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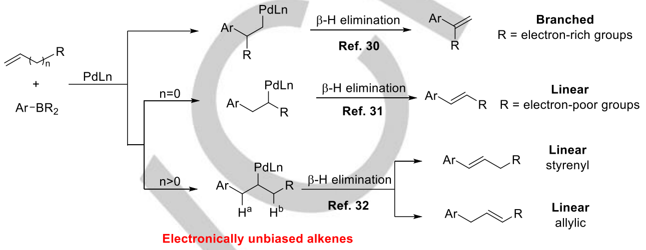
Constructing mononuclear palladium catalysts by precoordination/solvothermal polymerization platform: a recyclable catalyst for regioselective oxidative Heck reaction

Wen-Hao Li,[a] Cun-Yao Li,[b] Huan-Yan Xiong,[a] Yang Liu,[c] Wen-Yong Huang,[a] Guang-Jun Ji,[b] Zheng Jiang,[c] Hai-Tao Tang,*[a] Ying-Ming Pan*[a] and Yun-Jie Ding*[b]

Abstract: Heterogeneous metal single-site catalysts often exhibit higher catalytic performances than other catalysts because of their maximized atom efficiency with 100%. We reported herein a precoordination/solvothermal polymerization strategy to fabricate a stable mononuclear Pd-metalized porous organic polymer catalyst (Pd@POP). Pd@POP was easy to apply in regioselective organic reactions because its internal structure of this Pd@POP can be adjusted easily. Hence, we hoped to use our catalyst to solve the Intractable regioselective problems of Heck reaction. Results showed that Pd@POP-9 can efficiently activate the end of olefins, thereby leading to high selectivity for substitution at the external position. To understand the reason underlying the high selectivity and activity of the catalyst, the systemic characterization of the Pd@POP-9 and density functional theory calculations were provided in detail. This is the first report that Heck reaction can be catalyzed by a recyclable mononuclear metal catalyst with unprecedented catalytic activity and regioselectivity.

Compared with the homogeneous metal/ligand catalytic mode, the heterogenization of corresponding homogeneous catalysts is an attractive tool to achieve recyclable catalysts and highly selective organic synthesis.[1-4] For heterogeneous catalysts, decreasing the size of catalytic metals can maximize the utilization of precious metals, and only a small number of metal particles with appropriate size distribution can be used as catalytic active sites, whereas particles of other sizes are either inert or cause side reactions.[5-7] Dispersing metal active sites into isolated metal atoms (ions) is an effective strategy to solve these problems. Therefore, many atomically dispersed catalysts with single atoms or mononuclear metal complexes (single metal ions) have been prepared for this purpose.[8-11] For atomically dispersed catalysts, support is very important.[12] Unfortunately, in the existing works, most supports do not play the role of ligands, thereby preventing its large-scale application in ligand-controlled regioselective organic reactions.[13] For metal-catalyzed organic chemistry, ligands generally play a significant role. In some organic reactions, the costs of ligands are more expensive than those of the corresponding metal catalysts.[14,15] Therefore, the development of a highly efficient ligand that can be recycled and applied as supports to a mononuclear metal catalyst supports will result in the great development of modern organic synthesis.



Scheme 1. Different products of the Heck reaction.

Porous organic polymers (POPs) have remained a perennial focus as an intriguing platform for incorporating homogeneous metal/ligand catalytic system into heterogeneous supports.[16-19] In our previous research,[20-23] we demonstrated the advantages of phosphorus-doped POPs in the catalytic regioselective and chemoselective reactions and as an effective metal support for single-site catalyst. When P-doped POPs are used as support, mononuclear metal catalyst with 100% metal dispersion can be efficiently synthesized by a traditional polymerization/coordination method.[23] However, this method only works when expensive P-doped POPs are used as supports. For example, when cheaper NHC ligands are used as supports, some metal particles agglomerate under solvent conditions to form large nanoparticles under the same conditions (we will describe this phenomenon in detail in Figure 2).

Mizoroki–Heck reaction is one of the most common examples of using metal/ligand catalytic system to synthesize multiple substituted olefins by introducing an aromatic group to the C=C bond.[24-26] The key issue of this reaction is to regulate the position where an aromatic group is inserted into olefins.[27-29] Electronically biased olefins have been well studied with high regioselectivity successfully.[30-31] When electronically unbiased alkenes are used as substrates, a complex and inseparable mixture of products is created.[32] Generally, ligands play a crucial role in controlling the regioselectivity Heck reactions. Several homogeneous ligand-controlled, highly branched selective Heck have been developed (Scheme 2, L2–L5).[33-38] Sigman et al. reported the first oxidative Heck reaction that delivers high selectivity for (E)-styrenyl products by using unbiased alkenes as substrates with a NHC ligand (Scheme 2,

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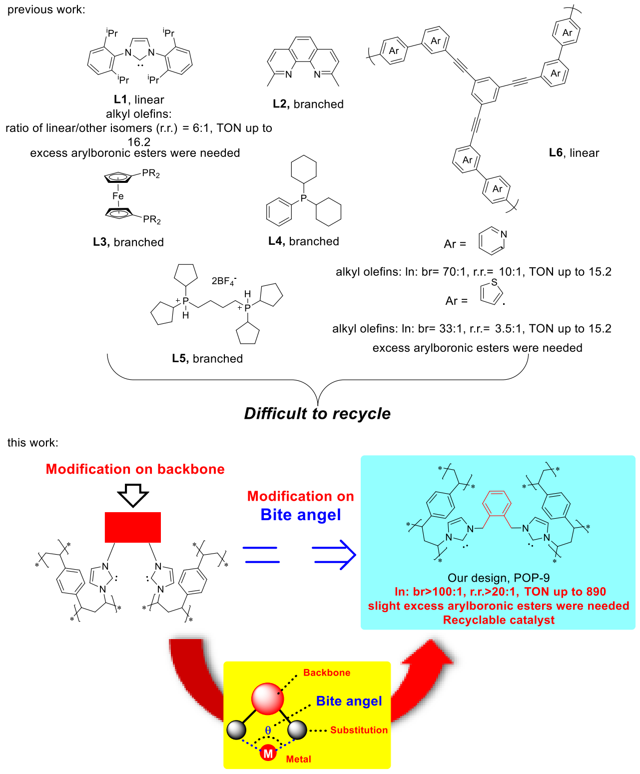

Scheme 2. Designs of ligands for the selective Heck reaction.

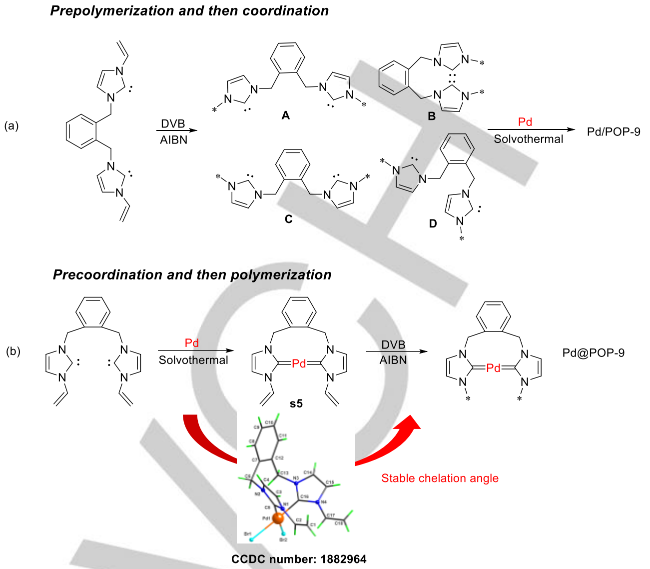

Figure 1. Two different synthesis modes of the catalysts.

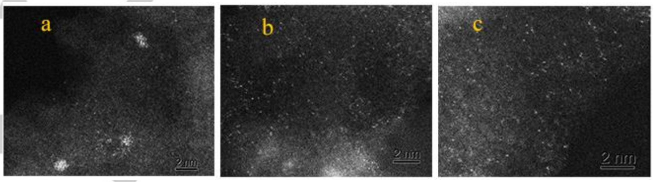

Figure 2. a) HADDF-STEM images of Pd/POP-9. b) HADDF-STEM images of Pd@POP-9. c) HADDF-STEM images of the used Pd@POP-9.

L1).[39] The only example of a heterogeneous catalysis reported by Zhan et al. showed that employing CMP materials as a heterogeneous ligand produces highly linear-selective oxidative Heck product from simple olefins(Scheme 2, L6).[40,41] However, under the existing oxidized Heck reaction conditions, excessive boric acid ester is needed due to borate ester self-coupling.[39-41] Among these developed methods, NHC ligands are certainly the most promising and possesses the highest developmental value compared with unstable and expensive phosphine and alkyne ligands.[42-43] NHC ligands can efficiently promote oxidative addition and consecutive ligand dissociation because of the characteristics of the strong σ-donor.[39,42] Thus, according to Sigman et al. and Zhan et al., we attempted to design and prepare a series of metallized NHC-doped POPs. When we used Pd@POP-9 as a recyclable mononuclear palladium catalyst for the selective Heck reaction of unbiased olefins. With the slight excess of arylboronic esters, Pd@POP-9 can achieve a selectivity of 100:1 (linear: branched), which is higher than the selectivity in the existing literature.

According to the traditional polymerization/coordination method,[23] we first prepared Pd-metallized NHC-doped POPs (Pd/POP-9) (Figure 1a). When we used Pd/POP-9 as a catalyst to catalyze the Heck reaction, we obtained different selective products each time even under the same conditions. This special phenomenon caught our attention. We supposed that the instability of the ratio may be due to the polymerization of the monomer causing the coordination unit to generate various bite angles (Figure 1a, isomers A–D), thereby affecting the reaction result. Catalysts fabricated under the classical prepolymerization/coordination conditions were mostly cluster-type ones (Figure 2a). To avoid the production of different isomers (A–D) during monomer polymerization, we improved the synthesis method. We used a novel synthesis mode in which the monomer through a precoordinated and polymerized process instead of the initial prepolymerization/coordination synthesis mode (Figure 1b). This new strategy can fix the stable chelation angle of the catalytic system via the strong coordination between the transition metal and the ligand. The angle was also be retained after polymerization. The coordination function can also be used to counterbalance the rapidly increasing surface free energy of the metals dispersed into mononuclear particles, which can effectively prevent the aggregation of small clusters.[44] The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image also showed that the Pd@POP-9 prepared through the precoordination/polymerization strategy was a 100% atomically dispersed Pd catalyst on NHC POPs with Pd loading reaching up to 0.37 % (determined by ICP-AES). In order to understand the coordination of Pd and ligands, the monomer **s5** was successfully separated. The ^{13}C NMR spectra of **s5** provided evidence of the metalation, the peak at 162.01 ppm could be ascribed to the palladium coordinate with carbene carbon atoms

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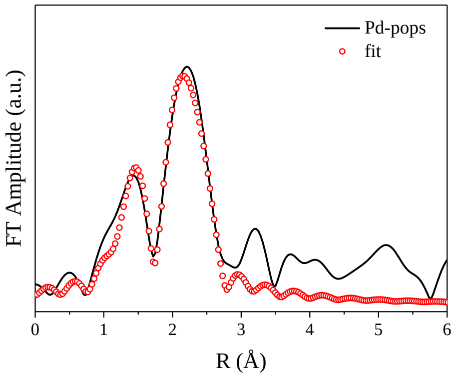


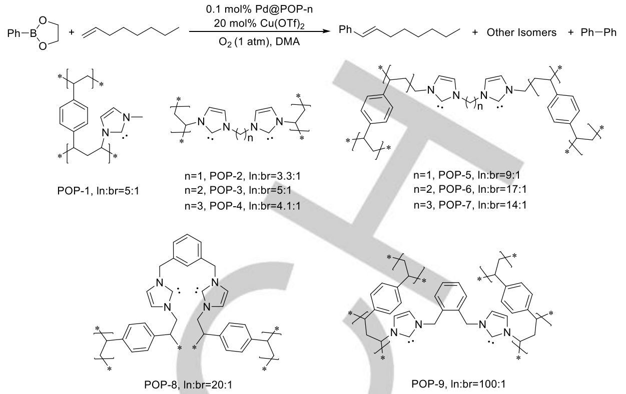
Table 1. Structural parameters extracted from quantitative EXAFS curve-fitting

Sample	Shell	N	R(Å)	ΔE_0 (eV)	$\sigma(10^{-3}Å^2)$	R factor
Pd foil	Pd-Pd	12.0	2.74	-4.5	5.0	0.004
Pd@POP-9	Pd-C	2.0	1.92	-10.0	4.2	0.017
	Pd-N	4.0	2.42	-2.8	9.2	
	Pd-Br	2.0	2.53	13.5	4.2	

N, coordination number; R, distance between absorber and backscatter atoms; ΔE_0, inner potential correction; σ^2, Debye-Waller factor to account for both thermal and structural disorders; The obtained S_0^2 of Pd foil was 0.77 and it was fixed in the subsequent fitting of Pd K-edge data for the sample.

of **s5** (supporting information, pages S18 and S68), which were consistent with those observed in previous studies.[45] The structure of **s5** was further confirmed through single-crystal X-ray structure analysis, and the single crystal data clearly showed the Pd-C coordinating mode (supporting information, pages S69-S72). For polymer catalyst (Pd@POP-9), the EXAFS was characterized. As shown in the table 1, EXAFS data clearly revealed the surrounding environment of Pd species. Pd-C coordination number was 2, Pd-Br coordination number was 2, and there were four nitrogen atoms around the palladium atom. These data were consistent with our single crystal data of monomer **s5**. And no strong Pd–Pd signal in the FT spectrum (Table 1) was observed for Pd@POP-9, suggesting that the Pd clusters have been removed by the coordination leaving only mononuclear Pd sites. Other relevant characterizations were performed to characterize this catalyst further (See supporting information). The TG curves of POP-9 and Pd@POP-9 demonstrated that the polymer can remain intact at temperatures of up to 250 ℃ (Figure S1). The nitrogen adsorption-desorption analysis (Figure S4 and S5) showed that all polymers possessed hierarchical porosity, large pore volumes and high surface areas, which could be further confirmed by SEM images (Figure S6). Additionally, XPS of our catalyst has been characterized to check the valence of Pd species. The result indicted that palladium existed in the form of Pd^{2+}. (Figure S7).

To study the influence of the polymer internal structure on regioselective Heck reaction, we synthesized a series of Pd-metallized NHC-doped POPs. First, we used monodentate Pd@POP-1 and bidentate Pd@POP-5 as catalysts and electronically biased 1-octene as the reaction substrate. The results showed that monodentate Pd@POP-1 can effectively



Scheme 3. Optimization of different Pd@POPs.

control the reaction selectivity (ln:br = 5:1), while bidentate Pd@POP-5 possessed higher selectivity than Pd@POP-1 (ln:br = 9:1). According to our previous studies, the bite angle formed by the two coordination centers of the bidentate ligands and the transition metal catalytic center possesses different regulatory effects on many reactions. Hence, we successfully designed and synthesized different bidentate NHC-doped POPs by fine-tuning the backbone of the ligand unit to regulate the chelation angle. When Pd@POP-9 was used as a catalyst, the linear product can achieve an excellent ln/br selectivity of 100:1. In previous studies, self-polymerizing P-doped ligand polymers often increase the catalyst reactivity and selectivity due to their high ligand concentrations and complex electronic properties. However, in the present study, Pd-metallized NHC-doped POPs showed the opposite result. The higher the concentration of the ligand units was, the poorer selectivity and the yield of the products will be (Table S2). As mentioned earlier, the typical oxidized Heck reaction required three equivalents of arylboronic esters to ensure the formation of the olefin coupling products because the self-coupling reaction of the arylboronic esters tend to occur. However, when we used Pd@POP-9 as a catalyst, the self-coupling products cannot be observed. Therefore, we only need a slight excess of arylboronic esters to promote the reaction due to the excellent chemoselectivity of the catalyst.

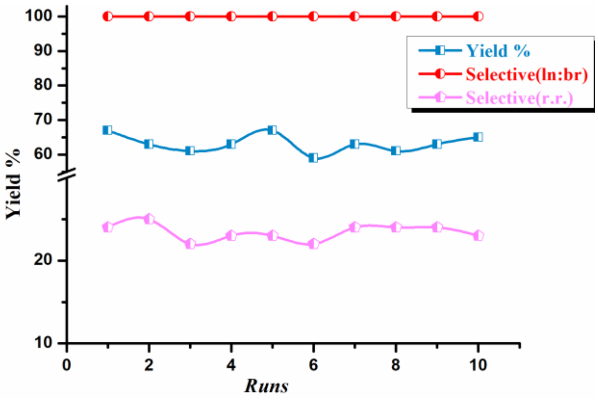


Figure 3. Studies on recycling of Pd@POP-9 for the oxidative Heck reaction.

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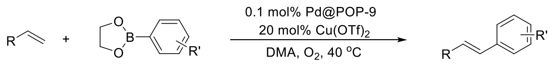
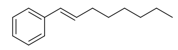
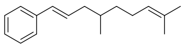
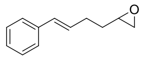
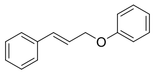
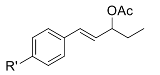
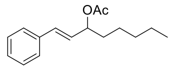
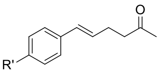
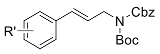
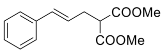
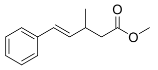
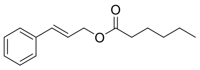
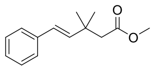
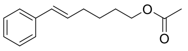
Table 2. Scope of oxidative Heck reaction.[a]



Entry	Prouct	% Yield^b (% Yield[e])	linear:branched[d]
1		67 (19)	100:1
2		74	100:1
3		87	40:1
4		83	80:1
			
5	R'= Cl	83 (7)	>100:1
6[g]	R'= H	86	>100:1
7	R'= OMe	71 (22)	>100:1
8	R'= CF_3	89	>100:1
9[c],[f]		43	>100:1
			
10	R'= Cl	54 (37)	20:1
11	R'= H	69	>100:1
12	R'= CF_3	65 (12)	>100:1
			
13	R'= H	93	>100:1
14	R'= *m*-F	61 (25)	>100:1
15	R'= *p*-OMe	92	>100:1
16		68	>100:1
17[c]		86	33:1
18[c],[f]		47 (36)	>100:1
19		81	20:1
20[g]		75	>100:1

[a] Reaction conditions: olefins (0.4 mmol), arylboronic esters (0.48 mmol), Pd@POP-9 (0.1 mol %), $Cu(OTf)_2$ (20 mol %), DMA (3 mL), 40 °C, O_2 (1 atm), 48 h. The selectivity (r.r.) for desired product was >20:1. [b] Isolated yield. [c] Using 0.8 mmol % arylboronic esters. [d] Determined by ^1H NMR spectroscopy. [e] Recovered starting material. [f] Reating 72 h. [g] The selectivity (r.r.) for desired product was >10:1.

Reusability is one of the core features of our heterogeneous catalysts. To the best of our knowledge, reusable heterogeneous catalyst on controlling regioselective Heck reactions have not been reported to date. We repeated the Heck reaction with Pd@POP-9 (Figure 3) up to 10 times. After each run, Pd@POP-9 was recovered via vacuum evaporation and washed sequentially with DMA, water, and acetone. Pd@POP-9 can be used for at least 10 runs without affecting regioselectivity and catalytic activity. The STEM images showed that Pd@POP-9 lacked notable aggregation after the 10th run (Figure 2b and 2c). Another possible reason for the high regioselectivity and activity of the catalysts was fact that NHC ligand can maintain a stable pKa because it contains large number of anions.

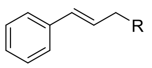
To test and verify the scope of the substrate of Pd@POP-9, we used a variety of electronically unbiased alkenes and arylboronic esters as substrates (Table 2). The Pd@POP-9 catalytic system facilitated the formation of the (E)-linear product and proved to be tolerant of various electrical functional groups. For example, olefins such as a ketone (Table 2, entries 10–12), an ether (Table 2, entries 3 and 4) or an ester (Table 2, entries 9, 16–20) all accessed linear-(E) products with good to excellent yields. Good yield and excellent selectivity were still observed for several allyl esters, especially substrates that tent to undergo competitive oxidative addition with the presence of Pd catalysts (Table 2, entry 5–9). A doubly protected allylic amine with a broad range of arylboronic esters can also access the linear-(E) products with excellent yields and selectivity under this catalysis system (Table 2, entries 13–15).

Long-chain aliphatic olefins are generally the most representative and challenging substrates for Heck reaction due to the absence of inductive effects and chelation. Studies on branched- and linear-selective have received extensive attention. However, the majority of the overall selectivity (r.r.) in these studies remains at 10:1. In the present study, the selectivity under the Pd@POP-9 catalyst system was improved compared with these studies. The ratio of the linear products to branched products reached 100:1, and the overall selectivity (r.r.) can reach up to 20:1 (Table 2, entries 1 and 2). To the best of our knowledge, no catalytic system can achieve such excellent catalytic results for selective Heck reaction. Therefore, the chelation of the ligand to the metal center plays an important role in the catalytic system.

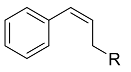
Table 3. DFT-Calculated Thermodynamic and Kinetic Population (%) for Different Products.

Product	ΔG[a]	$\%_{Thermo}$	*m*-$\Delta\Delta G^{\neq}$[b]	$\%_{kinetic}$	*b*-$\Delta\Delta G^{\neq}$[b]	$\%_{kinetic}$
A	0	96.63%	0.0	58.92%	0.0	71.35%
B	2.6	1.41%	1.2	7.76%	1.4	6.71%
C	2.8	1.15%	0.7	18.06%	0.7	21.87%
D	3.0	0.81%	0.8	15.26%	4.1	0.07%

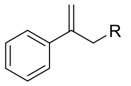
[a] DFT-Calculated free energy of possible products relative to product **A**. [b] Calculated using free energy values of transition states from Gaussian 16 A. 03. software package according to Eyring equation. *m* denotes monodentate and *b* denotes bidentate.



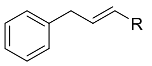
A



B



C



D

To further confirm the observed selectivity, DFT (Density Functional Theory) calculation is employed to shed light on the catalytic mechanism of the Heck reaction catalyzed by Pd catalyst. Both bidentate NHC ligand and monodentate NHC ligand are taken into consideration. 1-Butene is chosen as the substance for computational modeling. We firstly compared the free energy results among four different products. The DFT calculated results indicate **A** is most stable product thermodynamically, the calculate ratio of different products based on Boltzmann distributions suggests A is the dominant product (96.63%) among others. The origin of such difference can be attributed to a better conjugation effect between phenyl and the C=C bond in product **A**. With these understandings in mind, we then explore different reaction pathways of selectivity-determining step (Please see SI). The TSs (transition states) leading to different products are located and the $\Delta\Delta G^{\neq}$ are summarized in Table 3. The calculated results suggest the TS yield product **A** has the lowest energy barrier in both two catalysts. Noteworthily, the population of product **A** increases by nearly 12% when replacing the monodentate ligand with bidentate ligand, which is qualitatively in line with the experimental observations. The rate-determining step is found to be the insertion of phenyl group into C=C bond of 1-butene, which is found to be lowered by 5.5 kcal/mol (Please see Figure SI: A-IM2→A-TS1:24.2 kcal/mol; B-RC→B-TS1:18.7 kcal/mol) when using bidentate ligand. Thus, it requires less energy penalty for the catalyst using bidentate NHC ligand to furnish the most stable product. Moreover, the catalyst using bidentate ligand is more stable thermodynamically due to the entropy effect. Therefore, the bidentate NHC ligand can increase regioselectivity of product **A**.

In summary, compared with traditional polymerization/coordination methods, we used a precoordination/polymerization strategy to prepare a series of mononuclear Pd catalysts. Pd@POP-9 was easy to apply in the highly linear-selective oxidative Heck reaction of simple olefins because the internal structure of this Pd@POP can be adjusted easily. The Pd@POP-9 used in this study is the first example that uses reusable heterogeneous catalyst in controlling regioselective Heck reactions. This work also created a new catalytic system that incorporated NHC ligands, mononuclear metal catalysis, and POPs. This catalytic system can be used as a new regioselective tool to regulate complex organic synthesis in achieving high selectivity and reactivity that cannot be achieved under homogeneous conditions. Mononuclear metal catalytic system developed under this efficient synthesis mode can possess extensive applications in the future.

Experimental Section

To a solution of arylboronic esters (0.48 mmol) and electronically unbiased alkenes (0.4 mmol) in DMA (4 mL), $Cu(OTf)_2$ (20 mol%) and palladium catalyst (0.1 mol%) were added and the mixture was stirred at 40 ºC for 48 h under O_2 atmosphere (1 atm.). When the reaction was completed (monitored by TLC), the solution was filtered and washed with EtOAc and ether. The filtered solution was evaporated under vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product.

Acknowledgements

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Keywords: mononuclear metal catalysts • NHC-doped POPs • oxidative Heck reaction • prepolymerization/coordination synthesis mode • regioselectivity

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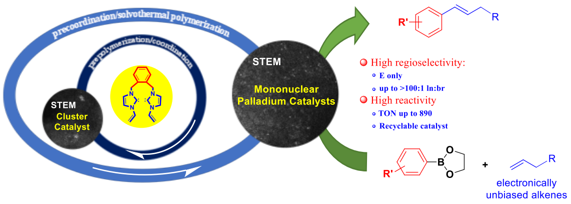

We reported herein a precoordination/solvothermal polymerization strategy to fabricate a stable atomically dispersed mononuclear Pd-metalized NHC-doped porous organic polymer catalyst (Pd@POP). This is the first report that Heck reaction can be catalyzed by a recyclable catalyst (Pd@POP-9) with unprecedented catalytic activity and regioselectivity.

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