

## Supramolecular Catalysts by Encapsulating Palladium Complexes within Dendrimers

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Dendrimers<sup>1</sup> are of great interest as new materials for applications in many areas such as catalysts.<sup>2</sup> A characteristic feature of dendrimers is the presence of internal cavities, which can host organic molecules<sup>3</sup> and metal nanoparticles.<sup>4</sup> Using this property, the catalytic active species can be introduced in the interior spaces of dendrimers to construct nanoreactors, which have received considerable attention because of their unique catalysis.<sup>4</sup> Recently, we have reported on the substrate-specific hydrogenation of olefins based on the hydrogen bonds between the tertiary amino groups inside a poly(propylene imine) (PPI) dendrimer and substrates.<sup>4a</sup> This success has provided us with a new strategy for the design of dendrimer-encapsulated metal catalysts that utilize the inner nano-environment of the dendrimers. In this communication, we describe the novel immobilization of a Pd complex catalyst within the cavity of dendrimers through ionic bonds.<sup>5</sup> The dendrimers encapsulating Pd complexes act as unique nanoreactors for Heck reactions and allylic aminations. Moreover, the dendritic nanoreactor could readily be recovered using thermomorphic system. To date, there are only a few examples of the positive dendritic effects on the activity of catalysts, in which the active sites are incorporated inside the dendrimers.<sup>6</sup>

PPI dendrimer was chosen as a nanoreactor because of the high density of tertiary amino groups in its interior. Peripheral amino groups on the third to fifth generation of the PPI dendrimer **1–3** were modified with decanoyl chloride and 3,4,5-triethoxybenzoyl chloride,<sup>4b</sup> respectively, to give the alkylated (**1a–3a**) and arylated (**1b**) dendrimers. 4-Diphenylphosphinobenzoic acid **4** was used as the phosphine ligand to fix the Pd complex inside the dendrimers through ionic bonds between the carboxyl group and an internal amino group of the dendrimer.

<sup>1</sup>H NMR studies in *d*<sub>8</sub>-toluene of **1a** showed that the addition of **4** caused downfield shifts of the  $\alpha$ -methylene protons of the tertiary amino groups, from the initially observed shift at 2.29 to 2.34–2.58 ppm, in ratios of **4/1a** = 1–6. These shifts can be explained as protonation of the tertiary amino groups of the dendrimer.<sup>7</sup> Similarly, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra also showed interactions between **1a** and **4**.<sup>8</sup> [PdCl(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] was added to the above mixture of **1a** and **4** to form the dendrimer-encapsulated Pd complex. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the resulting Pd complex (P/Pd = 1) showed a characteristic singlet at 23.1 ppm, whereas metal-free **4** exhibited a single resonance at –3.8 ppm. The  $\alpha$ -methylene proton signal of the tertiary amino group remained at about 2.40 ppm during the metal complexation. It can be said that the Pd complex is encapsulated through ionic bonds between the carboxyl group of **4** and amino groups within the dendrimer as shown in Figure 1. The local structure around Pd has been well characterized using Pd K-edge EXAFS data.<sup>8</sup>

Initially, as shown in Table 1, the potential ability of the dendrimers encapsulating Pd complexes as nanoreactors was investigated in the Heck reaction.<sup>9,10</sup> The dendritic Pd complexes efficiently catalyzed the Heck reaction of iodobenzene with *n*-butyl

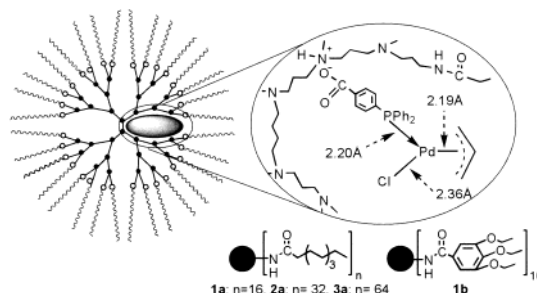


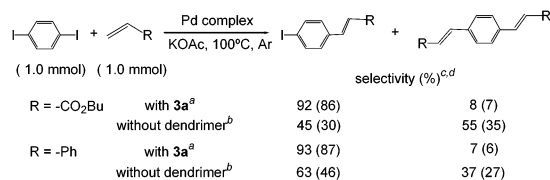
Figure 1. Proposed structure of dendrimer-encapsulated Pd complex.

Table 1. Heck Reaction Catalyzed by Dendrimer-Encapsulated Pd Complexes<sup>a</sup>

$\text{ArX} + \text{CH}_2=\text{CH-R} \xrightarrow[\text{toluene, KOAc, 100}^\circ\text{C}]{\text{Dendr-Pd}} \text{Ar-CH}_2\text{-CH(R)-CH}_3 + \text{HX}$					
entry	ArX	R	dendrimers	P/Pd	yield (%) <sup>b</sup>
1 <sup>c</sup>	PhI	–CO <sub>2</sub> Bu	<b>1a</b>	1	72
2	PhI	–CO <sub>2</sub> Bu	<b>1a</b>	2	59
3	PhI	–CO <sub>2</sub> Bu	<b>2a</b>	2	89
4	PhI	–CO <sub>2</sub> Bu	<b>3a</b>	1	92
5	PhI	–CO <sub>2</sub> Bu	<b>3a</b>	2	89
6	PhI	–CO <sub>2</sub> Bu	<b>3a</b>	3	37
7	PhI	–CO <sub>2</sub> Bu	<b>3a</b>	4	19
8	1-C <sub>10</sub> H <sub>7</sub> I	–CO <sub>2</sub> Bu	<b>3a</b>	1	83
9	PhI	–CO <sub>2</sub> Bu	none	1	<1
10 <sup>c,d</sup>	PhI	–CO <sub>2</sub> Bu	<b>3a</b>	1	38
11 <sup>e</sup>	PhI	–Ph	<b>3a</b>	1	99
12 <sup>e</sup>	1-C <sub>10</sub> H <sub>7</sub> I	–Ph	<b>3a</b>	1	99

<sup>a</sup> [PdCl(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (0.005 mmol), dendrimer (0.01 mmol), toluene (10 mL), aryl halide (1.0 mmol), olefin (1.4 mmol), KOAc (1.4 mmol), 2 h. <sup>b</sup> Determined by GC analysis. <sup>c</sup> Decomposition of Pd complexes was observed. <sup>d</sup> PPh<sub>3</sub> was used instead of **4** as a ligand. <sup>e</sup> For 12 h.

acrylate, while the reaction hardly occurred in the absence of the dendrimer under the present conditions (entry 9). The reaction rates increased with increasing generations of the dendrimers (entries 2, 3, and 5); the generation effect was most pronounced between the third and fourth generations. In the case of **3a**, the reaction rates decreased as the molar ratio of **4**/Pd was increased (entries 4–7). Notably, an active Pd species could be encapsulated to prevent its decomposition even in a **4**/Pd ratio of 1 (entry 4), while the use of **1a** resulted in the precipitation of Pd metals (entry 1). Moreover, using PPh<sub>3</sub> instead of **4** also gave a poor result (entry 10). Generally, the stabilization of homogeneous Pd(0) active species requires the addition of excess phosphine ligands.<sup>9</sup> The fifth generation dendrimer acts as an effective nanoreactor with high catalytic activity and stability for the Pd(0) species in a low P/Pd ratio. It can be reasoned that the dense amino groups inside the dendrimer provide a polar nanoenvironment around the active Pd species and coordinate to the Pd species, which leads to the high catalytic activity and the stability for the encapsulated Pd complex.

**Scheme 1.** Heck Reaction of *p*-Diiodobenzene with Olefins Using Pd Complexes<sup>a–d</sup>


<sup>a</sup> [PdCl(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (0.005 mmol), **3a** (0.01 mmol), **4** (0.01 mmol), toluene (10 mL), KOAc (1.4 mmol). <sup>b</sup> [PdCl(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (0.005 mmol), **4** (0.02 mmol), DMF (10 mL), KOAc (1.4 mmol). <sup>c</sup> Determined by LC analysis at a complex consumption of olefins. <sup>d</sup> Yields are given in parentheses.

**Table 2.** Allylic Amination Using Dendrimer-Encapsulated Pd Complexes<sup>a</sup>

entry	dendrimers	P/Pd	yield (%) <sup>b</sup>	L/B (-)
1	<b>1a</b>	2	78	8.5
2	<b>2a</b>	2	67	8.5
3	<b>3a</b>	1	36	9.0
4	<b>3a</b>	2	52	9.0
5 <sup>c</sup>	<b>3a</b>	2	>99	9.0
6	<b>3a</b>	4	19	9.0
7	none	2	83	5.1
8 <sup>d</sup>	<b>1a</b>	2	35	4.8
9 <sup>d</sup>	none	2	33	4.1

<sup>a</sup> [PdCl(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (0.0025 mmol), dendrimer (0.005 mmol), toluene (10 mL), cinnamyl methyl carbonate (1.0 mmol), morpholine (1.2 mmol), 30 min. <sup>b</sup> Determined by GC analysis. <sup>c</sup> For 12 h. <sup>d</sup> PPh<sub>3</sub> was used instead of **4** as a ligand.

The fifth generation dendrimer encapsulating the Pd complex can be applied to other Heck reactions. For example, 1-iodonaphthalene was reacted with *n*-butyl acrylate and styrene to give high yields of *n*-butyl 3-(1-naphthyl)acrylate and 1-styryl-naphthalene, respectively (entries 8 and 12). Moreover, in the reaction of *p*-diiodobenzene with *n*-butyl acrylate, *n*-butyl *p*-iodocinnamate as a monosubstituted product was obtained in 92% selectivity using the nanoreactor, whereas a nearly equimolar mixture of mono- and disubstituted products was obtained without the dendrimer. A similar phenomenon was also observed using styrene instead of *n*-butyl acrylate. As summarized in Scheme 1, these results strongly support that the Heck reaction occurs inside the dendrimers.

Furthermore, the dendrimers encapsulating Pd complexes can also act as unique nanoreactors for allylic amination. The results of allylic amination of cinnamyl methyl carbonate with morpholine at 20 °C are summarized in Table 2.<sup>11</sup> The reaction rates increased with decreasing generations of the dendrimers (entries 1, 2, and 4), which was also observed in the hydrogenation of olefins using our dendrimer-encapsulated Pd nanoparticles.<sup>4a</sup> The surface congestion of the higher-generation dendrimers can suppress the penetration of substrates into the dendrimers. However, such filter effect on the reaction rates was not observed in the above Heck reaction.<sup>12,13</sup> Molar ratios between linear and branched products (L/B) were 8.5, 8.5, and 9.1 with **1a**, **2a**, and **3a**, respectively (entries 1, 2, and 4), whereas the reaction in the absence of the dendrimers gave L/B = 5.1 (entry 7). L/B values increased with increasing polarity of solvents:<sup>14</sup> L/B = 5.1 (toluene), 7.7 (THF), 12.2 (acetone), and 14.1 (DMSO).<sup>15</sup> Regioselectivity was controlled by the local polarity around the Pd species within the dendrimers.<sup>16</sup> Using PPh<sub>3</sub> instead of **4** led to a low L/B value, with or without the dendrimers (entries 8 and 9).

Recycling the dendritic catalysts has been attempted by solvent precipitation<sup>17</sup> and membrane filtration,<sup>5a,18</sup> which often resulted in some losses of the catalytic activities. The solubility of the dendrimers can be tuned by their surface modifications with keeping their inner nanoenvironment intact.<sup>1</sup> Modification of the PPI dendrimer with 3,4,5-triethoxybenzoyl chloride instead of decanoyl chloride afforded dendrimer **1b** which was not soluble in aliphatic hydrocarbons such as heptane, but possessed high solubility in polar solvents such as DMF. In the allylic amination of cinnamyl methyl carbonate with piperidine, the thermomorphic two phases of DMF and heptane became homogeneous during the reaction and then could be readily separated by cooling the reaction mixtures.<sup>13,19</sup> The DMF phase containing the dendritic nanoreactor could be recycled after decantation of the heptane phase. The highly catalytic activity was retained during reuse experiments; yields of *N*-cinnamylpiperidine in the heptane phase were 46% (first), 99% (second), 99% (third), and 99% (fourth).

In summary, we have demonstrated that the Pd complexes could be encapsulated within the PPI dendrimers through ionic interactions. The specific nanoenvironment created by the dense amino groups inside the dendrimers can provide high catalytic activity and stability for the Pd complexes. The employment of a thermomorphic system allowed the recycling of the dendritic Pd catalysts.

**Supporting Information Available:** Experimental details and curve-fitting analysis (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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