

A Highly Active and Reusable Self-Assembled Poly(Imidazole/Palladium) Catalyst: Allylic Arylation/Alkenylation**

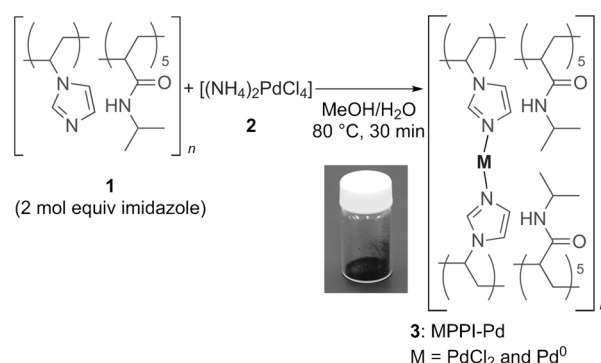
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Metalloproteins, supramolecular composites of polymeric peptides and metal species, are essential organic transformation systems for maintaining vital activity to promote highly efficient enzymatic reactions.^[1] For example, the metalloprotein catalase provides extremely high turnover efficiencies of $40\,000\,000\text{ sec}^{-1}$. However, metalloproteins are easily disassembled and exhibit substrate specificity. Therefore, the development of a metalloprotein-inspired polymeric metal catalyst is an important objective for organic, organometallic, and supramolecular chemistry, as well as sustainable and industrial process chemistry.^[2] These catalysts are expected to provide highly active and selective organic transformation systems with high reusability, safety, cleanness, ease of use, and substrate tolerance. In metalloproteins, the basic imidazole unit within histidine plays an important role for binding with metal species, thus forming catalytic sites within a supramolecular structure; therefore imidazole ligands are widely utilized as the building blocks of artificial metal-organic self-assembled supramolecules for functional materials including catalysts.^[3] We believe that some insoluble self-assembled complexes of amphiphilic polymeric imidazoles and metal species could offer catalytic activities as high as that of metalloproteins, but with much greater reusability.

We recently reported the preparation of highly active, reusable, heterogeneous polymeric metal catalysts for organic transformations, also known as molecular convolution, where a soluble linear polymer having multiple ligand groups is convoluted (noncovalently cross-linked) with transition metals through coordinative or ionic complexation.^[4] We envisioned applying this concept to the preparation of metalloprotein-inspired polymeric imidazole metal catalysts to produce highly active, reusable, heterogeneous, self-assembled catalysts. Herein we report the development of a novel polymeric imidazole/acrylamide palladium catalyst that

was utilized for the allylic arylation/alkenylation of allylic esters with aryl/alkenylboronic acids and tetraaryl borates. Even 0.8–40 ppm of the catalyst efficiently promoted the allylic arylation/alkenylation in alcohol or water with a catalytic turnover number (TON) of 20000–1250000, and the catalyst was reusable without loss of catalytic activity. We found that our molecular convolution methodology provided the globular-aggregated, self-assembled structure of the catalyst.

The metalloprotein-inspired polymeric imidazole/palladium catalyst **3** (MPPI-Pd) was readily prepared as follows. When the coordinative convolution of $[(\text{NH}_4)_2\text{PdCl}_4]$ (**2**; 1 mol equiv Pd) and poly[(*N*-vinylimidazole)-co-(*N*-isopropylacrylamide)]₅ (**1**; 2 molequiv imidazole) was carried out in a methanol/water (1:1) solution at 80 °C for 30 minutes, the resulting compound **3** (brown powder) was precipitated out (Scheme 1). The precipitates were hardly soluble in water, methanol, DMF, EtOAc, CH_2Cl_2 , or *n*-hexane. As shown in the top left panel of Figure 1, scanning electron microscopy



Scheme 1. Preparation of a metalloprotein-inspired polymeric imidazole palladium catalyst (MPPI-Pd; **3**).

(SEM) images revealed that the precipitates formed a globular-aggregated, self-assembled structure similar to the quaternary structure of proteins. The globules ranged from 100 to 1000 nm in diameter, and aggregated to construct a mesoporous suprastructure. X-ray photoelectron spectroscopy (XPS) of the palladium showed a major peak at 336 eV and a minor peak at 334 eV, which were assigned as Pd^{II} and Pd^0 , respectively (Figure 1; bottom left). Transmission electron microscopy (TEM) observation revealed the formation of palladium nanoparticles having a diameter of $(4.9 \pm 2.5)\text{ nm}$ (Figure 1; center left); these nanoparticles were obtained by reduction with MeOH. These results suggested that the

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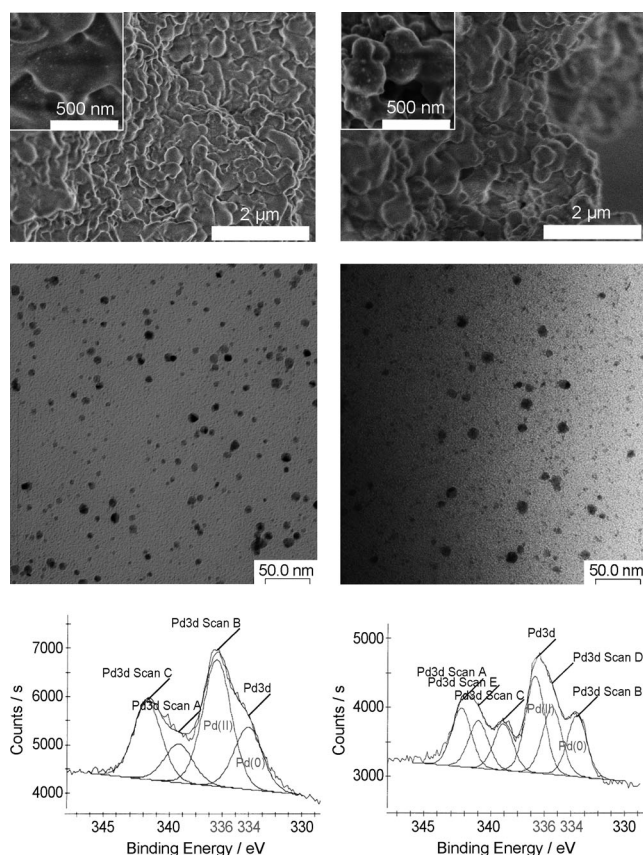


Figure 1. SEM images of **3** before use (top left) and after the 5th reuse (top right). TEM images of the **3** before use (center left) and after the 5th reuse (center right). XPS images of the **3** before use (bottom left) and after 5th reuse (bottom right).

catalyst was a composite of the polymeric imidazole **1**, palladium complexes, and palladium nanoparticles. In the composite, the palladium complexes should act as cross-linkers of **1** through palladium–imidazole coordination, and the imidazole units in **1** could serve to stabilize the palladium nanoparticles. Elementary analysis and ICP-AES analysis of the palladium supported the structure shown in Scheme 1.

The catalytic activity and reusability of the novel catalyst **3** were examined for allylic arylation/alkenylation of allylic esters with tetraaryl borates and arylboronic acids. Although there are numerous reports on aryl–aryl coupling with aryl boron reagents (Suzuki–Miyaura coupling), little attention has been paid to allyl–aryl coupling, which often requires a relatively high reaction temperature with a large amount (1–10 mol %) of catalyst.^[6] We previously reported the allylic arylation of allylic esters and tetraaryl borates using a microchannel reactor with poly(acrylamide triarylphosphine palladium) catalytic membrane.^[7] However, both the reactivity and substrate generality were insufficient. The results led us to the idea that newly developed catalysts could be applied to the allylic arylation to provide high catalytic activity and reusability as well as high substrate tolerance.

When the allylic arylation was examined using cinnamyl acetate (**4a**) and sodium tetraphenylborate (**5a**) in *i*PrOH/

H₂O (1:1) with 40 ppm palladium (0.004 mol % Pd) using **3**, the reaction proceeded smoothly to give 1,3-diphenylpropene (**6a**) quantitatively after 4 hours (Table 1, entry 1). In the reaction, the turnover number and frequency were 25 000 and 6250 h^{−1}, respectively, which are the highest numbers for allylic arylation to date. Moreover, **3** was reused five times without any loss of catalytic activity to give **6a** quantitatively. The coupling reaction with the reused (5th) catalyst did not show evidence of leaching of the palladium species into the reaction mixture (ICP-AES analysis; entry 6). SEM and TEM observations,^[8] and XPS analysis of **3** and reused **3** indicated that the catalyst was undamaged and unchanged under the reaction conditions (Figure 1; top, center, and bottom right panels). The reaction in water without the use of any organic solvents also proceeded smoothly to give **6a** in 98 % yield (entry 7). The phenyl vinyl carbinol ester **4b** gave **6a** with a yield of 96 % (entry 8). Electron-donating and electron-withdrawing substituents on the cinnamyl esters **4c–4g** reacted with substituted tetraaryl borates **5a–d** and were efficiently converted into the corresponding products **6b–i** with yields in the range of 93–98 % (entries 9–16).

It is interesting to note that the alkyl vinyl carbinol esters **4h–j** underwent palladium-catalyzed (40 ppm) allyl–aryl coupling to yield the corresponding coupling products **6j–l** quantitatively (Table 1, entries 17–20). The reaction of alkyl vinyl carbinol esters must proceed via the corresponding π -allylpalladium intermediate bearing the β hydride on the sp^3 -carbon center, a species that often suffers from the β -hydride elimination under palladium-catalyzed conditions to give undesirable 1,3-dienes.^[9,10] However, no trace of 1,3-dienes was observed in the reactions. The palladium-catalyzed (40 ppm) reaction of **4i** was also performed in water to give **6k** quantitatively (entry 19).

Furthermore, the coupling of aliphatic 2-alkenyl acetates is more challenging than that of cinnamyl acetates in terms of reactivity. However, geranyl acetate (**4k**), neryl acetate (**4l**), prenyl acetate (**4m**), and 2-hexenyl acetate (**4n**) efficiently led to the corresponding phenylated compounds **6m–p** with yields in the range of 96–99 % (Table 1, entries 21–25). Isomerization was not observed in the reactions, and water was used as a reaction solvent (entry 23). Alicyclic acetates **4o** and **4p** were readily converted into the corresponding products **6q** and **6r** with yield of 96 % (entries 26 and 27); the reaction of *cis*-**4p** proceeded through net inversion to give *trans*-5-methoxycarbonyl-3-phenyl-1-cyclohexene (**6r**) as a single diastereomer (entry 27).

The heterogeneous catalyst **3** (40 ppm) also promoted allylic substitution with aryl/alkenylboronic acids, which are versatile and readily available boron reagents (Table 2). Thus, the reaction of **4a** with phenylboronic acid (**7a**) and methanolic or aqueous KF at 70 °C yielded **6a** quantitatively (entries 1 and 2). The substituted arylboronic acids **7b–d** readily underwent carbon–carbon bond formation under similar conditions to give **6h**, **6s**, and **6t** with a yield of 98 % (entries 3–5). The alkyl vinyl carbinol esters **4i–j**, neryl acetate (**4l**), and cyclohexenyl acetate (**4o**) were converted into the corresponding alkenes **6k**, **6l**, **6n**, and **6q** with yields in the range of 97–99 % (entries 6–9). Allylic alkenylation, the allyl–alkenyl coupling reaction, of allylic acetates with

Table 1: Allylic arylation of allylic acetates with tetraarylborates.^[a]

$ \begin{array}{c} \text{R}^1\text{CH}=\text{CH}\text{CH}(\text{R}^2)\text{OAc} + \text{R}^3\text{BNa} \xrightarrow[\text{50 } ^\circ\text{C, 4 h}]{\text{3 (40 ppm), } i\text{PrOH/H}_2\text{O or H}_2\text{O}} \text{R}^1\text{CH}=\text{CH}\text{CH}(\text{R}^2)\text{R}^3 \\ \text{4} \qquad \qquad \qquad \text{5} \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{6} \end{array} $				
Entry	Allylic ester 4	5 (R ³)	Product 6	Yield [%]
1		4a 5a (Ph)		6a 99
2		4a 5a	6a (3 : 1st reuse)	99
3		4a 5a	6a (3 : 2nd reuse)	99
4		4a 5a	6a (3 : 3rd reuse)	99
5		4a 5a	6a (3 : 4th reuse)	99
6		4a 5a	6a (3 : 5th reuse)	99 ^[b]
7 ^[c]		4a 5a	6a	98
8		4b 5a	6a	96
9		4c 5a		6b 97
10		4d 5a		6c 93
11		4e 5a		6d 96
12		4f 5a		6e 98
13		4g 5a		6f 98
14		4a 5b (4-MeC ₆ H ₄)		6g 98
15		4a 5c (4-ClC ₆ H ₄)		6h 96
16		4a 5d (4-FC ₆ H ₄)		6i 98
17		4h 5a		6j 98
18		4i 5a		6k 99
19 ^[c]		4i 5a		6k 99
20		4j 5a		6l 97
21		4k 5a		6m 96
22		4l 5a		6n 97
23 ^[d]		4l 5a		6n 99
24		4m 5a		6o 98
25		4n 5a		6p 97
26		4o 5a		6q 96
27		4p 5a		6r 96

[a] Reaction conditions: **4** (0.5 mmol), **5** (1 mmol), **3** (20 nmol), *i*PrOH/H₂O (0.75 mL each) or H₂O (1.5 mL), 50 °C, 4 h. [b] Palladium species were not detected in the reaction mixture (ICP-AES). [c] The reaction was carried out in water for 8 h. [d] The reaction was carried out in water for 24 h.

alkenylboronic acids is more challenging in terms of reactivity as well as isomerization of olefins compared to allylic arylation.^[11] However, the reaction of **4a** with (*E*)-1-pentenylboronic acid (**7e**) proceeded smoothly with 40 ppm of **3** under similar reaction conditions to give (1*E*, 4*E*)-1-phenyloctadiene (**6u**) in a 98 % yield, wherein no isomerization occurred (entry 10). Neryl acetate (**4l**) was also coupled with alkenylboronic acid **7e** to give the triene **6v** in a 98 % yield (entry 11). Furthermore, the allylic vinylation efficiently proceeded under similar conditions. Thus, the allylic vinylation of **4a** and **4h** with dibutyl vinylboronate (**7f**) yielded the corresponding *exo*-dienes **6w** and **6x** in 95 % yield without the formation of isomers (entries 12 and 13).

Since **3** promoted efficient allylic arylations and alkenylations, 0.8 ppm of **3** was used for the reaction of **4a** and **5a** under similar reaction conditions (Scheme 2). We were pleased to find that the desired product **6a** was obtained quantitatively, wherein the TON and TOF were more than one million (1250000) and 104000 h⁻¹, respectively. To the best of our knowledge, this is the highest TON and TOF for allylic arylation.

In conclusion, the novel globular-aggregated, self-assembled supramolecular composite **3** of a polymeric imidazole and a palladium species was developed. Catalyst **3** (0.8–40 ppm Pd) efficiently catalyzed the allylic arylation/alkenylation in alcohol or water under mild reaction conditions. The catalyst **3** provided the highest TON and TOF for allylic arylation/alkenylation, and was reused five times without loss of catalytic activity.

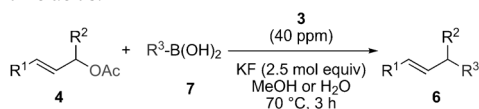
Experimental Section

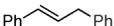
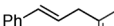
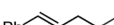


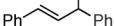
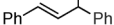
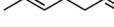


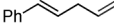
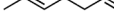
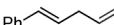

Preparation of MPPI-Pd (3**):** An aqueous solution of [(NH₄)₃PdCl₄] (**2**; 108 mg, 0.379 mmol; 5 mL) was slowly added to a solution of the imidazole polymer **1** (500 mg, 0.758 mmol) in methanol (5 mL) at 25 °C. The resulting brown suspension was heated at 80 °C for 45 min before the precipitates were filtered off through a glass filter. The precipitates were washed with H₂O and MeOH, successively, at 80 °C for 30 min in a flask. The precipitates were filtered off, washed with MeOH on the glass filter, and dried under reduced pressure to give **3** (583 mg, 92 %). Anal. Calcd for C₇₀H₁₂₂N₁₄O₁₀Cl₂Pd·5H₂O: C, 52.97; H, 8.38; N, 12.35; Cl, 4.47; Pd, 6.70. Found: C, 53.07; H, 8.30; N, 12.82; Cl, 4.64; Pd, 6.96. IR (KBr): 3285, 2972, 2875, 1658, 1530, 1453, 1386, 1236, 1172, 928, 834, 728, 655 cm⁻¹.

General procedure for allylic arylation catalyzed by MPPI-Pd (3**):**

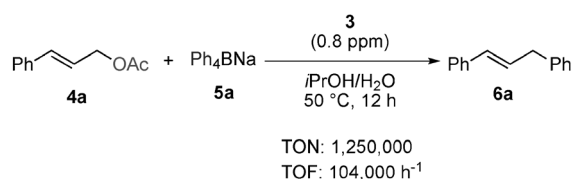
Reaction of cinnamyl acetate (**4a**) with sodium tetraphenylborate (**5a**): A 2.5 mL glass vessel was charged with sodium tetraphenylborate (**5a**; 342 mg, 1 mmol), **3** (0.03 mg, 40 ppm) in 2-propanol and water (1:1; 0.75 mL each). Cinnamyl acetate (**4a**; 88 mg, 0.5 mmol) was added to the reaction mixture, and the reaction vessel was then shaken using a PetiSzyer (HiPep Laboratories, Japan) at 50 °C for 4 h. The reaction mixture was filtered, and the recovered **3** was washed with Et₂O (4 × 3 mL). The combined filtrate was dried over MgSO₄ and concentrated

Table 2: Allylic arylation/alkenylation of allylic acetates with arylboronic/alkenylboronic acids.^[a]



Entry	Allylic ester	7 (R ³)	Product	Yield [%]
1	4a	7a (Ph)		6a 97
2 ^[b]	4a	7a		6a 99
3	4a	7b (4-ClC ₆ H ₄)		6h 98
4	4a	7c (4-MeOC ₆ H ₄)		6s 98
5	4a	7d (3,4-(MeO) ₂ C ₆ H ₃)		6t 98
6	4i	7a		6k 99
7	4j	7a		6l 99
8	4l	7a		6n 98
9	4o	7a		6q 97
10	4a	7e ((<i>E</i>)- )		6u 98
11	4l	7e		6v 98
12	4a	7f [CH ₂ =CHB(O- <i>n</i> Bu) ₂]		6w 95
13	4h	7f		6x 95

[a] Reaction conditions: **4** (0.5 mmol), **7** (0.6 mmol), **3** (20 nmol), MeOH (1.5 mL), 70 °C, 3 h. [b] The reaction was carried out in water for 60 h.



Scheme 2. Allylic arylation of **4a** with **5a** catalyzed by 0.8 ppm of **3**.

under reduced pressure. The residue was chromatographed on silica gel (*n*-hexane/ethyl acetate 9:1) to give **6a** in 99% yield.

Reaction of cinnamyl acetate (**4a**) with phenylboronic acid (**7a**): A 2.5 mL glass vessel was charged with phenylboronic acid (**7a**; 73.1 mg, 0.6 mmol), potassium fluoride (72.5 mg, 1.25 mmol), **3** (0.03 mg, 40 ppm), and MeOH (1.5 mL). Cinnamyl acetate (**4a**; 0.5 mmol) was added to the mixture, and the reaction mixture was then shaken using a PetiSzyer (HiPep Laboratories, Japan) at 70 °C for 3 h. The reaction mixture was filtered, and the recovered **3** was washed four times with Et₂O on the filter (4 × 3 mL). The combined filtrate was dried over MgSO₄ and then concentrated under reduced

pressure. The residue was chromatographed on silica gel (*n*-hexane/ethyl acetate 9:1) to give (*E*)-1,3-diphenylpropene (**6a**) in 97% yield.

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- [8] The mean diameter of the palladium nanoparticles in the reused (5th) catalyst was (4.8 ± 2.4) nm.
- [9] For excellent palladium-catalyzed arylation of secondary allylic acetates possessing β -hydrides on sp^2 - or sp^3 -carbon centers, see:
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