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A heterometal (Pd–Pb) organic framework: synthesis, structure and heterogeneous catalytic application

Yanwei Ren*, Ou Jiang, Jiawei Li and Hang Zeng

A heterometallic organic framework {Pb[Pd(bpydc)Cl_2]DMF}$_n$ (1) (H_2bpydc = 2,2′-bipyridine-5,5′-dicarboxylic acid) was synthesized via a one-pot solvothermal method and characterized using thermogravimetric analysis, X-ray photoelectron spectroscopy as well as powder and single-crystal X-ray diffraction. The crystal structure of 1 indicates that, in metalloligand Pd(bpydc)Cl_2, every Pd atom adopts a square planar coordination mode with two chloride ions and two nitrogen atoms from bpydc, and the carboxyl groups of Pd(bpydc)Cl_2 connect Pb atoms to form a one-dimensional chain along the crystallographic *a*-axis, which is interlinked via metalloligands to form a two-dimensional layer structure. This complex is highly active, stable and recyclable as a catalyst for the Suzuki–Miyaura and Heck reactions of a wide range of aryl halides including electron-rich and electron-poor aryl iodides/bromides, affording the corresponding products in good to excellent yields. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: metal–organic framework; palladium(II) complex; heterogeneous catalyst; Suzuki–Miyaura reaction; Heck reaction

Introduction

Homogeneous palladium (Pd)-mediated catalysts have been extensively applied in the petrochemical industry, fine chemicals and other fields based on their good selectivity and catalytic performances during the past few decades.[1–7] However, the major problem with many homogeneously catalyzed organic reactions is the recycling of the catalysts from the reaction media. From the sustainable development viewpoint, it is very important to develop heterogeneous Pd catalysts that combine the advantages of both homogeneous and heterogeneous catalysis.[8] Heterogenization of homogeneous catalysts, through immobilizing active complexes on supports,[9–12] has been shown to be a promising method for preparing heterogeneous catalysts with higher activity and recyclability.

Metal–organic frameworks (MOFs) have attracted tremendous interests[13] and an enormous amount of MOFs have been designed and synthesized for energy-, environment- and medicine-relevant applications, such as gas sorption,[14] luminescence,[15] sensors[16] and so on. Especially, MOFs used as heterogeneous catalysts have been developed dramatically during the past decade and many MOF-based catalysts containing various types of catalytic sites have been reported.[17–30] Among them, the most intensively investigated topic is MOF-based Lewis acid catalysts that utilize the coordinatively unsaturated metal centers in MOFs. However, these MOF catalysts often suffer from the possible collapse of frameworks after catalytic reaction since the coordinatively unsaturated metal centers are also responsible for the stability of the frameworks. To overcome this problem, a more rational strategy is to utilize metalloligands involving well-defined catalytic sites rather than pure organic ligands to construct MOF catalysts.[22–30] For example, we have reported two Ni(salen)-based MOFs that could be used as efficient and recyclable heterogeneous catalysts for the synthesis of cyclic carbonates by the cycloaddition of CO_2 with epoxides using the Ni(salen) moieties as Lewis acid catalytic sites.[23,24] Recently, the bipyridine palladium complex Pd(H_2bpydc)Cl_2 (H_2bpydc = 2,2′-bipyridine-5,5′-dicarboxylic acid) has been used as metalloligand to prepare MOF catalysts, such as Pd/Ln-MOFs,[25] Pd/Y-MOF,[26] doped UiO-67 and MOF-253,[27,28] which all exhibit good heterogeneous catalytic activity for C-C coupling reactions. Compared to many employments of MOFs as scaffolds for the encapsulation of Pd(0) nanoparticles,[31–34] a literature survey shows that there are only a few examples reporting the synthesis of MOFs incorporating molecular Pd(II) complexes as heterogeneous catalysts.[25–28,35,36]

Herein, we present the synthesis and characterization of a new stable heterometallic organic framework {Pb[Pd(bpydc)Cl_2]DMF}$_n$ (**1**). This complex shows high activity in the Suzuki–Miyaura reaction (SMR) and Heck reaction (HR) of a variety of aryl bromides. Importantly, Pd(II) leaching is largely inhibited due to the binding interaction between Pd(II) and the MOF framework, which renders **1** recoverable and reusable for at least five cycles with slight loss of catalytic efficiency.

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* *Correspondence to: Yanwei Ren, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510641, China. E-mail: renyw@scut.edu.cn*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510641, China

Experimental

General methods

Unless otherwise noted, all commercial reagents and solvents were used without further purification. Elemental analyses for C, H and N were carried out using a Vario EL III elemental analyzer. Infrared (IR) spectra were measured with a Nicolet Nexus 470 FT-IR spectrometer in the range 400–4000 cm^{-1}. NMR spectra were obtained with a Bruker AM-400 (400 MHz) spectrometer using tetramethylsilane as an internal standard. Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 powder diffractometer at 40 kV, 40 mA with Cu Kα radiation ($\lambda = 1.5406$ Å), with a scan speed of 17.7 s per step and a step size of 0.02° (2θ). Thermogravimetric analysis (TGA) was performed with a Q600 SDT instrument under a flow of nitrogen at a heating rate of 10 °C min^{-1} from ambient temperature to 800 °C. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD system with a base pressure of 10^{-9} Torr. The morphology of **1** was investigated using a cold field emission scanning electron microscope (SEM; S-4800, Hitachi). The content of Pd(II) ions was determined using inductively coupled plasma atomic emission spectrometry (TJA IRIS(HR)). GC–MS was conducted using a Shimadzu GCMSQP5050A system that was equipped with a 0.25 mm × 30 m DB-WAX capillary column.

Single-crystal X-ray diffraction data for **1** were collected with a Rigaku Mercury CCD diffractometer using Mo Kα radiation. The empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on F^2 by the full-matrix least-squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Crystal data are given in Table 1. The selected bond distances and angles are listed in Table S1 (supporting information). CCDC: 1406659.

Synthesis of $\{Pb[Pd(bpydc)Cl_2]DMF\}_n$ (1)

A mixture of H_2bpydc (24 mg, 0.1 mmol) and $Pd(CH_3CN)_2Cl_2$ (26 mg, 0.1 mmol) in a solution of DMF (5 ml) and EtOH (0.5 ml) was stirred at 25 °C for 1 h. Then, $Pb(NO_3)_2$ (33 mg, 0.1 mmol) was added to the solution. The resulting mixture was sealed in a 10 ml tube and heated to 90 °C, at which temperature it was held for 72 h. The produced yellow rod-like crystals of **1** were filtered, washed with DMF and EtOH, and dried at ambient temperature. Yield: 63 mg, 0.09 mmol, 90%. Anal. Calcd for $C_{15}H_{13}Cl_2N_3O_5PbPd$ (%): C, 25.74; H, 1.87; N, 6.00. Found (%): C, 25.18; H, 1.75; N, 6.11. IR (KBr, cm^{-1}): 3449(s), 1614(m), 1558(m), 1379(s), 1128(w), 1049(m), 849(m), 776 (m), 710(m).

Typical procedure for SMR

A 20 ml glass vessel was charged with **1** (0.5 mol%), aryl halide derivatives (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (0.75 mmol) and toluene (5 ml). The reaction mixture was stirred at the desired temperature under nitrogen atmosphere. After the mixture was cooled to room temperature, the solution was filtered and washed with brine, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash silica gel chromatography to afford pure product, which was identified using GC–MS, ^{1}H NMR and ^{13}C NMR analyses.

Typical procedure for HR

A 20 ml glass vessel was charged with **1** (0.5 mol%), aryl halide derivatives (0.5 mmol), olefin (0.75 mmol), Et_3N (1.5 mmol) and DMF (5 ml). The reaction mixture was stirred at the desired temperature under nitrogen atmosphere. After the mixture was cooled to room temperature, the solution was filtered and concentrated under vacuum. The crude residue was purified by flash silica gel chromatography to afford pure product, which was identified using GC–MS, ^{1}H NMR and ^{13}C NMR analyses.

Typical procedure for catalyst recovery

Once the reaction was finished, the mixture was centrifuged and the solvent was removed using a syringe with a syringe filter. The washing/centrifugation sequence was repeated four additional times until no product was detected in the liquid phase using TLC. The residual solvent was removed under reduced pressure affording the recovered **1**, which was directly used in the same tube with fresh reagents for the next run.

Results and discussion

Synthesis and crystal structure of 1

Firstly, reaction of $Pd(CH_3CN)_2Cl_2$ and H_2bpydc in DMF and EtOH at room temperature afforded $Pd(bpydc)Cl_2$ as a metalloligand, in which Pd(II) ion might preferentially coordinate to the two nitrogen atoms of H_2bpydc according to hard–soft acid–base theory. Subsequently, oxophilic metal Pb(II) ions were added and coordinated to the carboxylate groups of the metalloligand to afford yellow rod-like crystals of **1** under solvothermal conditions. The product is stable in air atmosphere and insoluble in water and common organic solvents. TGA of **1** indicates that it is thermally stable up to 240 °C, and a weight loss of 9.7% at about 240–285 °C (Fig. 1) corresponds to the loss of one DMF molecule. SEM observation indicates that the solid sample of **1** consists of rod-like crystallites on a scale of 200 μm (Fig. 2). The experimental PXRD pattern of **1** is in agreement with the simulated pattern, which indicates that the structure of the bulk sample is the same as that of the single crystal (Fig. 3).

Single-crystal X-ray diffraction study reveals that every Pd atom adopts a square planar coordination mode with two chloride ions and two nitrogen atoms from bpydc (Fig. 4(a)). Each Pb atom is coordinated by six oxygen atoms from four separate carboxylate metalloligands, and one oxygen-coordinated DMF molecule, adopting a distorted seven-coordinated capped octahedral geometry. All carboxyl groups of metalloligand $Pd(bpydc)Cl_2$ adopt a κ^1-κ^2-μ^2 mode to connect the Pb atoms to one-dimensional chain along the crystallographic *a*-axis (Fig. 4(b)), which is interlinked via metalloligands to form a two-dimensional layer structure (Fig. 4 (c)). The adjacent $Pd(bpydc)Cl_2$ planes locate in the inverse parallel position with short Pd···Pd interactions (4.536 Å), as is reported that square planar Pd(II) centers have a tendency to aggregate in the solid state.[37]

SMR catalyzed by 1

The Pd-catalyzed SMR is well known as an effective method for forming C-C bonds in organic synthesis. The initial studies were focused on the SMR of aryl halide derivatives with phenylboronic acid to evaluate the catalytic activity of **1** (Scheme 1). Firstly, the coupling reaction between bromobenzene and phenylboronic acid

Table 1. Crystal data and structure refinements for **1**

Empirical formula	$C_{15}H_{13}Cl_2N_3O_5PbPd$
Formula weight	699.77
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
	$a = 15.578(3)$ Å; $\alpha = 90°$
	$b = 7.5968(15)$Å; $\beta = 114.00(3)°$
	$c = 17.030(3)$ Å; $\gamma = 90°$
Volume (Å^3)	1841.2(6)
Z	4
Density (calcd g cm^{-3})	2.524
Absorption coeff. (mm^{-1})	10.432
F(000)	1304
Crystal color and shape	Yellow, rod-like
θ range data collection	2.99 to 27.47
Limiting indices	$-20 \le h \le 20, -9 \le k \le 9, -21 \le l \le 21$
Reflections collected	14 719
Unique	4086 [R(int) = 0.0622]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4086/0/244
Goodness-of-fit on F^2	1.084
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0445$, $wR_2 = 0.1037$
R indices (all data)	$R_1 = 0.0489$, $wR_2 = 0.1111$

was selected as a model reaction in order to screen the reaction parameters. After several reaction variables such as base, temperature, time and solvent were investigated (Table 2), the optimized reaction conditions involved phenylboronic acid, aryl halide and K_2CO_3 as base in toluene in the presence of 0.5 mol% of **1** at 100 °C (Table 2, entry 3). A blank control shows that no expected product was obtained when the coupling reaction between bromobenzene and phenylboronic acid was performed in the absence of catalyst (Table 2, entry 5). In addition, under the optimized conditions, a three-dimensional Pd-free MOF, namely $[Pb(bpdc)]_n$[38] (bpdc =4,4′-biphenyldicarboxylic acid), gave no conversion for this reaction, confirming the need for Pd to perform the coupling reaction (Table 2, entry 9). When the same amount of Pd(bpy)Cl_2 (bpy = 2,2′-bipyridine)[39] as homogeneous catalyst was used to replace **1**, the yield decreased slightly (Table 2, entry 10). The higher activity of **1** compared to its homogeneous counterpart could be related to the surface effect of MOF and the difference in the electron configuration of the bpydc moiety in **1** from that of the bpy molecule in Pd(bpy)Cl_2. These results showed that the Pd(II) ions in **1** are catalytic active centers for the SMR.

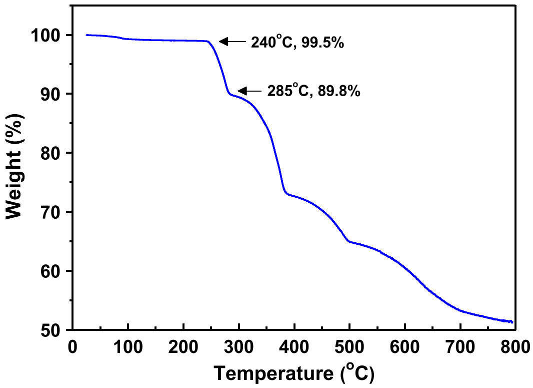


Figure 1. TGA curve of **1**.

Figure 2. SEM image of **1**.

The scope of 1-catalyzed coupling reactions of a variety of aryl halides with phenylboronic acid was further investigated. As evident from Table 3, **1** could catalyze the coupling reactions very well for various aryl bromides bearing electron-withdrawing groups, such as -CN and -COMe, while relatively low yields were obtained when aryl bromides bearing electron-donating substituents (-Me and -OMe) were used. These results are in agreement with the known general conclusion that electron-deficient aryl bromides exhibit higher activity than electron-rich ones. Iodobenzene and 4-iodoanisole are active under the standard conditions, giving corresponding products with excellent yields (Table 3, entries 6 and 7). Compared with the high reactivity of aryl iodides/bromides, using chlorobenzene derivatives as substrate led to very much lower yields (Table 3, entries 9 and 10), perhaps owing to the higher bond energy of the C-Cl bond.

HR catalyzed by 1

The Pd-catalyzed HR between olefins and aryl halides is also an important reaction for the formation of C-C bonds in synthetic chemistry. Thus, the catalytic activity of **1** for HR of aryl halides with olefins was examined (Scheme 2). Firstly, we chose bromobenzene and styrene as a model reaction to screen the reaction parameters. An excess of olefin with respect to aryl halide was used to avoid the

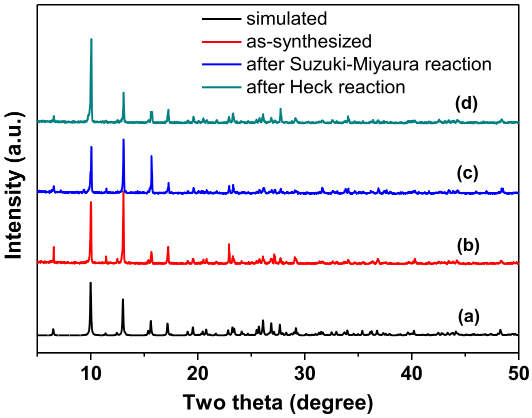


Figure 3. PXRD patterns of **1**: (a) simulated pattern from crystal structure; (b) as-synthesized sample; (c) after the SMR for one-run catalysis cycle; (d) after the HR for one-run catalysis cycle.

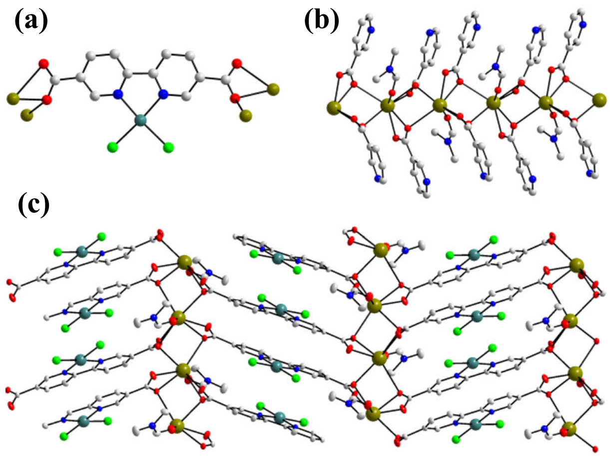
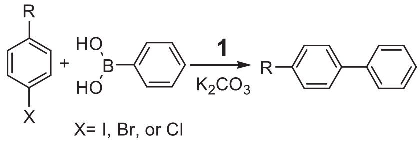


Figure 4. Crystal structure of **1**: (a) Pd(bpydc)Cl_2 moiety; (b) $[PbO_2]_\infty$ chain; (c) two-dimensional framework formed by the interlink of $[PbO_2]_\infty$ chains. Grey, C; blue, N; red, O; green, Cl; purple blue, Pd; yellow grey, Pb.



Scheme 1. General scheme for the SMR catalyzed by **1**.

Table 3. SMR of various aryl halides catalyzed by **1**[a]

Entry	Aryl halides	Yield (%)[b]
1	C_6H_5Br	92
2	4-CNC_6H_5Br	96
3	4-$CH_3COC_6H_5Br$	95
4	4-$CH_3C_6H_5Br$	90
5	4-$CH_3OC_6H_5Br$	85
6	C_6H_5I	98
7	4-$CH_3OC_6H_5I$	96
8	C_6H_5Cl	<5
9	4-$CH_3OC_6H_5Cl$	<5
10	4-$CH_3COC_6H_5Cl$	9

[a] Reaction conditions: aryl halides (0.5 mmol), phenylboronic acid (0.6 mmol) and K_2CO_3 (0.75 mmol) under nitrogen atmosphere, 6 h.

[b] Pure product isolated yield after purification by flash column chromatography.

formation of homocoupling by-products. The reaction proceeded smoothly after 12 h when DMF was used as solvent and K_2CO_3 was used as base under nitrogen atmosphere, which afforded the desired product in 82% yield (Table 4, entry 3). An increase of temperature from 100 to 120 °C did not promote the reaction significantly (Table 4, entry 4). The use of DMF–EtOH mixture as solvent was not obviously effective for this reaction (Table 4, entry 5), although it was reported that alcohol can act as a hydrogen bond donor and then promote the break of halides and facilitate HR.[40] The substitution of K_2CO_3 by the organic base Et_3N enhanced the yield markedly (Table 4, entry 6), partly owing to the good solubility and the stabilization effect of Et_3N for the Pd species.[41] When Et_3N was used as solvent and no additional base was added, the reaction also proceeded well with a yield of 91% (Table 4, entry 7). For comparison, under the optimized conditions (Table 4, entry 6), a blank control indicates that no product was obtained in the absence of catalyst (Table 4, entry 8), and also the Pd-free MOF [Pb(bpdc)][38] presented no any activity in this reaction (Table 4, entry 9). The homogeneous counterpart Pd(bpy)Cl_2 gave reduced yield (Table 4, entry 10), as in the SMR. These results showed that the Pd(II) ions in **1** are catalytic active centers for the HR.

Table 2. Optimization of SMR of bromobenzene and phenylboronic acid[a]

Entry	Catalyst	Solvent	Base	*T* (°C)	Time (h)	Yield (%)[b]
1	**1**	DMF	K_2CO_3	100	4	68
2	**1**	Toluene	K_2CO_3	100	4	82
3	**1**	Toluene	K_2CO_3	100	6	95
4	**1**	Toluene	—	100	6	0
5	—	Toluene	K_2CO_3	100	6	0
6	**1**	Toluene	Na_2CO_3	100	6	85
7	**1**	Toluene	K_2CO_3	80	6	78
8	**1**	Toluene	K_2CO_3	80	12	86
9	[Pb(bpdc)]	Toluene	K_2CO_3	100	6	0
10	Pd(bpy)Cl_2	Toluene	K_2CO_3	100	6	80

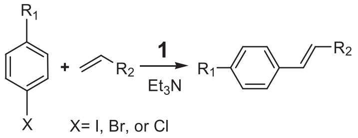
[a] Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol) and base (0.75 mmol) under nitrogen atmosphere.

[b] Yield of coupling product determined by GC–MS.

Similarly, under the optimized conditions, the presence of electron-withdrawing groups (CN and COMe) in the *para* position of aryl bromides was beneficial to the occurrence of this reaction (Table 5, entries 2 and 3), while in the presence of electron-donating substituents, the yields decreased significantly (Table 5, entries 4 and 5). Due to the higher bond energy of the C-Cl bond, aryl chlorides are difficult to activate (Table 5, entries 8 and 9). Furthermore, various alkenes, such as 4-methylstyrene, methyl acrylate and ethyl acrylate, reacted successfully with bromobenzene, giving the corresponding products in excellent yields (Table 5, entries 10–12).

Catalyst stability and recyclability

A crucial issue for heterogeneous catalysts is the possibility that some of active sites can migrate from the solid support to the liquid phase and these leached species could become responsible for a significant part of the catalytic activity. Therefore, leaching tests were performed to estimate whether the active Pd species in **1** would leach easily from MOF to the liquid phase during the catalytic reaction. Firstly, when a model reaction (bromobenzene and phenylboronic acid in the SMR) had taken place for 1 h with a yield of about 25% for biphenyl, the reaction solution was split into two fractions, in which one had the catalyst while the other was without the catalyst. As shown in Fig. 5, after an additional 5 h, the yields of biphenyl of the two fractions are 95% (with catalyst) and 24% (without catalyst). These results undoubtedly indicate that **1** has a good heterogeneous nature and no active



Scheme 2. General scheme for the HR catalyzed by **1**.

Table 4. Optimization of HR of bromobenzene and styrene[a]

Entry	Catalyst	Solvent	Base	*T* (°C)	Time (h)	Yield (%)[b]
1	**1**	DMF	K_2CO_3	100	4	56
2	**1**	DMF	K_2CO_3	100	8	65
3	**1**	DMF	K_2CO_3	100	12	82
4	**1**	DMF	K_2CO_3	120	12	85
5	**1**	DMF + EtOH	K_2CO_3	100	12	80
6	**1**	DMF	Et_3N	100	12	96
7	**1**	Et_3N	—	100	12	91
8	—	DMF	Et_3N	100	12	0
9	[Pb(bpdc)]	DMF	Et_3N	100	12	0
10	Pd(bpy)Cl_2	DMF	Et_3N	100	12	82

[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.75 mmol) and base (1.5 mmol) under nitrogen atmosphere.

[b] Yield of coupling product determined by GC–MS.

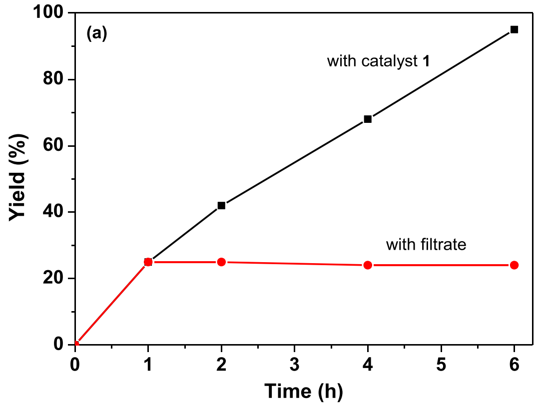


Figure 5. Leaching tests for the SMR of bromobenzene and phenylboronic acid.

species leached into the liquid phase under catalytic conditions. Similarly, the heterogeneous nature of **1** was also verified in the HR using leaching tests (Fig. S4, supporting information). In addition, only a trace of dissolved Pd (32 ppb for the SMR and 45 ppb for the HR) could be detected in the filtrate after catalytic reaction. These results indicated that the loss of Pd species was negligible, and the coupling reactions would proceed on the MOF catalyst surface.

Another important advantage of heterogeneous catalysts is their recyclability. Therefore, tests of the recyclability of **1** were carried out using model reactions, i.e. the SMR of bromobenzene and phenylboronic acid and the HR of bromobenzene and styrene. After each cycle, the catalyst could be easily recovered by centrifugation to remove the supernatant, and then washed with toluene (or DMF) several times. As depicted in Fig. 6, the recovered catalyst was subsequently used in five successive cycles with only slight loss of catalytic efficiency. PXRD patterns of the reused catalyst showed that the structural integrity of the MOF framework was mostly maintained after the catalytic reaction (Fig. 3). Moreover, reduction of Pd(II) ions to Pd(0) clusters (Pd black formation is a general process for Pd catalysts) could be excluded at least to a great extent, since the color change of the catalyst related to Pd(0) formation was not observed during the reaction. To further confirm that the Pd remained in its divalent form after the catalytic reactions, we performed XPS analysis for as-synthesized **1** and the recovered **1** after being used in the SMR. They both exhibit a Pd $3d_{5/2}$ band at around 338 eV and a Pd $3d_{3/2}$ band at around 343.5 eV (Fig. 7), respectively, which are characteristic of divalent Pd.[26–28] Moreover, XPS analysis showed that the Pb and Pd contents of the recovered **1** are 2.01 and 2.16 at.%, respectively. These results illustrate that **1** was stable and recyclable under the investigated reaction conditions. Therefore, based on the above studies, a plausible mechanism is suggested in that the coupling reaction the Pd(II) of **1** seems to undergo a reversible process, in which Pd(II) is reduced to Pd(0) and immediately oxidized back to the initial Pd(II) state *in situ* after the catalytic cycle. The role of Pb(II) of **1** is only to maintain the stability of the MOF framework that can be considered as a polymer ligand to bind Pd(II) ions, preventing the formation of Pd(0) nanoparticles and the agglomeration of Pd(0) species into Pd black.

Table 5. HR of various aryl halides and olefins catalyzed by **1**[a]

Entry	Aryl halides	Olefin	Yield[b] (%)
1	C_6H_5Br	Styrene	96
2	4-CNC_6H_5Br	Styrene	96
3	4-$CH_3COC_6H_5Br$	Styrene	95
4	4-$CH_3C_6H_5Br$	Styrene	60
5	4-$CH_3OC_6H_5Br$	Styrene	52
6	C_6H_5I	Styrene	91
7	4-$CH_3OC_6H_5I$	Styrene	95
8	C_6H_5Cl	Styrene	<5
9	4-$CH_3COC_6H_5Cl$	Styrene	<5
10	C_6H_5Br	4-Methylstyrene	92
11	C_6H_5Br	Methyl acrylate	96
12	C_6H_5Br	Ethyl acrylate	93

[a] Reaction conditions: aryl halides (0.5 mmol), olefins (0.75 mmol) and Et_3N (1.5 mmol) under nitrogen atmosphere, 12 h.

[b] Pure product isolated yield after purification by flash column chromatography.

Conclusions

In summary, we have successfully synthesized a new two-dimensional heterometallic (Pb–Pd) organic framework via a one-pot solvothermal method. This complex is highly active, stable and recyclable for the SMR and HR of a wide range of aryl halides

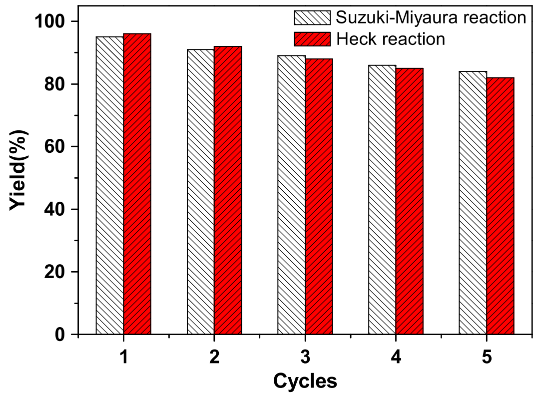


Figure 6. Recyclability of **1** in the SMR of bromobenzene and phenylboronic acid and the HR of bromobenzene and styrene.

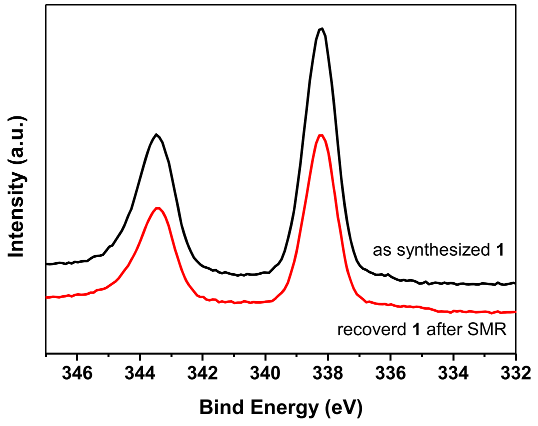


Figure 7. XPS spectra of **1** and of **1** recovered after SMR.

including electron-rich and electron-poor aryl iodides/bromides, affording the corresponding products in good to excellent yields. A further study of catalytic applications of this MOF for other Pd-catalyzed transformations is in progress.

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