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Incorporation of PdCl₂P₂ complexes in Ni-MOF as catalysts for Heck arylation of functionalised olefins.

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Abstract

Two palladium complexes of a PdCl₂P₂ type with P=tri(1-piperidiny)phosphine (Pd-1) and triphenylphosphine (Pd-2) were successfully immobilised on [Ni₈(OH)₄(OH₂)₂(L)₆]_n (Ni-MOF) material (L=4,4'-(benzene-1,4-diyl-diethyne-2,1-diyl)bis(1-H-pyrazole)) to form Pd@Ni-MOF composites. The presence of big octahedral cavities in the Ni-MOF structure (2.4 nm) enabled incorporation of PdCl₂P₂ molecules inside the Ni-MOF, as confirmed by physicochemical measurements and computer simulation. The Pd@Ni-MOF composites catalysed arylation of estragole by iodobenzene with efficiency higher than corresponding PdCl₂P₂ compounds without MOF. Arylation of eugenol by PhB(OH)₂ unexpectedly resulted in formation of ether as the main product. This was explained by the dominating activity of the Cu@MOF catalyst, formed in situ in reaction conditions.

Introduction

Palladium complexes are recognised as highly active catalysts of various C-C bond forming reactions leading to arylated products.[1-9] In this area, the arylation of olefins already bearing one phenyl ring, occupies a special place as a method enabling preparation of differently substituted stilbenes for the pharmaceutical industry. [10-13] Arylation of olefinic substrates can be performed according to the Heck procedure, using aryl halide as a source of the aryl group.[14-16] Alternatively, in the Heck-type reaction, phenylboronic acid donates a phenyl group to the substrate and addition of the oxidant is necessary to reoxidise the palladium.[17-20] Both methods work very efficiently, although the first one, Heck coupling is more universal. However, the problem which is often addressed in a homogeneous system is good separation of the catalyst from the reaction mixture to guarantee metal-free products.[1] The recommended solution is immobilisation of the catalyst using inorganic or organic support. [21-26] In the past,

metal-organic frameworks (MOFs) have been studied as potential carriers for metal catalysts.[27-30]

Metal-organic frameworks (MOFs) present an attractive class of materials due to their highly porous nature and their chemical and structural diversity. The special nature of these compounds is evidenced by a wide range of applications in numerous areas, such as sensing, medicine, gas separation and catalysis.[31-34] Due to the permanent porosity and accessibility of voids, MOFs are perfectly suited to host other molecules and, as a result, to create composites with new properties. In most cases, the incorporation primarily concerned gases, organic compounds and metal nanoparticles as guest molecules.[35-37] In contrast, encapsulation of metal complexes in MOFs are scarce, probably due to pore size limitations and the stability of MOFs. To date, only a few examples have been reported on the successful incorporation and release of ruthenium non-conventional anticancer drugs such as [Ru(p-cymene)Cl₂(pta)] (RAPTA-C) to the CPO-27-Ni and [Ni₈(μ₄-OH)₄(μ₄-OH₂)₂(μ₄-4,4'-(buta-1,3-diyne-1,4-diyl)bispyrazolato)₆]_n MOFs. [38-39]

It is worth mentioning the remarkable approach reported by Grela et al. in which ruthenium alkylidene complexes were successfully supported inside (Al)MIL-101-NH₂·HCl MOF and used as catalysts an olefin metathesis in a flow system. [40] A typical photocatalyst, a [Ru(bpy)₃]²⁺ complex, was incorporated into numerous MOFs such as ZJU-100, PCN-99, UiO-66, MIL-125-NH₂. [41-44] Che and coworkers introduced pincer platinum(II) complexes into a series of MOFs materials as efficient catalysts for photoinduced dehydrogenation reactions.[45] Wang et al. reported luminescent organogold (III) photocatalyst immobilised in MOF1 and ZJU-28 materials.[46] The original synthetic strategy, based on a direct incorporation of Pd(H₂bpydc)Cl₂ (H₂bpydc = 2,2'-bipyridine-5,5'-dicarboxylic acid) in the UiO-67 type MOF, has been applied to obtain a single-site catalyst for C-Cl bond activation [47].

Phosphine ligands play an important role in the creation of highly active metal catalysts, creating an optimal environment for substrates activation through electronic and steric influence.[48] In palladium catalytic systems, phosphines stabilise metal complexes and promote a homogeneous reaction pathway. Immobilisation of such a catalyst on the solid carrier can facilitate a heterogeneous mechanism and solve separation problems. However, the incorporation of the phosphine complexes into a MOF material has never been examined yet. The previously reported Pd-phosphine-MOF composites were formed by the direct coordination of Pd to the ligand used as a linker. [49]

Herein, we report the successful encapsulation of two palladium phosphine complexes of a PdCl_2P_2 type in the cavity of a pyrazolate Ni-MOF. The Ni-MOF was chosen as the support, based on the following considerations: (i) the strength of the Ni–azolate bonds conferring high stability of the Ni-MOF material, (ii) the large-pores of Ni-MOF with two types of nanocages, octahedral and tetrahedral voids of about 2.4 nm and 1.1 nm inner size, respectively.[50] The Pd@Ni-MOF composites were used as catalysts in the model Heck and Heck-type arylation of estragole and eugenol.

Results and discussion

Synthesis and characterisation of Pd@Ni-MOF

The highly porous and robust MOF material $[\text{Ni}_8(\text{OH})_4(\text{OH}_2)_2(\text{L})_6]_n$ (Ni-MOF) where $\text{L}=4,4'$ -(benzene-1,4-diyl)diethyne-2,1-diyl)bis(1-H-pyrazole) [50] was chosen as a platform for the incorporation of two phosphine palladium complexes of PdCl_2P_2 type containing tri(1-piperidinyl)phosphine (Pd-1) and triphenylphosphine (Pd-2) as the P-ligands. The Ni-MOF shows remarkable thermal and chemical stability, high porosity and robustness. It was expected therefore, that its structure would be preserved in catalytic reaction conditions. Additionally, octahedral voids of about 2.4 nm are big enough for the encapsulation of the phosphine palladium complexes (Figure 1). According to the computer simulation (grand canonical Monte Carlo) two molecules of Pd-1 and three molecules of Pd-2 could be accommodated in the Ni-MOF structure (see supplementary material).

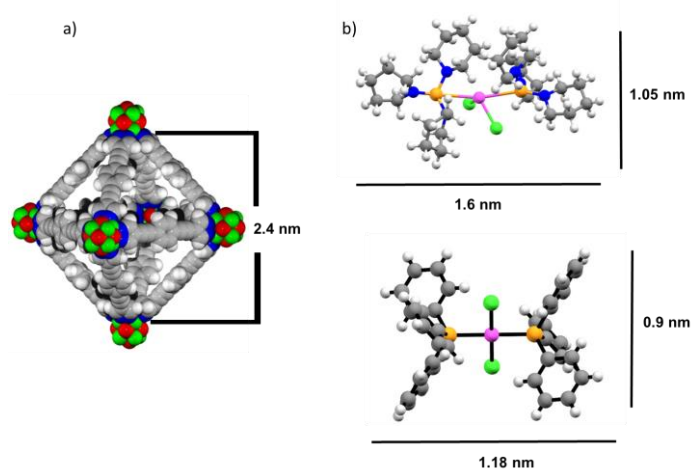


Figure 1. View of the octahedral voids in (a) the structure of Ni-MOF and (b) the structure of the Pd-1 (above) and Pd-2 (below) complexes.

The Pd-1 and Pd-2 complexes were immobilised by suspending the activated Ni-MOF in toluene or dichloromethane solutions of the palladium complexes.

The BET surface area of the Ni-MOF was estimated at $3020 \text{ m}^2 \text{ g}^{-1}$ which was higher than that reported by Navarro et al. ($2215 \text{ m}^2 \text{ g}^{-1}$). [50] The difference was most likely caused by the lower content of DMF in the studied Ni-MOF. Figure 2 a-b shows the N_2 adsorption-desorption isotherm for Pd-1@Ni-MOF and Pd-2@Ni-MOF. The surface area decreased to $1967 \text{ m}^2 \text{ g}^{-1}$ for Pd-1@Ni-MOF and to $2225 \text{ m}^2 \text{ g}^{-1}$ for Pd-2@Ni-MOF as a result of incorporation of palladium complexes inside the Ni-MOF (Table 1).

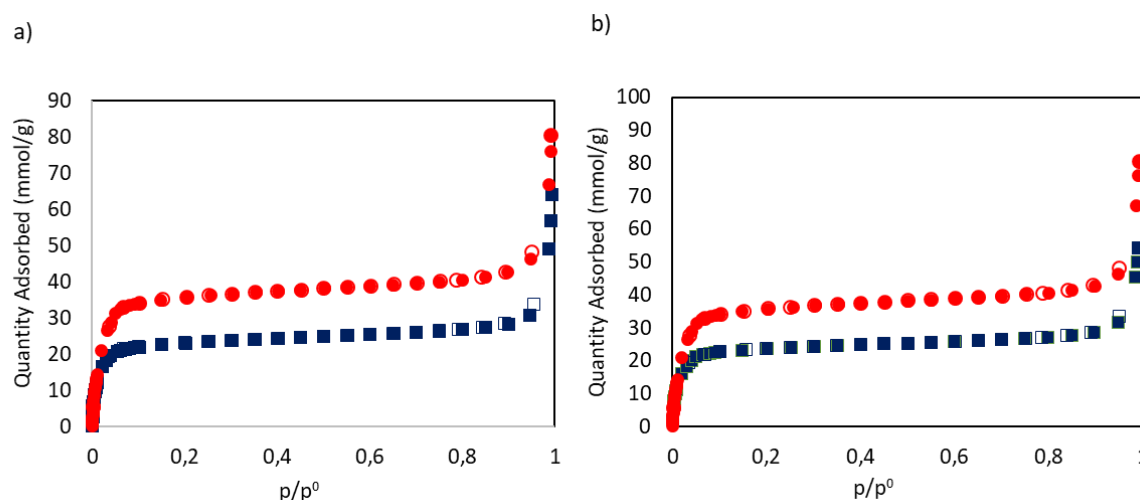


Figure 2. a) and b) N_2 (77 K) adsorption isotherms for Ni-MOF (red), a) Pd1@Ni-MOF and b) Pd2@Ni-MOF (blue). Empty symbols denote desorption.

Table 1. BET surface area and total pore volume for Ni-MOF, Pd-1@Ni-MOF and Pd-2@Ni-MOF.

	BET Surface Area (m^2/g)	Total pore volume (cm^3/g)
Ni-MOF	3020(24)	1.48
Pd-1@NiMOF	1967(11)	0.98
Pd-2@NiMOF	2225(46)	1.09

The XRPD method evidenced that after bonding of the Pd complexes, the Ni-MOF material maintained its crystallinity (Figure 3).

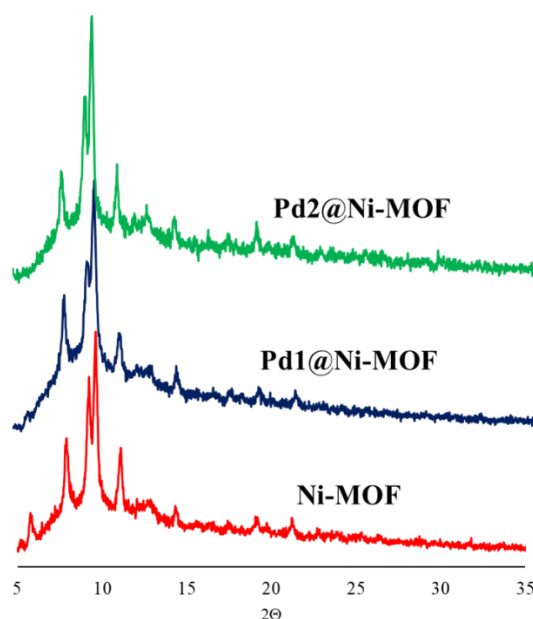


Figure 3. XRPD patterns of Ni-MOF as synthesised, Pd-1@Ni-MOF, Pd-2@Ni-MOF.

The XPS spectra revealed two peaks at 337.1 and 342.2 eV for Pd-1@Ni-MOF and at 337.6 and 342.9 eV for Pd-2@Ni-MOF assigned to the $3d_{5/2}$ and $3d_{3/2}$ core levels of divalent palladium (Table 2). Additionally, the P2p binding energy equal to 132.3 eV for Pd-1@Ni-MOF and 131.6 eV for Pd-2@Ni-MOF were close to the values determined in Pd(II) complexes with phosphine ligands. [51-52]

Table 2. XPS data (BE, eV) for Pd-1@Ni-MOF and Pd-2@Ni-MOF

	Pd-1@Ni-MOF	Pd-2@Ni-MOF
P2p	132.3	131.6
Pd $3d_{3/2}$	337.1	337.6
Pd $3d_{5/2}$	342.3	342.9

In contrast, analysis of the IR spectrum was not informative about the presence of Pd-1 and Pd-2 complexes in the porous Ni-MOF matrix. The positions of $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{N})$ bands of the pyrazole ring of the ligand in the Pd-1@Ni-MOF and Pd-2@Ni-MOF spectra were almost identical compared to pristine Ni-MOF. A small difference was observed only for the $\nu(\text{P}-\text{C})$ band situated at ca. 1090 cm^{-1} in the Ni-MOF and Pd-2@Ni-MOF spectra.

Catalytic activity of Pd@MOF in Heck and Heck-type reactions.

The obtained Pd@Ni-MOF catalysts were employed in Heck and Heck-type couplings of eugenol and estragole. It was expected that both substrates would be transformed to corresponding stilbenes, 1 or 2 by arylation with iodobenzene (Heck coupling) or with phenylboronic acid (Heck-type coupling) (Figure 4). Formation of some amounts of products 1b and 2b was also expected on the basis of our earlier experience with the Pd(OAc)₂ catalyst [53].

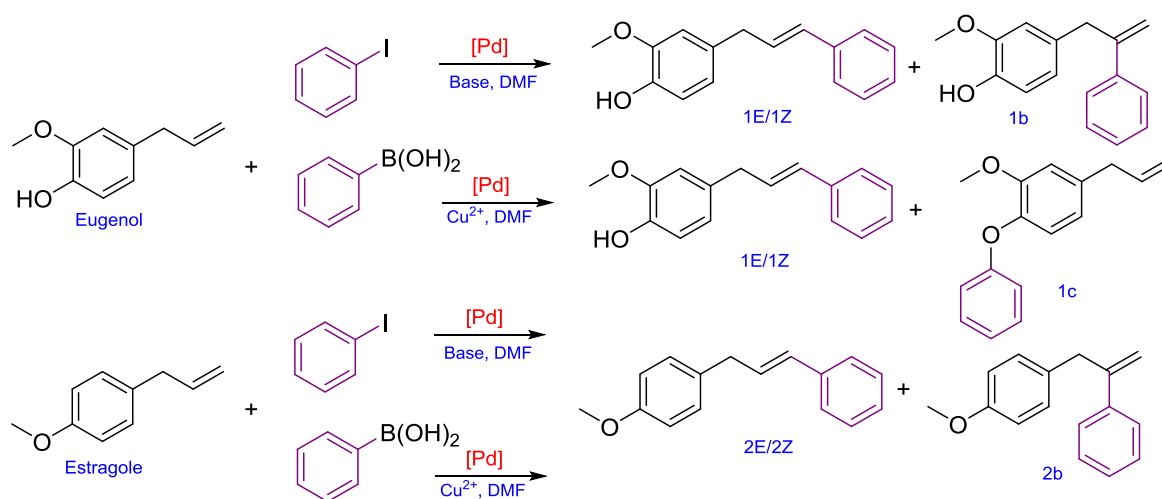


Figure 4. Heck and Heck-type reactions of eugenole and estragol catalysed by Pd@Ni-MOF.

The first tests, carried out using a low amount of Pd@Ni-MOF, 0.1 mol%, showed that in Heck conditions only Pd-1@Ni-MOF was active and it converted 33% of estragole to the desired products (Table 3). However, this catalyst did not form any product from eugenol. In the same conditions the second catalyst, Pd-2@Ni-MOF, was not active in the Heck coupling of either, eugenol and estragole substrate. Better results were obtained in a Heck-type coupling with phenylboronic acid as the source of the phenyl group. Conversion of estragole was relatively low for both catalysts and Pd-2@Ni-MOF provided better results, with 25% of product 2 as a mixture of E and Z isomers. Unexpectedly, arylation of eugenol resulted in formation of a new product, ether 1c, as the main one for both catalysts. Ether 1c was not observed in our earlier studies carried out using Pd(OAc)₂ under similar conditions. On the other hand, formation of ethers in copper-mediated reactions of phenylboronic acid and phenol derivatives is known as the Chan-Lam process.[54-56] In order to explain the presence of 1c in our reactions, additional experiments were performed in the absence of the Pd@Ni-MOF catalyst. Elimination of Pd@Ni-MOF from the reaction mixture resulted in formation of 35% of 1c as the only product (Table 4). A similar result, 30% of 1c, was achieved in the presence of pure Ni-MOF without

palladium (Table 4). These results indicated that ether 1c was formed in the Chen-Lan process by the contribution of the $\text{Cu}(\text{OAc})_2$ used in our system as an oxidant of palladium. Domination of the $\text{Cu}(\text{OAc})_2$ activity over that of palladium led to the formation of product mixture, composed of 2 and 1c.

Table 3. Results of the arylation of eugenol and estragole with iodobenzene and phenylboronic acid catalysed by Pd@Ni-MOF catalysts.

Entry	Catalyst	Base	ArX	Olefin	Conversion of PhI or olefin (%)	1 (E/Z) or 2 (E/Z) (%)	1c (%)
1	Pd-1@Ni-MOF	K_2CO_3	PhI	eugenol	-	-	-
2	Pd-2@Ni-MOF				-	-	-
3	Pd-1@Ni-MOF			estragole	33	22/12	-
4	Pd-2@Ni-MOF				-	-	-
5	Pd-1@Ni-MOF	-	$\text{PhB}(\text{OH})_2$	eugenol	40	6/3	31
6	Pd-2@Ni-MOF				42	13/9	20
7	Pd-1@Ni-MOF			estragole	8	6/2	-
8	Pd-2@Ni-MOF				25	15/9	1

Reaction conditions: PhI (1 mmol) or $\text{PhB}(\text{OH})_2$ (1.5 mmol), olefin (1 mmol), K_2CO_3 or $\text{Cu}(\text{OAc})_2$ (2 mmol), [Pd] (1×10^{-6} mol), DMF (5 mL), 110°C , 6h. Yield based on GC-MS.

Catalytic activity of Pd-1@MOF

Further studies on the activity of Pd@Ni-MOF catalysts were undertaken using a higher amount of palladium: 1 mol% for the Heck coupling of substrates with iodobenzene and 0.5 mol% for the coupling with phenylboronic acid (Table 4). First, Pd-1@Ni-MOF was tested and the Pd-1 complex without MOF was also used as a reference. Interestingly, Heck arylation of estragole gave better results (76% conversion) with immobilised Pd-1@MOF than with the Pd-1 complex only (67%). Both catalysts selectively formed the expected stilbene and two stereoisomers, 1E and 1Z, were identified with the main one being 1E. Attempts to recycle Pd-1@Ni-MOF gave positive results and the reaction was repeated three times with the same catalyst sample. However, conversion of iodobenzene decreased from 76% to 53% indicating some loss of catalytic efficiency. A possible reason for this could be decomposition of the catalyst and leaching of palladium. In fact, ICP analyses of the Pd-1@Ni-MOF catalyst recovered after the third run evidenced a decrease of palladium content to 0.042%.

The second series of arylation reactions with Pd-1@Ni-MOF was carried out using eugenol as the substrate. The reference reaction with the Pd-1 catalyst resulted in 100% conversion of

eugenol to the corresponding stilbene, present in two isomeric forms, E and Z, in comparable amounts. The reactivity of Pd-1@Ni-MOF appeared quite different as besides the expected stilbene, product 1c was also formed with a 20% yield. In this reaction, conversion of eugenol was 50% and it decreased to 33% for the recovered catalyst. Moreover, in five subsequent runs the selectivity changed and 1c became the main product. It could therefore be assumed that the palladium immobilised in the MOF was active only in the first run and formed product 2. In the next runs, the yield of product 2 decreased significantly and formation of ether 1c should be assigned to the activity of Cu(OAc)₂ only.

Table 4. Results of the arylation of eugenol and estragole catalysed by Pd-1 and Pd-1@Ni-MOF.

Entry	Catalyst	Run	ArX	Olefin	Conversion of PhI or olefin (%)	1 (E/Z) or 2 (E/Z) (%)	1c (%)
1	Pd-1 ^a	-	PhI	estragole	54	32/18	-
2	Pd-1	-			67	36/22	-
3	Pd-1@Ni-MOF	1			76	48/22	-
4		2			65	50/15	-
5		3			53	53/0	-
6	Without catalyst	-	PhB(OH) ₂	eugenol	35	-	35
7	Ni-MOF	-			30	-	30
8	Pd-1	-			100	53/42	-
9	Pd-1@Ni-MOF	1			50	15/13	20
10		2			33	8/8	17
11		3			34	6/6	20
12		4			28	3/3	18
13		5			48	3/3	36
14		6			36	2/2	28

Heck reaction conditions: PhI (1 mmol), olefin (1 mmol), K₂CO₃ (2 mmol), [Pd] (1×10⁻⁵ mol), ^a [Pd] (0.5×10⁻⁵ mol) DMF (5 mL)

Heck-type reaction conditions: PhB(OH)₂ (1.5 mmol), eugenol (1 mmol), Cu(OAc)₂ (2 mmol), [Pd] (0.5×10⁻⁵ mol), DMF (5 mL). Yield based on GC-MS.

Pd-1 - Dichlorobis[tri(1-piperidinyl)phosphine]-palladium(II)

Catalytic activity of Pd-2@Ni-MOF

Results obtained with the application of Pd-2@Ni-MOF catalyst are presented in Table 5. The positive effect of Ni-MOF on the substrates conversion is seen clearly when the productivities of Pd-2 and Pd-2@Ni-MOF were compared. Thus, the Pd-2 complex provided 54% of stilbene

while Pd-2@Ni-MOF formed 68% of product 1. Recycling of Pd-2@Ni-MOF was performed five times with satisfactory results. The yield of products decreased to 58% but it was still comparable with results obtained in a homogeneous system with a Pd-2 complex. The composition of the products was stable within the series of reuse experiments and the desired stilbene was mainly formed. The amount of side product 1b remained at the level of ca. 6%.

In the next step of the studies, the Pd-2 catalyst was employed as a pure complex and in an immobilised form, Pd-2@Ni-MOF, to the arylation of eugenol with phenylboronic acid. In this case, the Pd-2 complex was more active than Pd-2@Ni-MOF with conversion of 86% versus 58%. Similarly, as in the reaction with Pd-1@Ni-MOF, product 1c was also formed in this system. The yield of 1c increased in subsequent catalytic runs from 11% in the first reaction to 23% in the fourth one. At the same time, the amount of stilbene decreased from 43% to 8%. The trend of the changes was analogous to that observed for Pd-1@Ni-MOF. It is seen that the activity of Pd-2@Ni-MOF catalyst decreased fast in the Heck-type conditions, namely in the presence of an excess of Cu(OAc)₂. In order to explain the reason for this phenomenon, SEM/EDX studies of the recovered catalyst were undertaken. In the sample of the isolated Pd-2@Ni-MOF, only a small amount of palladium was found, ca. 0.1 weight%. In contrast, a high amount of copper was present, ca. 50 weight%. Most probably, the copper covered completely the catalyst surface and blocked access of the substrates to the active palladium centres. Moreover, partial exchange of nickel centres by copper centers should be considered. It has been recently shown that such process occurred effectively in mild conditions [57].

It was therefore interesting to check whether such a catalyst would be useful in the catalytic process. The answer was positive because the reaction of eugenol with phenylboronic acid performed in the presence of the recovered catalyst produced 23% of ether 1c.

Table 5. Results of the arylation of eugenol and estragole catalysed by Pd-2 and Pd-2@Ni-MOF.

Entry	Catalyst	Run	ArX	Olefin	Olefin conversion (%)	1 (E/Z) or 2 (E/Z) (%)	1b or 2b (%)	1c (%)
1	Pd-2 ^a	-	PhI	estragole	46	26/12	5	-
2	Pd-2	-			57	36/16	5	-
3	Pd-2@Ni-MOF	1			75	44/25	6	-
4		2			68	35/27	6	-
5		3			63	29/28	6	-
6		4			57	28/23	6	-

7		5			58	26/26	6	-
8		6			58	27/25	6	-
9	Pd-2	-	PhB(OH) ₂	eugenol	86	48/35	3	-
10	Pd-2 ^b	-			84	49/31	4	-
11	Pd-2@Ni-MOF	1			58	23/20	3	11
12		2			43	12/7	-	17
13		3			38	5/5	1	21
14		4			38	4/4	1	23

Heck reaction conditions: PhI (1 mmol), olefin (1 mmol), K₂CO₃ (2 mmol), [Pd] (1×10⁻⁵ mol), ^a [Pd] (0.5×10⁻⁵ mol) DMF (5 mL)

Heck-type reaction conditions: PhB(OH)₂ (1.5 mmol), eugenol (1 mmol), Cu(OAc)₂ (2 mmol), [Pd] (0.5×10⁻⁵ mol), ^b [Pd] (1×10⁻⁵ mol), DMF (5 mL). Yield based on GC-MS.

Pd-2 Dichlorobis[triphenylphosphine]-palladium(II)

Unfortunately, we did not succeed in the conversion of eugenol to the coupling product in the Heck reaction with iodobenzene. No product was obtained at low (Table 3) or higher catalyst concentrations (1 mol%). It can be assumed that the presence of the OH group in the eugenol molecule hindered access to active palladium centers in the MOF structure and blocked the reaction.

Conclusions

In summary, we presented the first example of the immobilisation of two palladium complexes of PdCl₂P₂ type on [Ni₈(OH)₄(OH₂)₂(L)₆]_n (Ni-MOF). The efficiency of the synthetic strategy, based on simple impregnation from the organic solution, was confirmed by different analyses, such as SEM/EDX, ICP, XRPD and BET surface area measurements. In addition, the computer simulation indicated the possible incorporation of PdCl₂P₂ compounds in the octahedral cavities of the Ni-MOF. The immobilisation of PdCl₂P₂ complexes on the Ni-MOF resulted in an increase of the catalytic activity in the arylation of estragole by iodobenzene. This positive effect can be explained by the improvement of the contact between the catalyst and the reactants in the porous Ni-MOF matrix. The heterogenised Pd@Ni-MOF catalyst was successfully separated and used in the next catalytic runs, however, some decrease in its productivity was noted, probably because of some decomposition. In the arylation of eugenol carried out with PhB(OH)₂ in the presence of the Cu(OAc)₂ co-catalyst, instead of the desired stilbene, an ether was formed. It was found, that copper covered the surface of the Ni-MOF support completely and blocked the activity of the palladium. Consequently, copper activated the OH group of eugenol and facilitated etherification. Interestingly, the in situ formed Cu@MOF catalyst was also active in the formation of an ether. In this case, the ability of the Ni-MOF to form a

composite with transition metals changed the reaction selectivity from palladium-catalysed to a copper-catalysed one.

Experimental Section

All reagents and solvents were purchased from commercial sources. Copper(I) iodide, dichlorobis(triphenylphosphine) palladium(II), dichlorobis[tri(1-piperidinyl)phosphine] palladium(II), nickel(II) acetate tetrahydrate, 1-Boc-4-iodopyrazole and 1,4-diethynylbenzene were purchased from Sigma-Aldrich and used without purification.

XRPD data were collected on a Bruker D2-PHASER diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The compounds were manually grounded in an agate mortar, then deposited in the hollow of a zero background silicon sample holder. N₂ adsorption isotherms were measured at 77 K on a Micrometrics 3Flex surface characterization analyzer. Prior to measurement, the DMF molecules present in the powdered samples were exchanged with CH₂Cl₂ for 12 h. Next, the samples were heated at 130 °C for 7 h and outgassed at 10⁻⁵ bar. IR-ATR absorption bands were measured by spectrophotometer Bruker Tensor 27. Inductively Coupled Plasma Mass spectrometry (ICP-OES) measurements were recorded on a iCAP 7400 DUO (Thermo Fisher Scientific) spectrometer.

X-ray photoelectron spectra (XPS) were conducted on a Kratos Axis Ultra-DLD X-ray photoelectron spectrometer equipped with Al K α radiation (1486.6 eV). Elemental (C, H, N) analyses were obtained in a THERMO SCIENTIFIC Flash 2000 instrument.

The organic products of the catalytic experiments were analyzed with a GC (HP 5890II) and MS (HP 5971a).

Synthesis of the MOF

[Ni₈(OH)₄(H₂O)₂(L)₆]*n*-solv (Ni-MOF) was prepared according to a reported procedure [50].

Pd-1@Ni-MOF

150 mg of the activated MOF and 67 mg of Pd-1 were placed in 20 mL of dichloromethane. The content of the vial was stirred at RT for 24 h. The solid was collected by centrifugation and washed with dichloromethane (2 x 10 mL). Green solid was dried overnight at RT.

IR (ATR, cm^{-1}): 1498 (m) [$\nu(\text{C}=\text{C}+\text{C}=\text{N})$], 1369 (w), 1251 (vw), 1161(w) [$\nu(\text{C}-\text{N})$], 1058 (m), 1020 (w), 835 (s) [$\gamma(\text{C}-\text{H}_{\text{AR}})$] 642 (m).

Pd (ICP) 2.45 wt%; Pd (EDX) 1.14 wt%; P (EDX) 1.10 wt%

Pd-2@Ni-MOF

150 mg of the activated MOF and 78 mg of Pd-2 were placed in 20 mL of toluene. The content of the vial was stirred at RT for 24 h. The solid was collected by centrifugation and washed with toluene (2 x 10 mL) and acetone (1 x 10 mL). Green solid was dried overnight at RT.

IR (ATR, cm^{-1}): 1497 (m) [$\nu(\text{C}=\text{C}+\text{C}=\text{N})$], 1367 (m), 1224 (m) [$\nu(\text{C}-\text{N})$], 1098(vw) [$\nu(\text{P}-\text{C})$], 1060 (w), 1018 (w), 837 (m) [$\gamma(\text{C}-\text{H}_{\text{AR}})$], 642 (m), 532 (w)

Pd (ICP) 1.22 weight%; Pd (EDX) 1.18 weight%; P (EDX) 0.53 weight%

Heck reaction

The reaction was carried out in a 50 mL Schlenk tube. The solid substrates, K_2CO_3 (2 mmol), and the Pd catalyst (1×10^{-6} – 1×10^{-5} mol) were weighed and placed in the Schlenk tube under an N_2 atmosphere. Next, olefin (1 mmol), iodobenzene (1 mmol), and 5 mL of the DMF were added with a pipette. The Schlenk tube was closed with a rubber plug, and the reaction mixture was stirred at 110 °C in oil bath. After the given reaction time, the Schlenk tube was cooled down, and the organic products were separated by extraction with diethyl ether (three times with 5, 4, and 2 mL). For better phase separation, 5 mL of water was added, and the products were GC-MS analyzed with mesitylene (0.1 mL) as the internal standard.

Heck-type reaction

The reaction was carried out in a 50 mL Schlenk tube. The solid substrates, copper (II) acetate (2 mmol), phenylboronic acid (1.5 mmol), and the Pd catalyst (1×10^{-6} – 1×10^{-5}) were weighed and placed in the Schlenk tube under an N_2 atmosphere. Next, olefin (1 mmol) and 5 mL of the solvent (DMF) were added with a pipette. The Schlenk tube was closed with a rubber plug, and the reaction mixture was stirred at 110 °C in oil bath. After the given reaction time, the Schlenk tube was cooled down, and the organic products were separated by extraction with diethyl ether (three times with 5, 4, and 2 mL). For better phase separation, 5 mL of water was added, and the products were GC-MS analyzed with mesitylene (0.1 mL) as the internal standard.

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