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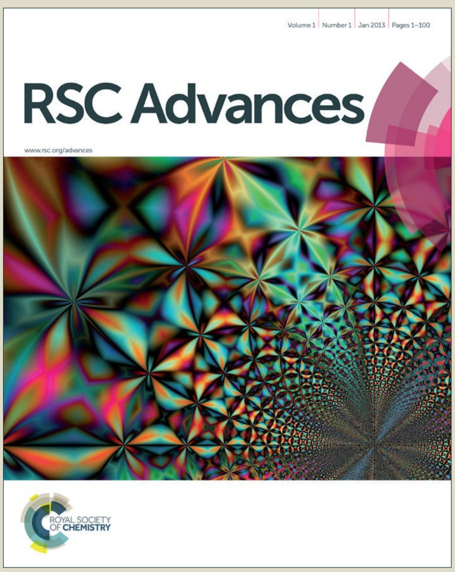

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COMMUNICATION

MOF-253-Pd(OAc)$_2$: A Recyclable MOF for Transition-Metal Catalysis in Water

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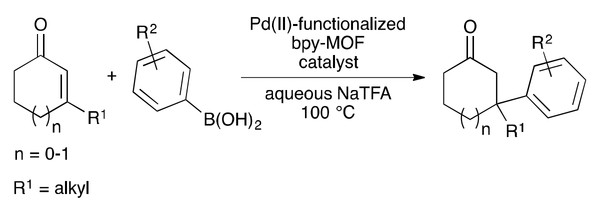
We report palladium(II)-functionalized MOF-253 (MOF-253-Pd(OAc)$_2$) as a recyclable catalyst to form all-carbon quaternary centers via conjugate additions of arylboronic acids to β,β-disubstituted enones in aqueous media. We demonstrate MOF-253-Pd(OAc)$_2$ can be reused 8 times to form ketone products in yields above 75% while maintaining its crystallinity. Additions of a range of stereoelectronically diverse arylboronic acids to a variety of β,β-disubstituted enones catalyzed by MOF-253-Pd(OAc)$_2$ occur in modest-to-high yields (34-95%).

The ability to carry out chemical reactions in the most efficient, economical, and environmentally responsible manner is critical to a sustainable chemical enterprise.[1] To this end, synthetic chemists have sought to develop processes that minimize hazardous reagents while increasing atom economy and energy efficiency.[2] In many reactions, organic solvents constitute the majority of the chemical matter and are the primary source of hazardous waste.[3] As a result, studies to replace hazardous organic solvents with more environmentally benign aqueous media have become a priority.[4]

Homogeneous transition-metal catalysts with outstanding activity and selectivity have been developed as a means to improve atom economy and energy efficiency in a broad range of reactions.[5] Unlike classical heterogeneous catalysts, which often lack the activity and selectivity of their homogeneous counterparts, homogeneous transition-metal catalysts are often difficult or impossible to recover and reuse.[6] Metal-organic frameworks (MOFs) have emerged as a promising platform for catalysis at the interface of traditional homogeneous and heterogeneous catalysis.[7] In recent years, MOFs containing 2,2´-bipyridyl linker units (bpy-MOFs) have been shown to be capable of supporting a variety of transition-metal complexes. The utility of these transition metal-functionalized bpy-MOFs as recyclable catalysts has been demonstrated in a wide variety of organic transformations including: cross-coupling reactions;[8] reductions of carbon dioxide[9] and alkenes;[10] oxidations of alcohols,[11] water,[9b, 12] arylboronic acids,[13] and alkenes;[14] oxidative coupling of amines;[9b] C-H borylation and silylation of arenes;[10, 15] hydrosilylation of ketones;[15a] and hydroborations[10] of alkenes, aldehydes and ketones.[16] These transformations are typically carried out in aprotic reaction media and the structures of the bpy-MOFs are known to be relatively stable even at high temperatures. Much less is understood about the structural stability of bpy-MOFs and metalated derivatives in polar, protic solvents, especially at elevated reaction temperatures.[17] As a result, metal-functionalized bpy-MOFs as catalysts of reactions run in polar, protic solvents remain underexplored.



Scheme 1 Formation of All-Carbon Quaternary Centres via Conjugate Addition in Aqueous Media Catalysed by Pd(II)-Functionalized bpy-MOFs

We recently reported palladium(II) complexes of 2,2′-bipyridine that catalyse conjugate additions of arylboronic acids to β,β-disubstituted enones in aqueous media.[18] However, the palladium species formed upon completion of the reaction cannot be reused as the catalyst. The ability of MOFs to support active metal complexes and prevent bimolecular deactivation processes[9b, 12, 19] prompted us to study palladium(II)-functionalized bpy-MOFs as potentially recyclable catalysts for these conjugate addition reactions and a platform for green catalysis in water. Herein, we report studies to develop palladium(II)-functionalized bpy-MOFs as recyclable catalysts to form all-carbon quaternary centres via

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conjugate additions of arylboronic acids to β,β-disubstituted enones in aqueous media (Scheme 1).

MOF-253 and bpy-UiO-67, two prototypical MOFs containing 2,2′-bipyridyl linkers, were synthesized via reported protocols from [2,2′-bipyridine]-5,5′-dicarboxylic acid and either $ZrCl_4$ or $AlCl_3 \cdot 6H_2O$.[20] Powder X-ray diffraction (PXRD) patterns and nitrogen physisorption analyses of the bpy-MOFs are consistent with reported data (Figures S1-S4). The postsynthetic metalation of bpy-UiO-67 and MOF-253 was performed by treating the bpy-MOFs with $Pd(OAc)_2$ in acetone at ambient temperature to afford bpy-UiO-67-$Pd(OAc)_2$ (**C1**) and MOF-253-$Pd(OAc)_2$ (**C2**) (Figure 1). The integrity of the bpy-MOFs was maintained after metalation based on PXRD patterns (Figure S1 and S2). The palladium content of the catalysts was determined quantitatively by inductively coupled plasma-mass spectrometry (ICP-MS).

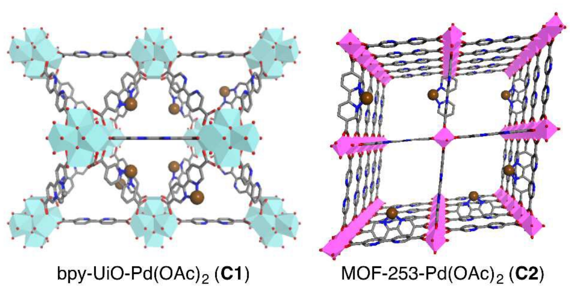


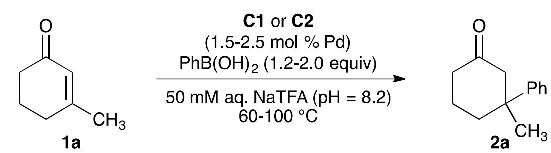
Figure 1 Idealized structures of bpy-UiO-67-$Pd(OAc)_2$ (**C1**) and MOF-253-$Pd(OAc)_2$ (**C2**). Cyan and pink octahedra represent Zr and Al clusters, respectively, while brown, red, blue, and gray spheres represent $Pd(OAc)_2$ species, O, N, and C atoms, respectively; H atoms are omitted for clarity.

With bpy-UiO-67-$Pd(OAc)_2$ and MOF-253-$Pd(OAc)_2$ in hand, we studied the model reaction of phenylboronic acid with 3-methylcyclohex-2-en-1-one **1a** to evaluate the utility of these Pd(II)-functionalized MOFs as catalysts in polar, protic media (Table 1). The reaction of enone **1a** with 1.2 equivalents of phenylboronic acid in the presence of bpy-UiO-67-$Pd(OAc)_2$ (**C1**) (1.5 mol % total palladium based on **1a**) did not form ketone **2a** at 60 °C and formed **2a** in 2% yield at 80 °C when the reactions were run in methanol (entries 1 and 2). Changing the reaction medium from methanol to 50 mM aqueous sodium trifluoroacetate (aq. NaTFA, pH = 8.2) led to the formation of ketone **2a** in 20% yield when the reaction was run at 80 °C (entry 3). Ketone **2a** was formed in 50% yield upon increasing the reaction temperature to 100 °C (entry 4).

We found that the total loading of palladium in the reaction, the number of equivalents of phenylboronic acid, and the weight percentage of palladium present in the MOF significantly impact the yield of our model reaction (entries 5-7). Increasing the total palladium content of the reaction from 1.5 mol % to 2.5 mol % and the amount of phenylboronic acid from 1.2 equivalents to 2.0 equivalents led to the formation of **2a** in 90% yield (entry 6). When the weight % Pd loaded in the MOF was increased from 5.0% to 8.1%, the reaction was complete after two hours and generated **2a** in 99% yield (entry 7). The reaction of phenylboronic acid with **1a** catalysed by MOF-253-$Pd(OAc)_2$ **C2** in place of **C1** also formed **2a** in 99% yield in two hours (entry 8). Reactions of **1a** with phenylboronic acid run in the presence of bpy-UiO-67 with no palladium and an analogous MOF without bipyridine sites, UiO-67-$Pd(OAc)_2$, did not occur to form the conjugate addition product **2a** (entries 9 and 10). These results are consistent with supported Pd(II)-bipyridine complexes as the active catalysts when MOFs **C1** and **C2** are used to promote the model reaction.

The palladium-functionalized MOFs bpy-UiO-67-$Pd(OAc)_2$ **C1** and MOF-253-$Pd(OAc)_2$ **C2** perform similarly as catalysts in the model reaction. Two features of MOF-253-$Pd(OAc)_2$ **C2** led us to select this material for additional catalytic studies. The larger pore size of MOF-253[21] compared to bpy-UiO-67[22] is attractive because the resulting larger pore volumes will be able to accommodate a wider array of enone and arylboronic acid substrates and will facilitate flux of reagents and products into and out of the pores. In addition, we found that MOF-253 could be consistently metalated with approximately 8 weight % Pd, while we observed significant batch-to-batch variations for metalation of bpy-UiO-67 with $Pd(OAc)_2$.

Table 1 Identification of Reaction Conditions[a]



entry	catalyst (mol % Pd)	wt. % Pd in MOF[b]	temp (°C)	$PhB(OH)_2$ (equiv)	yield (%)[c]
1[d]	**C1** (1.5)	5.0	60	1.2	0
2[d]	**C1** (1.5)	5.0	80	1.2	2
3	**C1** (1.5)	5.0	80	1.2	20
4	**C1** (1.5)	5.0	100	1.2	50
5	**C1** (2.5)	5.0	100	1.2	74
6	**C1** (2.5)	5.0	100	2.0	90
7[e]	**C1** (2.5)	8.1	100	2.0	99
8[e]	**C2** (2.5)	8.4	100	2.0	99
9[e]	bpy-UiO-67 (0.0)	0.0	100	2.0	0
10[e]	UiO-67-$Pd(OAc)_2$ (2.4)	2.4	100	2.0	0

[a] Reaction conditions: **1a** (0.500 mmol), $PhB(OH)_2$ (0.600-1.00 mmol), MOF catalyst (0.008-0.013 mmol Pd), reaction medium (0.33 mL), 16 h. [b] Weight % Pd loaded in the MOF determined by ICP-MS. [c] Determined by ^1H NMR spectroscopy using dibromomethane as an internal standard. [d] Reaction run in methanol. [e] Reaction run for 2 h.

To gain insight into the stability of MOF-253-$Pd(OAc)_2$ **C2** under our aqueous reaction conditions, we evaluated the recyclability of **C2** in our model addition of phenylboronic acid to enone **1a** (Scheme 2). Consistent with our data in Table 1, the initial reaction with pristine **C2** as catalyst formed ketone **2a** in 99% yield in less than two hours. Upon recovery of the catalyst and exposure to additional enone **1a**, phenylboronic acid, and aqueous NaTFA, the yield of ketone **2a** dropped to 92% in run 2 and 76-80% in runs 3 and 4 after 2-2.5 hour reaction times. The yield of **2a** could be increased to 90-99% for runs 5-9 by extending the reaction times.

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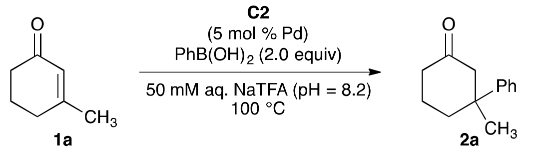


Run	1	2	3	4	5	6	7	8	9
Time (h)	2	2	2.5	2.5	4	4	8	8	16
Yield (%)[a]	99	92	76	80	96	90	99	99	99

Scheme 2 Recycling of **C2** in the addition of $PhB(OH)_2$ to enone **1a**. Reaction conditions: **1a** (1.50 mmol, 1.00 equiv), $PhB(OH)_2$ (3.00 mmol, 2.00 equiv), **C2** (0.075 mmol, 0.050 equiv) and aqueous 50 mM NaTFA (1.00 mL). [a] Determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard.

The results shown in Scheme 2 clearly demonstrate the ability to reuse MOF-253-Pd$(OAc)_2$ **C2** in conjugate additions of phenylboronic acid to enone **1a**. However, these results also show that, at minimum, partial degradation of the **C2** occurs over time. To verify that the solid MOF-supported 2,2′-bipyridine complex of Pd$(OAc)_2$ is the active catalyst in these reactions, we performed leaching tests to eliminate the possibility for MOF degradation into an active and homogeneous palladium species (see Supporting Information). Exposure of **C2** to the reagents and reaction conditions for two hours and analysis of the palladium content of the aqueous supernatant showed that 0.6% of the palladium had leached out of **C2**. However, the palladium found in the supernatant is not catalytically competent under our reaction conditions. Ketone **2a** is formed in 1% yield after two hours when the palladium contained in the supernatant is evaluated as a catalyst of the model reaction under the optimized reaction conditions.

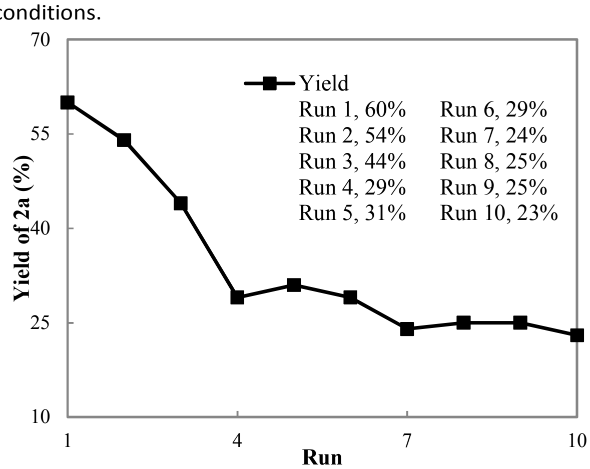
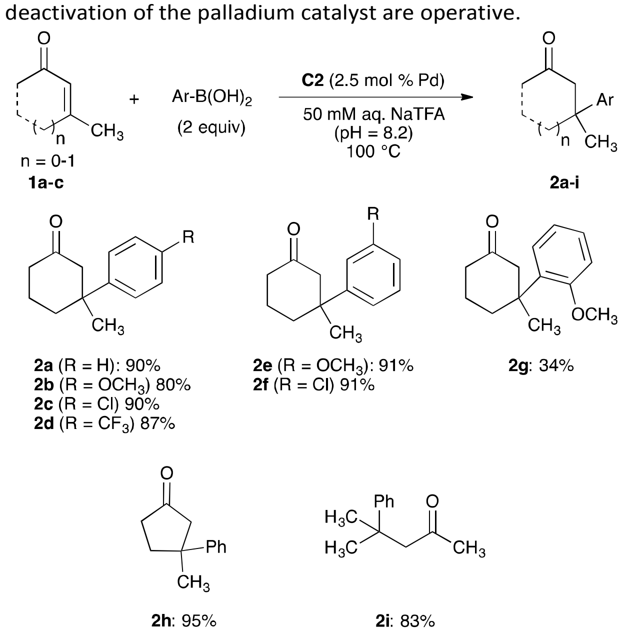


Figure 2 Low conversion recycling experiments. Reaction conditions: **1a** (1.50 mmol, 1.00 equiv), $PhB(OH)_2$ (3.00 mmol, 2.00 equiv), **C2** (0.075 mmol, 0.050 equiv), and aqueous 50 mM NaTFA (1.0 mL, pH = 8.2), 1 h reaction time. Yields of **2a** were determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard.

To develop an understanding of the rate of catalyst deactivation under our reaction conditions, we conducted an additional recycling study where **C2** was reused and the yield of the conjugate addition reaction was determined after one-hour reaction times (Figure 2). As expected from our initial recycling experiment, a slow decline in the activity of the catalyst is observed during the initial recycling runs. By the fourth run, the activity of the catalyst is halved and ketone **2a** is formed in 29% yield compared to 60% in the first run. However, the activity of the catalyst remains consistent in runs 4-10 and **2a** is formed in 23-30% yield after one hour.

The PXRD pattern of MOF-253-Pd$(OAc)_2$ **C2** after the 10th run remained unchanged from that of **C2** before catalysis (Figure S5). More importantly, the used **C2** possesses comparably high surface area relative to freshly prepared **C2** (Figure S6). However, the decrease in activity of the catalyst after two hours (run 2 in Figure 2) is not consistent with the quantity of palladium lost to leaching over two hours. The combination of these results suggests additional pathways for deactivation of the palladium catalyst are operative.



Scheme 3 Conjugate Addition of Arylboronic Acids to Enones 1a-c catalysed by MOF-253-Pd$(OAc)_2$ **C2**. Reaction conditions: **1a-c** (0.500 mmol), arylboronic acid (1.00 mmol), MOF-253-Pd$(OAc)_2$ **C2** (0.013 mmol of Pd), 50 mM aqueous NaTFA (0.33 mL, pH = 8.2), 100 °C, 2-18 h. Isolated yields are reported after purification by flash column chromatography.

With a robust palladium-functionalized MOF for catalysis in water identified, we evaluated the scope of the conjugate addition reaction. Additions of a variety of arylboronic acids to a selection of enones **1a**-**c** catalysed by MOF-253-Pd$(OAc)_2$ **C2** are summarized in Scheme 3. As demonstrated in our optimization studies, the addition of phenylboronic acid to 3-methylcyclohex-2-en-1-one **1a** occurs to form ketone **2a** in 90% yield. Additions of 4-substituted arylboronic acids containing electron-donating, electron-withdrawing, and halogen substituents to enone **1a** formed ketones **2b**-**d** in 80-90%. 3-Substituted arylboronic acids are also suitable substrates for conjugate additions catalysed by **C2**. Additions of 3-methoxy- and 3-chlorophenylboronic acids to enone **1a** generated ketones **2e** and **2f** in 91% yield. The addition of 2-methoxyphenylboronic acid to **1a** occurred to form ketone **2g** in 34% yield. However, additions of 2-substituted arylboronic acid lacking a strong electron-donating substituent did not form conjugate addition products. In these cases,

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protodeborylation of the 2-substituted arylboronic acid is the primary reaction pathway observed.[23]

MOF-253-Pd(OAc)$_2$ **C2** also catalyses conjugate additions of phenylboronic acid to additional cyclic and acyclic β,β-disubstituted enones. The addition of phenylboronic acid to 3-methylcyclopent-2-en-1-one **1b** forms ketone **2h** in 95% yield. The addition of phenylboronic acid to acyclic 4-methylpent-3-en-2-one **1c** generated ketone **2i** in 83% yield. However, additions of phenylboronic acid to 3-arylcyclohex-2-en-1-ones and 3-methylcyclohept-2-en-1-one occurred in <10% yield in the presence of MOF-253-Pd(OAc)$_2$ **C2**. The poor reactivity of these two enone substrates is consistent with analogous reactions carried out in aqueous media and catalysed by a complex of 2,2′-bipyridine and palladium trifluoroacetate that require higher catalyst and arylboronic acid loadings. Attenuated rates for catalysis by **C2** in combination with rates of protodeborylation that remain consistent regardless of the identity of the catalyst can lead to arene formation through protodeborylation as the primary reaction pathway for these more challenging substrates classes.

Conclusions

In summary, we have established two palladium(II)-functionalized bpy-MOFs, bpy-UiO-67-Pd(OAc)$_2$ and MOF-253-Pd(OAc)$_2$, as competent catalysts for conjugate additions of arylboronic acids to β,β-disubstituted enones in water. We have also demonstrated that MOF-253-Pd(OAc)$_2$ is a reusable catalyst system that promotes additions of a range of arylboronic acid to β,β-disubstituted enone reaction partners to form ketones containing quaternary carbon centres. The development of MOF-253-Pd(OAc)$_2$ as a platform for transition-metal catalysis in water sets the stage for new applications of this and related catalyst systems in the areas of green catalysis. Studies to improve the catalytic activities and stabilities of MOF-253-Pd(OAc)$_2$ and additional metalated derivatives for new catalytic transformations in aqueous environments are on-going.

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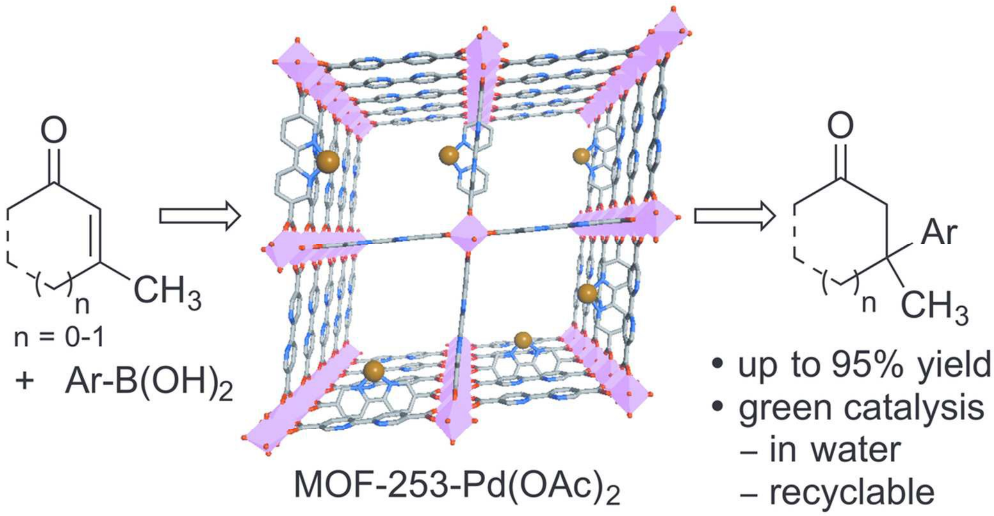

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