Self-assembled Dendrimer-bound Pd(II) Complexes via Acid-base Interactions and their Catalysis for Allylic Amination

Masahiko Ooe, Makoto Murata, Atsushi Takahama, Tomoo Mizugaki, Kohki Ebitani, and Kiyotomi Kaneda*
Department of Chemical Science and Engineering, Graduate School of Engineering Science, Osaka University,
1-3 Machikaneyama, Toyonaka, Osaka 560-8531

(Received May 12, 2003; CL-030405)

The Pd complexes were noncovalently attached on the periphery of poly(propyleneimine) dendrimers based on acid-base interactions. The dendritic Pd complexes were found to possess catalytic activities for allylic amination, and to be able to mimick the catalytic activity of the analogous monomeric Pd complex catalyst.

Dendrimers are hyperbranched macromolecules with monodispersed molecular weights, precisely determined cascade structures, and a specific number of end groups.[1] One of the promising application of metallodendrimers is in the field of catalysis.[2] Immobilization of metal complex catalysts onto soluble or insoluble polymers by covalent binding have often encountered the difficulties in mimicking the structures of parent complexes and mass transfer limitations, which results in decreases of the catalytic activities.[3] Organometallic dendrimers, however, because of their structurally well-defined and specific number of active sites as well as their congested surface regarded as solid supports, offer the potential for bridging the gap between homogeneous and heterogeneous catalysis.[4] Recently, we have reported the preparation of covalently phosphinated poly(propyleneimine) (PPI) dendrimer-bound $PdCl_2$ complexes and Pd(0) complexes, and their unique catalyses in the selective hydrogenation of dienes to monoenes[5] and the stereoselective allylic amination.[6] We wish to report here the alternative approach for the preparation of dendritic catalysts using ionic interactions between the carboxyl groups of phosphine ligands and the terminal amino groups on the PPI dendrimers,[7] and their catalysis in allylic amination.[8]

Based on the well-defined cascade structures and the specific number of primary amino groups on the periphery that are available for catalyst binding sites, the third and fifth generation PPI dendrimers (**1a**, **1b**) were chosen as the host supports. The dendrimer-bound Pd complexes (**3a** and **3b**) were prepared via two steps as shown in Figure 1.[9,10] Treatment of the PPI dendrimers **1** with 4-diphenylphosphinobenzoic acid (DPPBA) gave phosphinated dendrimers **2** (step **i**), followed by the addition of $[PdCl(\pi\text{-}C_3H_5)]_2$ to afford the self-assembled dendritic Pd complexes **3** (step **ii**).

The above dendrimers were characterized using IR and ^{31}P NMR. In IR spectra, addition of DPPBA(16 eq.) to **1a** showed a new band at $1534\,cm^{-1}$ due to the carboxylate of DPPBA and the band for free DPPBA at $1694\,cm^{-1}$ disappeared (**step i**). The $^{31}P\{^1H\}$ NMR spectrum exhibited a singlet signal for free DPPBA gave at −4.8 ppm, which shifted slightly upfield to −5.2 ppm for the dendritic hosts **2**. Furthermore, addition of $[PdCl(\pi\text{-}C_3H_5)]_2$ to **2** resulted in a shift of the DPPBA signal from −5.2 to 23.4 ppm. From these results, the Pd phosphine complexes were bound on the dendrimers through ionic interactions between the carboxyl group of DPPBA and the peripheral amino groups of **1** (Figure 1).

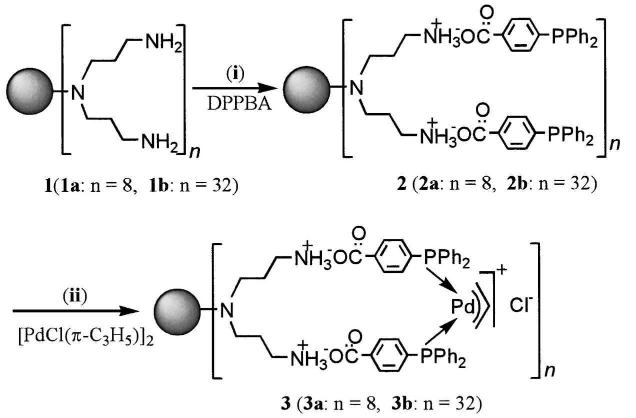
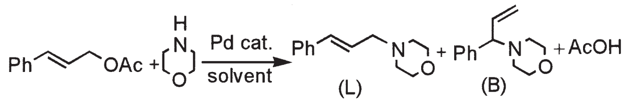


Figure 1. Preparation of self-assembled dendrimer-bound Pd complexes.

The catalytic performance of dendrimer-bound Pd complexes **3** for the allylic amination of cinnamyl acetate with morpholine are summarized in Table 1.[11] The allylic amination smoothly proceeded with the dendritic catalysts **3a** and **3b**, in which the reaction rates strongly dependent on the P/Pd ratio; the highest activity was obtained at P/Pd = 2 (Entries 2 and 8). Above P/Pd = 2, the catalytic activities decreased with increasing P/Pd ratios. Similar trend was also observed for the reactions in the absence of the dendrimers (Entries 12-16). Although the present dendrimer-bound Pd complexes were insoluble in DMF solvent, the allylic amination proceeded smoothly under such heterogeneous conditions (Entry 4). Generally, for many organic reactions, immobilization of metal complexes using organic polymers tends to decreases their catalytic activity as compared to the monomeric analogs,[3] which is attributable to the mass transfer limitation of substrates to the active sites within the polymer matrices.[12] It can be said that all the active Pd species attached to the periphery of the dendrimers act as active catalytic centers without the diffusion control even under heterogeneous conditions using DMF solvent.[5]

The stereoselectivity of the amination[12] was investigated using *cis*-3-acetoxy-5-carbomethoxy-1-cyclohexene with morpholine (Scheme 1). A 60% selectivity of the *cis* product was observed with the dendritic catalyst **3b**, whereas a 1:1 mixture of *cis*- and *trans* products was observed using **3a** and the dendrimer-free catalyst. Interestingly, in DMF solvent, the *cis*-selectivity was 62% in the case of **3a**. In our previous paper, higher stereoselectivity for this amination was obtained, when increasing the generation of the phosphinated dendrimer-bound

Table 1. Pd-catalyzed allylic amination of cinnamyl acetate with morpholine[a]

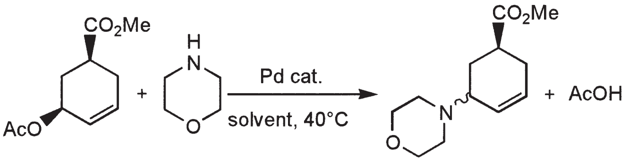


Entry	Catalyst	P/Pd	Time /min	Yield /%	L/B
1	**3a**	1	10	24	10
2	**3a**	2	10	51	10
3	**3a**	2	30	89	13
4[b]	**3a**	2	30	>99	25
5	**3a**	4	10	46	8
6	**3a**	6	10	26	10
7	**3b**	1	10	22	10
8	**3b**	2	10	47	10
9	**3b**	2	30	81	11
10	**3b**	4	10	30	9
11	**3b**	6	10	18	11
12[c]	dendrimer-free Pd	1	10	25	10
13[c]	dendrimer-free Pd	2	10	52	10
14[c]	dendrimer-free Pd	2	30	83	12
15[c]	dendrimer-free Pd	4	10	46	8
16[c]	dendrimer-free Pd	6	10	22	10

[a] Reaction conditions: cinnamyl acetate 3.0 mmol, morpholine 4.5 mmol, $[PdCl(\pi\text{-}C_3H_5)]_2$, 0.01 mmol, DPPBA 0.02-0.12 mmol, **1a** 1.25-7.50 µmol, **1b** 0.31-1.88 µmol, MeOH 16 mL, 5 °C.

[b] DMF was used as a solvent at 10 °C. [c] Without the dendrimers.

Pd(0) complex catalyst, in which the active sites were covalently attached to the periphery of the dendrimers.[6] It seems that, compared to the immobilization by covalent binding, the present immobilization of Pd complexes on the dendrimers by ionic interactions may afford active sites with high mobility on the surfaces,[7] even under the heterogeneous conditions. That is, the self-assembled dendrimer Pd catalysts can mimic low molecular weight Pd catalysts in terms of catalytic activity and selectivity.



Catalyst	Solvent	Select /% *cis* : *trans*
3a	MeOH	50 : 50
3a	DMF	62 : 38
3b	MeOH	60 : 40
3b	DMF	60 : 40
dendrimer-free Pd	MeOH	50 : 50

Reaction conditions: *cis*-3-acetoxy-5-carbomethoxy-1-cyclohexene 1.0 mmol, morpholine 1.0 mmol, catalyst (0.04 mmol of Pd, P/Pd = 2), solvent 16 mL, 40 °C. Selectivity was calculated at 30 % conversion of the allylic substrate.

Scheme 1. Generation dependence of stereoselectivity in allylic amination of *cis*-3-acetoxy-5-carbomethoxy-1-cyclohexene with morpholine.

In conclusion, we present the preparation of self-assembled dendritic Pd catalysts using noncovalent binding via acid–base interactions between dendritic hosts and phosphine ligands. Since the active Pd species are attached on the periphery of PPI dendrimers, high catalytic performance, which is comparable to that of the parent Pd complex for allylic amination, were observed under both homogeneous and heterogeneous conditions.

References and Notes

1 For reviews and books on dendrimers, see: a) D. A. Tomalia, H. Baker, J. R. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, and P. Smith, *Polym. J.*, **17**, 117 (1985). b) A. W. Bosman, H. M. Janssen, and E. W. Meijer, *Chem. Rev.*, **99**, 1665 (1999). c) "Dendrimers and Other Dendritic Polymers," ed. by J. M. J. Fréchet and D. A. Tomalia, J. Wiley & Sons, New York (2001). d) G. R. Newkome, C. N. Moorefield, and F. Vögtle, "Dendrimers and Dendrons: Concepts, Syntheses, Applications," Wiley-VCH, Weinheim (2001).

2 For reviews on dendritic catalysts, see: a) G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer, and P. W. N. M. van Leeuwen, *Angew. Chem., Int. Ed.*, **40**, 1828 (2001). b) D. Astruc and F. Chardac, *Chem. Rev.*, **101**, 2991 (2001). c) R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen, and J. N. H. Reek, *Chem. Rev.*, **102**, 3717 (2002).

3 For recent reviews on polymer-bound metal complex catalysts, see: a) N. E. Leadbeater and M. Marco, *Chem. Rev.*, **102**, 3217 (2002). b) D. E. Bergbreiter, *Chem. Rev.*, **102**, 3345 (2002).

4 a) J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. M. N. van Leeuwen, P. Wijkens, D. M. Grove, and G. van Koten, *Nature*, **372**, 659 (1994). b) M. T. Reetz, G. Lohmer, and R. Schwickardi, *Angew. Chem., Int. Ed. Engl.*, **36**, 1526 (1997). c) D. de Groot, E. B. Eggeling, J. C. de Wilde, H. Kooijman, R. J. van Haaren, A. W. van der Made, A. L. Spek, D. Vogt, J. N. H. Reek, P. C. J. Kamer, and P. W. N. M. van Leeuwen, *Chem. Commun.*, **1999**, 1623. d) N. J. Hovestad, E. B. Eggeling, H. J. Heidbuchel, J. T. B. H. Jastrzebski, U. Kragl, W. Keim, D. Vogt, and G. van Koten, *Angew. Chem., Int. Ed.*, **38**, 1655 (1999). e) E. B. Eggeling, N. J. Hovestad, J. T. B. H. Jastrzebsky, D. Vogt, and G. van Koten, *J. Org. Chem.*, **65**, 8857 (2000).

5 T. Mizugaki, M. Ooe, K. Ebitani, and K. Kaneda, *J. Mol. Catal. A: Chem.*, **145**, 329 (1999).

6 T. Mizugaki, M. Murata, M. Ooe, K. Ebitani, and K. Kaneda, *Chem. Commun.*, **2002**, 52.

7 a) D. de Groot, B. F. M. de Waal, J. N. H. Reek, A. P. H. J. Schenning, P. C. J. Kamer, E. W. Meijer, and P. W. M. N. van Leeuwen, *J. Am. Chem. Soc.*, **123**, 8453 (2001). b) R. van de Coevering, M. Kuil, R. J. M. K. Gebink, and G. van Koten, *Chem. Commun.*, **2002**, 1636.

8 M. Johannsen and K. A. Jorgensen, *Chem. Rev.*, **98**, 1689 (1998).

9 Recent report on heterogeneous Pd catalyst using polystyrene-based support functionalized with DPPBA, see: Y. Uozumi, H. Danjo, and T. Hayashi, *Tetrahedron Lett.*, **38**, 3557 (1997).

10 Typical procedures for the preparation of **3a** (P/Pd = 2) are as follows: **1a** (0.0025 mmol) and DPPBA (0.04 mmol) were dissolved in methanol (16 mL), and stirred for 30 min under an argon atmosphere. $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.01 mmol) was added to the above methanol solution and stirred at room temperature for 30 min under an argon atmosphere. ^{31}P NMR (109 MHz, CD_3OD, 30 °C): 23.4 ppm from H_3PO_4 as an external reference.

11 Typical procedures for the allylic amination of cinnamyl acetate with morpholine catalyzed by dendrimer-bound Pd complex **3a** are as follows: to a catalyst solution prepared according to reference 10, was added cinnamyl acetate (3.0 mmol) and morpholine (4.5 mmol). After vigorous stirring of the reaction mixture at 5 °C, the yields of products were determined by GC using an internal standard method.

12 B. M. Trost and E. Keinan, *J. Am. Chem. Soc.*, **100**, 7779 (1978).