

Letter

# Catalysis of dendrimer-bound Pd(II) complex Selective hydrogenation of conjugated dienes to monoenes

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## Abstract

Complexation of the diphenylphosphinomethylated dendrimer DAB-dendr-[N(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]<sub>16</sub> with PdCl<sub>2</sub>(PhCN)<sub>2</sub> gave a dendrimer-bound PdCl<sub>2</sub> complex. The dendritic Pd complex showed high catalytic activity for the selective hydrogenation of conjugated dienes to monoenes under mild reaction conditions. The catalytic activity of the dendritic Pd complex was higher than that of the corresponding low-molecular weight complex [PhN(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>PdCl<sub>2</sub>]. The dendritic catalyst was easily recovered from reaction mixtures and could be reused without any loss of the activity. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Diphenylphosphinomethylated dendrimer; Dendrimer-bound Pd(II) complex; Selective hydrogenation; Conjugated dienes; Catalyst reuse

## 1. Introduction

The dendrimers are novel macromolecules with the monodispersed molecular weights, precisely determined cascade structures, and specific number of the end groups [1–5]. Surface functional groups on the dendrimers can be easily modified with various ligand atoms capable of binding metal complexes to give a number of metal-containing dendrimers [6–8]. Then,

much attention has been paid to the dendritic metal complexes as catalysts because they have structurally well-defined and specific number of active sites seen in the traditional homogeneous catalysts as well as the possibility of recovery and reuse of the heterogeneous catalysts [9–12].

In the course of our studies on catalyst design of highly functionalized polymeric metal complexes [13–16], we chose the dendrimers as well-defined polymeric ligands and found that the dendrimer-bound Pd(II) complex showed high catalytic activity for the hydrogenation of conjugated dienes to monoenes. We report here the characteristic features of the dendrimer-bound Pd(II) complex catalysts, as compared

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with those of the corresponding monomeric complex and a typical polymeric Pd catalyst of the polystyrene-bound Pd(II) complex [17].

## 2. Experimental

The diphenylphosphinomethylated dendrimer DAB-dendr-[N(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]<sub>16</sub> (**1**) was synthesized from DAB-dendr-(NH<sub>2</sub>)<sub>16</sub> according to the method of Reetz et al. [7].<sup>1</sup> Complexation of **1** with PdCl<sub>2</sub>(PhCN)<sub>2</sub> afforded the dendrimer-bound PdCl<sub>2</sub> complex (**2**). [PhN(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>PdCl<sub>2</sub>] (**3**) as a low-molecular weight analogue of **2** was obtained by the literature procedure [18,19]. The structures of dendritic compounds **1** and **2** were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P nuclear magnetic resonance (NMR) spectra. In the <sup>31</sup>P NMR spectrum of **2**, a sharp signal at  $\delta = -28.0$  due to the metal-free dendrimer **1** completely disappeared and only a new signal was observed at  $\delta = +7.93$  corresponding to the phosphines coordinated to Pd complexes. Infrared (IR) spectrum of **2** had broad bands at 294 cm<sup>-1</sup> assigned as terminal, *cis* Pd–Cl stretching bands, which were similar to those observed in **3** [20]. X-ray photoelectron spectroscopy (XPS) spectrum of **2** showed two bands at 343.4 and 338.3 eV due to Pd 3d<sub>3/2</sub> and 3d<sub>5/2</sub>, respectively, and the binding energy of Cl 2p was 197.9 eV. The above values of binding energies are comparable with those of **3** and a typical Pd(II) complex of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.<sup>2</sup> From these results, the structure of the dendritic Pd complex **2** can be considered as a divalent DAB-dendr-[N(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Pd(II)Cl<sub>2</sub>]<sub>16</sub>.

The catalytic activity of **2** was examined in the hydrogenation of cyclopentadiene under an

atmospheric pressure of H<sub>2</sub> in EtOH, as compared with those of **3**, Pd/C, and Pd/Al<sub>2</sub>O<sub>3</sub>.<sup>3</sup> The timecourses of hydrogen uptakes are shown in Fig. 1. In the case of **2**, the hydrogen uptake drastically dropped after cyclopentadiene was consumed completely. At this stage, high selectivity for the formation of cyclopentene was observed; cyclopentene was an only product without cyclopentane. Further, the successive reduction of cyclopentene occurred at an extremely slow rate when the reaction was prolonged. Using Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, rates of the hydrogenation remained constant after the perfect consumption of the diene without such a turning point of the hydrogen uptake; a competitive reduction of cyclopentadiene and cyclopentene occurred to result in low selectivity for the monoene. A rate of the hydrogenation with **3** was extremely low among these Pd catalysts used. It has been reported that such a selective hydrogenation of dienes to monoenes using homogeneous Pd catalysts required high pressures of H<sub>2</sub> and SnCl<sub>2</sub> as an activating agent [21,22].

The initial rates of H<sub>2</sub> uptakes in the hydrogenation of various olefins are summarized in Table 1, accompanied by those using the polystyrene-bound Pd catalyst [17]. The dendritic catalyst **2** has high activity for the hydrogenation of several cyclic conjugated dienes to monoenes. Notably, the rates increase in the order of C<sub>5</sub> < C<sub>6</sub>–C<sub>8</sub>, while the size of substrates much influences the hydrogenation rates in the case of the polystyrene-bound Pd catalyst [17]. Reductions of non-conjugated diene and common monoolefins such as 1,5-COD and cyclooctene occurred slowly. An acetylenic com-

<sup>1</sup> The poly(amino)dendrimer DAB-dendr-(NH<sub>2</sub>)<sub>16</sub> was purchased from DSM Fine Chemicals.

<sup>2</sup> The binding energies of Pd 3d<sub>3/2</sub>, 3d<sub>5/2</sub> and Cl 2p of the complexes **3** and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> are as follows; 343.6, 338.5, and 198.0 eV for **3** and 343.6, 338.3, and 198.5 eV for PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

<sup>3</sup> Dendritic catalyst **2** (0.01 mmol Eq of Pd) was placed in a side-armed flask attached to a gas buret and a manometer. The system was evacuated and filled with H<sub>2</sub>, followed by addition of 5 ml of EtOH and stirred for half an hour at 25°C. Hydrogen uptake was measured just after the addition of cyclopentadiene (1.3 mmol).

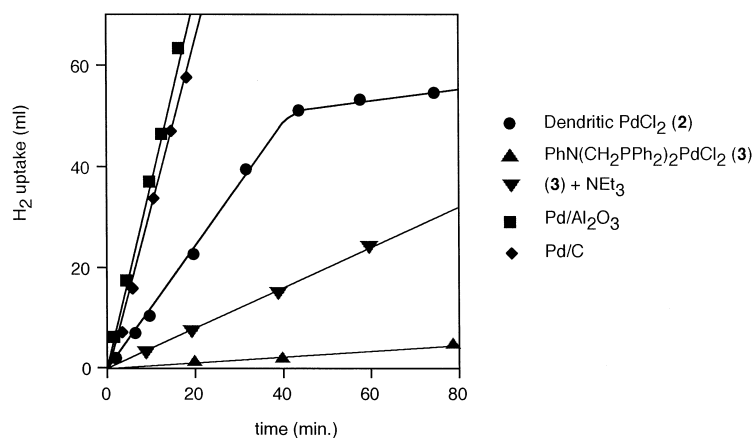










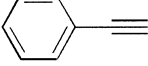
Fig. 1. Timecourses of H<sub>2</sub> uptakes using various Pd catalysts in the hydrogenation of cyclopentadiene.

pound of phenylacetylene was also hydrogenated to give styrene in 90% selectivity. Nitro, carbonyl, and nitrile compounds, e.g., ni-

trobenzene, benzaldehyde, acetophenone, and propionitrile were not reduced under the above reaction conditions.

Table 1

Hydrogenations of olefins catalyzed by dendrimer-bound Pd(II) complex (2) and polystyrene-bound Pd(II) complex (PS-PdCl<sub>2</sub>)<sup>a</sup>

substrate	initial rate (x 10 <sup>-1</sup> ml/min.)		substrate	initial rate (x 10 <sup>-1</sup> ml/min.)	
	2	PS-PdCl <sub>2</sub> <sup>b</sup>		2	PS-PdCl <sub>2</sub> <sup>b</sup>
	13.9	19.3		1.0 <sup>c</sup>	4.9
	21.7	17.1		3.3 <sup>c</sup>	3.3
	18.0	11.3		0.6 <sup>c</sup>	0.5
reuse	17.6			1.1	3.8
	18.2			4.9	13.9

<sup>a</sup>Reaction conditions: substrate 1.3 mmol, EtOH 5.0 ml, catalyst 0.01 mmol of Pd, 25 ± 1°C, H<sub>2</sub> 1 atm.

<sup>b</sup>Ref. [17]. Reaction conditions: substrate 4.3 mmol, benzene–EtOH (1:1) [13 – (volume of substrate)] ml, catalyst 0.04 mmol of Pd, 25 ± 1°C, H<sub>2</sub> 1 atm.

<sup>c</sup>Reaction temperature 40 ± 1°C.

### 3. Results and discussion

Table 2 shows the hydrogenation of 1,3-cyclooctadiene by **2** and **3** in the various solvents. Notably, in this hydrogenation, the catalytic activity of the dendritic complex **2** is higher than that of the low-molecular weight Pd analogue **3** in various solvents. Generally, heterogenization of metal complexes using organic polymers has disadvantages such as lowered reactivity induced by diffusion limitation of substrates, catalyst leaching, steric hindrance, and inability to totally mimic reactivity and selectivity attainable with the corresponding homogeneous ones [12]. It has been also reported that dendritic metal complex catalysts had lower activities than analogous monomeric complexes in many organic reactions [23–25].

Presumably, an active species for this hydrogenation may be a Pd(II) hydride species derived from the following scheme on the basis of hydrogenation using the polystyrene-bound Pd(II) catalyst [17].



L = bisphosphine ligand.

According to the above equilibrium equation, generation of the Pd–H can be accelerated by

Table 2

Hydrogenation of 1,3-cyclooctadiene in various solvents catalyzed by dendrimer-bound Pd(II) complex (**2**) and [PhN(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-PdCl<sub>2</sub>] (**3**)<sup>a</sup>

Solvent	Initial rate ( $\times 10^{-1}$ ml/min)	
	<b>2</b>	<b>3</b>
EtOH	18.0 (Hetero)	0.3 (Hetero)
MeOH	13.8 (Hetero)	0.6 (Hetero)
<i>n</i> -BuOH	12.9 (Hetero)	1.2 (Hetero)
<sup>i</sup> PrOH	9.1 (Hetero)	1.3 (Hetero)
THF	9.7 (Hetero)	1.5 (Hetero)
DMF	8.7 (Homo)	1.1 (Homo)
Acetone	7.0 (Hetero)	0 (Hetero)
Toluene	5.1 (Hetero)	0.2 (Hetero)
<i>n</i> -Hexane	1.2 (Hetero)	0 (Hetero)
Chloroform	0.5 (Hetero)	0 (Hetero)

<sup>a</sup>Reaction conditions: substrate 1.3 mmol, catalyst 0.01 mmol of Pd, solvent 5 ml, H<sub>2</sub> = 1 atm, 25 ± 1°C.

Hetero: heterogeneous reaction. Homo: homogeneous reaction.

the presence of bases. In a separated experiment, addition of triethylamine to the corresponding low-molecular weight catalyst **3** increased rates of the hydrogenation as shown in Fig. 1. The highly catalytic performance of **2** would be due to the dendrimer structure containing many amino moieties, as compared with **3**.

Interestingly, the solubility of **2** in various solvents did not strongly influence the catalytic activities. Among the solvents used in Table 2, EtOH was the most effective solvent although **2** was insoluble in EtOH. On the other hand, the hydrogenation proceeded homogeneously in DMF, but the rate of hydrogenation was not high. Since all active sites of **2** are located on the dendrimer surface, the substrates easily gain access to the active sites on the surface without steric hindrance and diffusion limitation, which might lead to the efficient hydrogenation even in the heterogeneous system using EtOH solvent. Vide supra, the fact that molecular size of dienes did not affect the hydrogenation rate could be explained by the above unique character of the functionalized dendrimer ligand. These phenomena are a sharp contrast to results of our previous hydrogenation using the polystyrene-bound Pd complex [17]; in order to swell the polystyrene support, a mixed solvent of benzene and EtOH must be used because many Pd active sites exist within the polystyrene matrix.

Recycling of **2** was carried out in the heterogeneous hydrogenation of 1,3-COD in EtOH. After the hydrogenation, the dendritic catalyst was separated from the reaction mixture by centrifugation and washed with EtOH in air, then dried in vacuo.<sup>4</sup> The spent Pd catalyst was used in the hydrogenation for the 2nd run. The catalytic performance of **2** about the activity and selectivity for the hydrogenation was kept in the 2nd run. The dendritic Pd catalyst maintained

<sup>4</sup> In the case of homogeneous hydrogenations in DMF solvent, **2** could be recovered as precipitates by adding an excess of ether to the reaction mixtures.

pale yellow color throughout the above reuse experiment. From XPS spectra of the spent catalyst, the binding energies of Pd 3d<sub>3/2</sub>, 3d<sub>5/2</sub> and Cl 2p were almost the same as those of the fresh ones. IR spectrum of the spent catalyst supported the *cis* configuration of the complex as was shown in fresh one.

#### 4. Conclusions

The dendrimer-bound PdCl<sub>2</sub> complex **2** has high catalytic activity for the selective hydrogenation of conjugated dienes to monoenes under an atmospheric pressure of H<sub>2</sub>. The catalytic activities is higher than those of the corresponding low-molecular weight complex. **2** can be easily recovered and reused without any loss of the activity.

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