal conditions found for the Heck cross-coupling reaction using **2** are t-C_4H_9OK as the base, DMF-H_2O (1:1) as the solvent, a temperature of 90 °C and a 9 h reaction time.

With the optimized reaction conditions in hand, the limitations of this transformation were studied (Table 3). A series of aryl halides and styrene have been employed as reactants in the Heck coupling to evaluate the catalytic performance of the Pd/Ln-CPs.

Table 3

Heck cross-coupling reaction of aryl halides and styrene using Pd/Ln-CPs 1–4.[a]



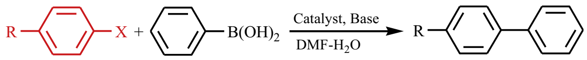
Entry	Catalyst[b]	Aryl halide	Time (h)	Product	Yield (%)[c]
1	**1**		9		98
2	**2**		9		99
3	**3**		9		98
4	**4**		9		96
5	**2**		9		99
6	**2**		9		83
7	**2**		9		87
8	**2**		9		90
9	**2**		9		58
10	**2**		12		9
11	**2**		9		12
12	**2**		12		Trace

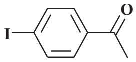
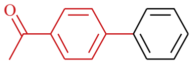
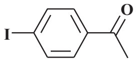
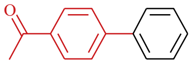
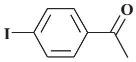
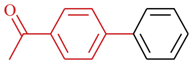
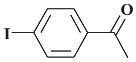
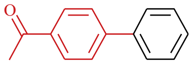
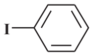
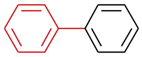
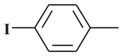
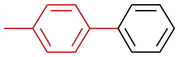
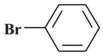
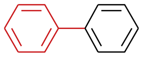
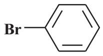
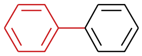
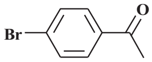
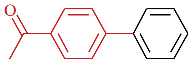
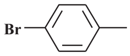
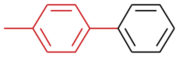
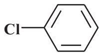
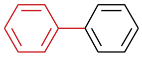
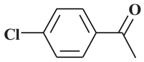
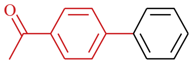
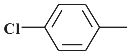
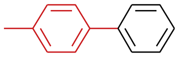
[a] Reaction conditions: aryl halide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2.0 mmol), t-C_4H_9OK (2.0 mmol), DMF-H_2O (1:1, 6 mL), catalyst (0.4 mol%), 90 °C.

[b] **1** [Pd/Nd-CPs], **2** [Pd/Sm-CPs], **3** [Pd/Eu-CPs], **4** [Pd/Dy-CPs].

[c] Yields were determined by GC analysis.

Table 4
Suzuki cross-coupling reaction of aryl halides and arylboronic acids using catalyst **2**.[a]



Entry	Catalyst[b]	Aryl halide	Time (h)	*T* (°C)	Product	Yield (%)[c]
1	**1**		7	80		97
2	**2**		7	80		98
3	**3**		7	80		97
4	**4**		7	80		95
5	**2**		7	80		98
6	**2**		9	80		82
7	**2**		9	80		73
8	**2**		9	80		62 [d]
9	**2**		9	80		78
10	**2**		9	80		62
11	**2**		12	90		18
12	**2**		12	90		31
13	**2**		12	90		7

[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 mL), catalyst (0.4 mol%).
[b] **1** [Pd/Nd-CPs], **2** [Pd/Sm-CPs], **3** [Pd/Eu-CPs], **4** [Pd/Dy-CPs].
[c] Yields were determined by GC analysis.
[d] Reaction conditions: bromobenzene (1.0 mmol), *t*-C_4H_9OK (2.0 mmol), DMF-H_2O (1:1, 6 mL), catalyst **2** (0.4 mol%).

As shown in Table 3, complexes **1**–**4** displayed approximately the same catalytic activity, leading to similar yields (Entries 1–4). Therefore, complex **2** was chosen as a model catalyst for further Heck reactions. The coupling of styrene with iodobenzene afforded the expected *trans*-stilbene in very high yield (98%; Entry 5) while the reaction with bromobenzene also led to a good yield (87%; Entry 7). However, a pronounced drop in activity was observed for the sluggish chlorobenzene (9%; Entry 10), even after a reaction time of 12 h. As should have been expected, the catalytic activity decreases from iodobenzene to bromobenzene and chlorobenzene because of the ever enhanced difficulty in activating the C–halide bond which is essential in the oxidative addition step of the catalytic cycle. The presence of a methyl group on the aromatic halide has a negative effect on the reaction yield (Entries 6 versus 5; 9 versus 7; 12 versus 10), suggesting that electron-donating substituents impede C–halide bond activation, thus resulting in a poor reactivity. Conversely, the presence of electron-withdrawing substituents on the aromatic halide greatly promotes the cross-coupling reaction leading to almost quantitative yields (99% for acetyl on 4-iodoacetophenone and 90% for acetyl on 4-bromoacetophenone; entries 2 and 8, respectively). Yet the effect of such substituents is much diminished in the case of aromatic chlorides (just 12% yield versus 9% yield; entry 11, versus 10).

The above results on the substrate behaviour can be rationalized by considering the involvement of the aryl halide bond in the oxidative addition step from the palladium catalytic cycle of **1**–**4**. On the contrary, the reductive elimination step appears to be greatly influenced by the base, the aqueous solvent and also the lanthanide, endowed with a strong reducing ability stemming from its electropositive nature.

3.3.2. Suzuki–Miyaura cross-coupling reaction

To our delight, catalysts **1**–**4** were also active in promoting the Suzuki–Miyaura cross-coupling reaction, displaying similar catalytic profiles (Table 4, Entries 1–4). As shown in this table, compound **2** readily catalyzes Suzuki–Miyaura coupling reactions in DMF-H_2O (1:1 vol.), at a low catalyst loading (0.4 mol%). In the case of this cross-coupling we found that K_2CO_3 is a much better base than *t*-C_4H_9OK, a result contrasting with data from the Heck reaction with the same catalyst **2** (Entries 7 versus 8). Then, reaction parameters such as substrate, time and temperature were varied to establish their influence on the product yields. The nature of the aryl halide plays a key role. The highest yields were obtained for aryl iodides (98%; entries 2 and 5 for iodobenzene and 4-iodoacetophenone after 7 h at 80 °C). However, for bromobenzene and 4-bromoacetophenone a longer time (9 h) was needed to obtain substantial yields (73% and 78%; entries 7 and 9, respectively). A similar trend of the electronic effects played by substituents on the aryl halides as in the Heck reactions was observed in Suzuki cross-couplings catalyzed by **2**. Electron-withdrawing substituents vigorously promote the reaction (exceptionally high yields of 98%) while the reverse holds true for electron-releasing substituents. Overall, substrate reactivity decreases in the following order of the substituents on the aryl halide: $-CH_3CO > -H > -CH_3$. Notwithstanding, the type of halide prevails over the role of the substituent with which it is equipped (biaryl yields of 98% for iodobenzene, after 7 h, and 73% for bromobenzene, after 9 h, whereas the difference in yields is smaller for the methyl-substituted counterparts: 82% *vs.* 62% for iodotoluene *vs.* bromotoluene. Table 4). Consequently, the electronic effect of the substituent is more easily noticeable on the less reactive aryl halides (yields of 31% for 4-acetyl-chlorobenzene, 18% for chlorobenzene and just 7% for 4-methyl-chlorobenzene, at the same temperature and reaction time; entries 11–13).

Our results demonstrate again the established role of aryl halides in the oxidative addition step of the palladium catalytic cycle with catalysts **1**–**4**, the rate determining step of the Suzuki–Miyaura reaction. By contrast, the base and aqueous solvent supposedly influence the transmetallation/ligand exchange and reductive elimination steps of the catalytic cycle. The lanthanides, besides their role as a charge vector within the catalyst matrix and their coordination abilities, also affect the reductive elimination step due to their electropositive propensity. An in-depth understanding of the detailed mechanism by which the lanthanides cooperate with palladium in these carbon–carbon cross-coupling processes would, however, need further exploration.

It should be emphasized that on most favourable substrates, like the aryl iodides commonly used in the Suzuki–Miyaura reaction, all our novel heterobimetallic catalysts provide excellent performance even under low catalyst loading and convenient reaction conditions like temperature and time and, importantly, in a more benign solvent mixture ($DMF-H_2O$).

4. Conclusions

In this contribution a series of new heterobimetallic Pd/Ln (Ln = Nd (**1**), Sm (**2**), Eu (**3**) and Dy (**4**)) polymeric frameworks have been conveniently prepared under hydrothermal conditions by the coordination of Pd(II) and Ln(III) ions through the heteroleptic ligand 2,2′-bipyridine-4,4′-dicarboxylic acid (H_2BPDC). Compounds **1**–**4** were proved to be isomorphous and to display similar 2D structures consisting of two distinct types of building blocks, Ln_2O_{16} and $Pd(BPDC)_2$. On testing their thermal stabilities we found that **1**–**4** do not degrade up to 400 °C. When applied in Heck and Suzuki–Miyaura C–C cross-coupling reactions, compounds **1**–**4** exhibited excellent catalytic activities leading to very high yields (up to 99% in Heck and 98% in Suzuki–Miyaura reactions with catalyst **2**), even at low catalyst loading and moderate temperatures and reaction times. Moreover, conditions were identified for both chemical transformations to proceed in an environmental-friendly medium. Overall the results point to an advantageous cooperation between palladium and lanthanides during the catalytic cycle, mediated by the bifunctional organic ligand.

Acknowledgments

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Appendix A. Supplementary data

CCDC 1432828 (**1**), 1432829 (**2**), 1432827 (**3**) and 1432826 (**4**) contains the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.04.032.

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