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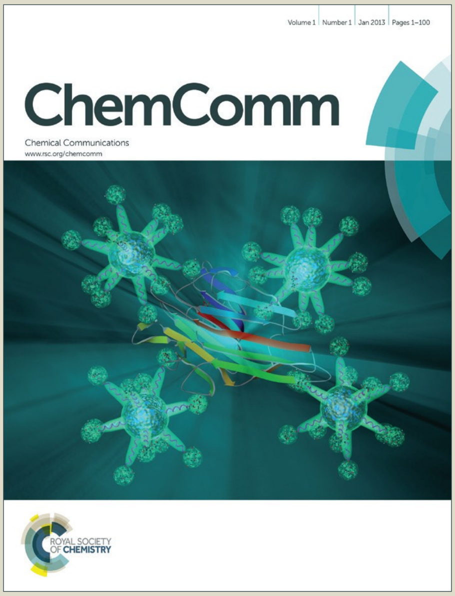

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N-Heterocyclic tetracarbene Pd(II) moiety containing Pd(II)-Pb(II) bimetallic MOF for three-component cyclotrimerization via benzyne

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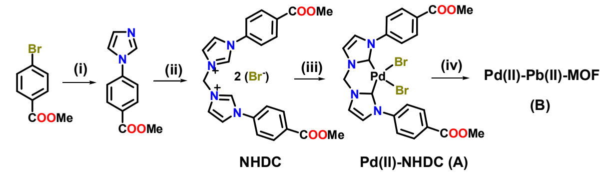
A novel Pd(II)-Pb(II) bimetallic metal-organic framework Pd(II)-Pb(II)-MOF (B) which contains a *N*-heterocyclic tetracarbene Pd(II) moiety was synthesized based on a chelating *N*-heterocyclic dicarbene Pd(II)-NHDC ligand (A) under solvothermal conditions. It can be a highly active heterogeneous catalyst for three-component cyclotrimerization via benzyne species.

Owing to the ever-increasing demand of environmental and natural resources, the development of reusable heterogeneous catalysts, especially those precious metal-containing catalysts, for organic reactions is imperative.[1] Compared to homogeneous catalytic systems, the heterogeneous catalysts are more eco-friendly and long-lived for recyclable use than their homogeneous counterparts.[2]

As is well-known, as an attractive class of composite solid materials, MOFs themselves are inherent heterogeneous catalysts due to their organic-inorganic hybrid composition and polymeric nature.[3] In addition, MOFs are still attractive platforms for immobilizing catalytic species via in situ or post-synthetic approach because of their ordered structural feature, porosity, thermal stability and high density of catalytic centres.

N-heterocyclic carbenes (NHCs) are a very important class of ligands in organometallic chemistry and have been widely and successfully used in binding various catalytic metal ions, for example palladium, ruthenium and silver, to organometallic homogeneous catalysts for promoting a variety of organic reactions such as cross coupling alkene and metathesis.[4] Besides post-synthetic approach,[5] the catalytic active NHC-metal moiety could be in principle incorporated into MOFs based on the two-step synthetic methodology for bimetallic MOFs; that is, starting with the use of pre-synthesized NHC-metal-containing organometallic metalligand with uncoordinated donors to combine with the other kind of metal ion.[6] Thus, the homogeneous catalytic active organometallic NHC-metal moiety could be turned into their heterogeneous counterparts.

In this contribution, we report a tetracarbene Pd(II) moiety containing bimetallic **Pd(II)-Pb(II)-MOF** (**B**) which is generated from a bidentate NHC-Pd(II)-containing carboxylic metalligand **Pd(II)-NHDC** (**A**) and Pb(II) ions under solvothermal conditions. The obtained bimetallic MOF **B** can be, the first of its kind, a highly active tetracarbene Pd(II)-based heterogeneous catalyst to promote benzyne cyclotrimerization and three-component coupling of benzyne, allylic bromides and arylboronic acids under mild reaction conditions.



[a] Reagents: (i) imidazole, CuI, Cs_2CO_3, DMF, 130°C, 12 h; (ii) CH_2Br_2, reflux, 24 h; (iii) $Pd(OAc)_2$, DMSO, 130°C, 4 h; (iv) $Pb(NO_3)_2$, $Na_2C_2O_4$, H_2O - EtOH, 150°C, 2 days.

Scheme 1. Synthesis of **Pd(II)-NHDC** (**A**) and bimetallic **Pd(II)-Pb(II)-MOF** (**B**).[a]

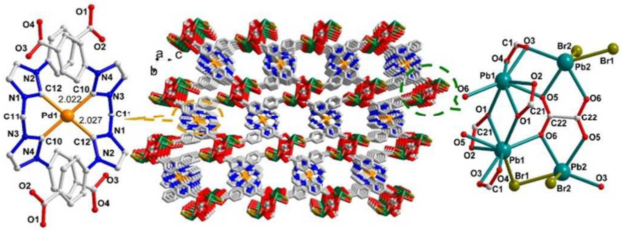


Fig. 1 3D framework and the coordination environments of Pd(II) and Pb(II) in **B**. The opposite Pd···Pd and Pb···Pb distances in the pore are 14.2 and 7.2 Å, respectively.

The chelating *N*-heterocyclic dicarbene **A** was synthesized according to the modified reported method (Scheme 1).[7] The synthetic pathway for *N*-heterocyclic tetracarbene Pd(II) moiety containing **B** (**$Pb_4PdL_2Br_4(C_2O_4)\cdot 11(H_2O)$**, **L** = $C_{21}H_{14}N_4O_4$) is described in Scheme 1. Treatment of **A** with

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Electronic Supplementary Information (ESI) available: single-crystal data (CIF), structural analysis, XRPD patterns, TGA, XPS spectrum and NMR spectra for the products can be found in the Supporting Information (PDF). See DOI: 10.1039/x0xx00000x

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$Pb(NO_3)_2$, in the presence of sodium oxalate in H_2O-EtOH mixed solvent system under solvothermal conditions (150°C, 2 days), afforded bimetallic **B** as the colourless crystals.

The formula of **B** was determined based on single-crystal X-ray diffraction studies and elemental microanalysis (ESI). Single-crystal analysis (Fig. S1) revealed that **B** crystallizes in the triclinic space group *P-1*, and exhibits a 3D framework consisting of Pd(II) and Pb(II) metal centers (Fig. 1 and Fig. S1). In the view of topology (Fig. 2a), each unit of $[(Pb(2))_2C_2O_4]$ can be seen as a 4-connected node, $[(Pb(1))_2O_2]$ is viewed as a 6-connected node, both bis(imidazolium) ligands which chelate palladium atom also act as a 6-connected node. Therefore, the whole framework can be simplified to (4, 6)-connected topological structures with a Schläfli symbol of $\{3^2.4^4.5^4.6^4.7\}_2\{3^2.6^2.7^2\}$. The simulated and measured XRPD patterns are identical, indicating that the bulk crystals were obtained in a pure phase and possess the same structure as the single crystal (Fig. 2b). The XPS spectrum confirmed that the Pd in **B** is bivalent (Fig. S2).

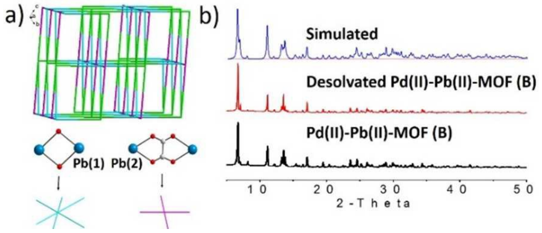


Fig. 2 a) Schematic representation of 3D network of **B**. b) Simulated (blue line) and measured XRPD patterns of **B** (black line) and desolvated **B** (red line, heated at 150°C for 3 h).

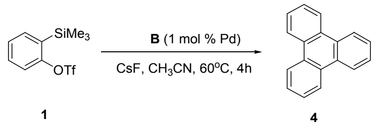
The encapsulated H_2O guest molecules in the framework can be completely removed by heating at 150°C (Fig. S3) and the desolvated framework is stable based on the XRPD pattern (Fig. 2b). The porosity of **B** was confirmed by the gas adsorption–desorption experiment (ESI). The surface area and the pore width of **B** are 33.56 $m^2 g^{-1}$ and 1.6 nm, respectively (Fig. S4). Such porous and thermal stable MOF with Pd(II)-NHC moiety could be used as the heterogeneous catalyst for organic reactions carried out at a relative high temperature.

It is well-known that Pd-NHC containing compounds are effective catalysts for many types of organic reactions such as C-C, C-N and C-O bond formation or deletion. On the other hand, arynes, which can be mildly generated by the fluoride-induced 1,2-elimination of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate,[8] are highly active intermediates to offer numerous applications in (i) nucleophilic additions or multicomponent reactions, (ii) σ-bond insertion reactions, (iii) [4 + 2]- and [2 + 2]-cycloaddition, and (iv) metal-assisted aryne reactions.[9] However, the organic phosphine ligands are the main theme in the palladium-catalysed cross-coupling reactions of benzyne. Compared to Pd(II)-phosphine complexes, Pd(II)-NHC species with better metal-binding properties,[10] however, have never been used in coupling reactions based on benzyne.

For evaluation of the catalytic performance of Pd(II)-NHC species for cross-coupling reactions based on benzyne, the benzyne cyclotrimerization catalysed by **1** was initially tested. When 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**) was treated with CsF and a catalytic amount (10 mol % Pd) of **A** in acetonitrile at 60°C for 2 h, triphenylene (**4**) was isolated as the product in 85 % yield, which is comparable to those reported Pd(II)-phosphine-catalyzed benzyne cyclotrimerization.[11] Furthermore, three-component cross-coupling reaction of 2-(trimethylsilyl)phenyl triflate (**1**) with allyl bromide (**2a**) and phenylboronic acid (**3a**) was also examined with **A** under the same reaction conditions. The result demonstrated that the three-component coupling reaction proceeded very smoothly to give 2-allylbiphenyl species and triphenylene in 70 and 24% isolated yields (4 h), respectively.

It is noteworthy to note that **A** herein and other reported Pd(II)-phosphine catalysts act as the homogeneous catalysts to promote the coupling reactions. Pd, a noble metal, is widely used in preparation of various highly active palladium-carbene catalysts for organic synthesis, therefore, the development of corresponding heterogeneous, eco-friendly, reusable, Pd(II)-NHC-type catalysts for the coupling reactions is a topic of great interest. Inspired by this, tetracarbene palladium containing bimetallic **B** (desolvated) was used instead of **A** to perform the benzyne cyclotrimerization and three-component coupling of benzyne.

Table 1. Pd(II)-Pb(II)-MOF-catalyzed the triphenylene of benzyne[a]



entry	catalyst (mol % Pd)	reagent	T (h)	T (°C)	yield of **4** (%)[b]
1	1%	CsF	4	60	83
2	1%	Bu_4NF	4	60	67
3	1%	KF	4	60	60
4	1%	CsF	4	r.t	70
5	0.5%	CsF	4	60	52
6	--	CsF	4	60	--
7	1%	--	4	60	--
8	1%	CsF	4	60	30[c]

[a] Reaction conditions: 2-(trimethylsilyl)phenyl triflate (**1**, 0.5 mmol), CsF (1.5 mmol), **B** (1 mol % Pd, finely ground) CH_3CN (3 mL), N_2. [b] Isolated yield. [c] The reaction was run 1h under the same conditions as entry 1, and then the MOF was removed.

To optimize the reaction conditions of the **B** catalyzed benzyne cyclotrimerization, exhaustive experimentation was carried out. As shown in Table 1, the best result (triphenylene, 83% yield) was obtained when the reaction was carried out in acetonitrile at 60°C with **B** (1 mol % Pd) and three equivalents of anhydrous CsF (entry 1). Use of other sources of fluorides

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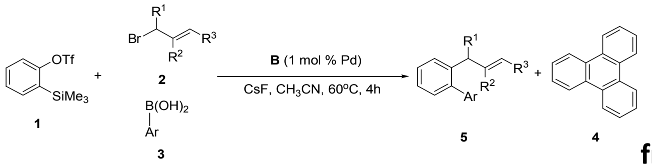
Table 2. Results of Pd(II)-Pb(II)-MOF (**B**)-catalyzed three-component reaction of benzyne precursors, allylic bromides, and arylboronic acids [a]



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entry	allylic bromide (**2**)	arylboronic acid (**3**)	conversion of **1** (%,)	yield of **5** (%) [b]	yield of **4** (%)[b]
1	$R^1 = R^2 = R^3 = H$ (**2a**)	Ar = C_6H_5 (**3a**)	93	**5a**, 68	25
2	$R^1 = R^3 = H$; $R^2 = CH_3$ (**2b**)	Ar = C_6H_5 (**3a**)	92	**5b**, 70	22
3	$R^1 = R^2 = H$; R^3 = Ph (**2c**)	Ar = C_6H_5 (**3a**)	95	**5c**, 65	30
4	3-bromocyclohexene (**2d**)	Ar = C_6H_5 (**3a**)	93	**5d**, 68	25
5	$R^1 = R^2 = R^3 = H$ (**2a**)	Ar = *m*-C_6H_5CN (**3b**)	92	**5e**, 67	25
6	$R^1 = R^2 = R^3 = H$ (**2a**)	Ar = *p*-C_6H_4F (**3c**)	94	**5f**, 63	33
7	$R^1 = R^2 = R^3 = H$ (**2a**)	Ar = *m*-$C_6H_4OCH_3$ (**3d**)	93	**5g**, 71	23
8	$R^1 = R^2 = R^3 = H$ (**2a**)	Ar = *p*-$C_6H_4CO_2CH_3$ (**3e**)	95	**5h**, 66	29
9	$R^1 = R^3 = H$; $R^2 = CH_3$ (**2b**)	Ar = *p*-C_6H_4F (**3c**)	93	**5i**, 69	23
10	3-bromocyclohexene (**2d**)	Ar = *p*-C_6H_4F (**3c**)	92	**5j**, 70	22

[a] Reaction conditions: 2-(trimethylsilyl)phenyl triflate (**1**, 0.5 mmol), allyl bromide (**2**, 0.5 mmol), phenylboronic acid (**3**, 0.6 mmol), **B** (1 mol % Pd), CsF (1.5 mmol), CH_3CN (3 mL), 60°C, N_2. [b] Isolated yields of the products. The ^1H NMR and ^{13}C NMR data for the products are provided in Supporting Information.

such as Bu_4NF (entry 2) and KF (entry 3) gave lower yields. Upon decrease of the reaction temperature (entry 4) or the catalyst amount (entry 5), the yield of triphenylene was proportionately reduced. It is noteworthy that no triphenylene was detected in 4 h when the reaction was carried out in absence of **B** (entry 6) or CsF (entry 7), indicating that **B** and CsF are essential species for the triphenlene formation. In order to gain insight into the heterogeneous nature of **B**, the hot leaching test was carried out. As indicated in Table 1 (entry 8), no further reaction took place without the MOF after about 1 h. This finding confirmed that **B** herein is a typical heterogeneous catalyst for benzyne cyclotrimerization (Fig. S5). Compared to **A**, only one- tenth amount of Pd was used for this reaction, but provided with a comparable yield, indicating the **B** herein is much more active than its homogeneous counterpart.

It is similar to **A**, **B** can also effectively catalyse the three-component coupling reaction of 2-(trimethylsilyl)phenyl triflate (**1**) with allyl bromides (**2**) and phenylboronic acids (**3**) under the same reaction conditions with excellent conversion. As indicated in Table 2 (entry 1), when **1** (0.5 mmol) was treated with **2a** (0.5 mmol) and **3a** (0.6 mmol) in the presence of **B** (1 mol % Pd) and CsF (1.5 mmol) in CH_3CN at 60°C for 4 h (monitored by TLC), the high conversion (93 %) of **1** is achieved. The *o*-substituted biphenyl product (**5a**) was isolated in 68 % yield, together with the by-product of triphenylene (**4**, yield, 25 %). When the catalyst amount was increased to 5 mol %, the corresponding conversion was increased to 95%, including 75 % of **5a** and 20 % of **4**.

Reaction time examination (Fig. 3) shows that the yield of **5a** continuously increased within 4 h, and the maximum yield appeared at 4 h. No more changes in the conversions can be observed after 4 h.

In addition to **2a**, substituted allyl bromides (**2b**-**2c**), including bromo-substituted cyclic olefin (**2d**), could also undergo the three-component reaction with **1** and **3a** to generate the corresponding 2-allylbiphenyl products in good yields under the optimized reaction conditions (Table 2). Thus, methallyl bromide (**2b**) afforded **5b** in 70% yield (entry 2). In a similar manner, cinnamyl bromide (**2c**) reacted with **3a** and **1** to provide **5c** in 65% yield (entry 3). The reaction of 3-bromocyclohexene (**2d**) with **1** and **3a** under the same conditions smoothly proceeded to give the corresponding product **5d** in 68% yield (entry 4).

The scope and generality of the present catalytic reaction can be further extended to substituted arylboronic acids. Under the optimized conditions, the combination of **1** and **2** (**2a**, **2b** or **2d)** with 3-cyanobenzeneboronic acid (**3b**), or 4-fluorobenzeneboronic acid (**3c**), or 3-methoxybenzeneboronic acid (**3d**), or 4-(methoxylcarbonyl)benzeneboronic acid (**3e**) gave the corresponding *o*-allylbiphenyl derivatives **5e - 5j** in 63 - 71 % yields (entries 5-10), respectively. In all cases, triphenylene (**4**) was always obtained as a by-product (yields, 22-30 %). The product mixture can be easily separated by column on silica gel using petroleum ether as the eluent.

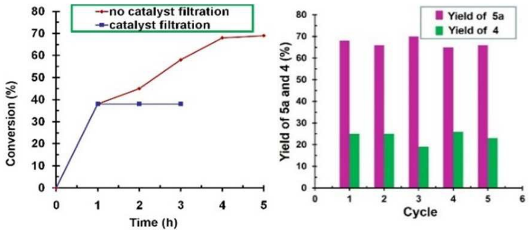

Fig. 3 Left: Reaction time examination and leaching test for coupling reaction based on **1, 2a and 3a**. Reaction conditions: N_2, **B** (cat. 1% mol Pd), **1** (0.5 mmol), **2a** (0.5 mmol), **3a** (0.6 mmol), CsF (1.5 mmol), CH_3CN (3 mL). The solid catalyst was filtrated from the reaction solution after 1 h, whereas the filtrate was transferred to a new vial and reaction was carried out under the same conditions for an additional 2 h. Right: recycling catalytic test.

For the three-component coupling reactions, **B** also exhibits a heterogeneous catalytic nature, and it can be recovered by centrifugation and filtration. After washed with H_2O/ethanol and dried at 90°C in vacuum, it was reused for the next run under the same reaction conditions. The hot leaching test (Fig. 3) demonstrated no further reaction took place without **B** after ignition of the three-component cyclotrimerization at 1 h. The inductively coupled plasma (ICP) measurement indicated that the Pb and Pd leaching amount from **B** is ca. 0.018 and 1.8 %, respectively, after the cyclic catalysis. This suggested that the Pd-NHC in **B** is catalytic active sites instead of Pd(II) cation, and the Pb(II)-framework is an ideal carrier to stabilize the Pd-NHC species during the catalytic process (ESI). In addition, the XRPD patterns of **B** and those after being reused for five consective catalytic cycles indicated that the structural integrity of **B** was well preserved (Fig. S6). As shown in Fig. 3, good conversion of **1** (89 %) and an ideal yield (66 %) of *o*-allylbiphenyl product were still obtained after five catalytic runs (Fig. 3). Although the catalytic mechanism of **2** is not clear, it is believed to be the same as those of reported molecular Pd(II)-complex.[12]

In summary, we report a novel bimetallic **B** generated from a **A** ligand and Pb(II) under solvothermal conditions. The obtained bimetallic **B** contains *N*-heterocyclic tetracarbene Pd(II)-moiety and it can be a highly efficient heterogeneous catalyst system for benzyne cyclotrimerization and three-component coupling reaction of benzyne, allylic bromides and arylboronic acids under mild reaction conditions. Studies aimed at extending the scope of other kind of *N*-heterocyclic carbene metal-moieties containing MOFs and their heterogeneous catalytic behaviours are currently underway in our laboratory.

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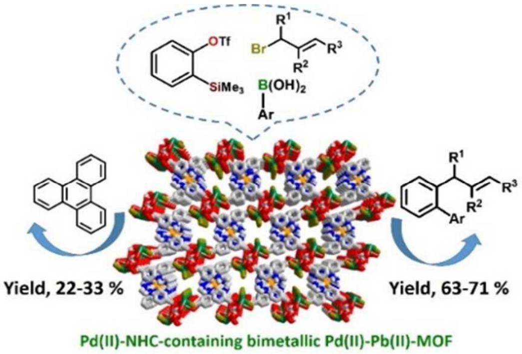

A *N*-heterocyclic tetracarbene Pd(II) moiety containing bimetallic metal-organic framework Pd(II)-Pb(II)-MOF, which can be a highly active heterogeneous catalyst for three-component cyclotrimerization, is reported.