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reduction of nitro aromatics\*

a polyamine dendrimer for chemoselective

Selective synthesis of Rh<sub>5</sub> carbonyl clusters within

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The selective synthesis of the  $[Rh_5(CO)_{15}]^-$  cluster within the PPI dendrimer was successfully demonstrated. The dendrimer-encapsulated  $[Rh_5(CO)_{15}]^-$  was resistant to decomposition under the catalytic reaction conditions and exhibited extremely high selectivity for the chemoselective reduction of nitro groups of various nitro aromatics with other reducible groups using CO/H<sub>2</sub>O as a reductant.

Dendrimers are well-defined macromolecules with a highly branched structure from the core to the surface. The physical and chemical properties of dendrimer molecules, e.g. size, flexibility, and solubility, can be adjusted by changing the components of the core, branch, and surface units of the dendrimer framework.<sup>1</sup> One of the structural features of dendrimers is an internal nanovoid consisting of well-regulated branch units. Organic molecules and metal species are easily accommodated in the internal nanovoids, which can allow the dendrimers to act as nanocarriers in drug delivery<sup>2a</sup> and bioimaging systems.<sup>2b</sup> The dendrimer nanovoids also serve as nanoreactors for the synthesis of unique compounds including metal nanoclusters,<sup>3*a,b*</sup> metal complex assemblies,<sup>3*c*</sup> and quantum dots.<sup>3d</sup> In addition, dendrimers encapsulating these metal species provide catalytic nanoreactors with unique activity, such as the condensation of substrates and size-selective activity based on the independent tunability of the core and surface units.<sup>4</sup> In this context, our research group has been developing several dendritic nanoreactors encapsulating metal species for selective molecular transformations, such as hydroformylations,<sup>5a</sup> allylic substitutions,<sup>5b</sup> hydrogenations,<sup>5c</sup> and oxidative coupling reactions.<sup>5d</sup>

In the present study, a  $[Rh_5(CO)_{15}]^-$  carbonyl cluster was synthesized successfully within a poly(propylene imine) (PPI) dendrimer. Conventionally, the selective synthesis of the  $[Rh_5(CO)_{15}]^-$ 

cluster is difficult and requires multiple steps.<sup>6</sup> However, this PPI dendrimer easily encapsulated a  $Rh_6(CO)_{16}$  precursor within the internal nanovoid and selectively transformed it into the  $[Rh_5(CO)_{15}]^-$  cluster in one step. Furthermore, the dendrimerencapsulated  $[Rh_5(CO)_{15}]^-$  promoted chemoselective reduction of aromatic nitro compounds having other reducible functional groups with greater than 99% selectivity, leading to a straightforward synthesis of functionalized anilines, which are important intermediates for dyes, pharmaceuticals, and rubber chemicals.<sup>7</sup> This is the first report of a selective synthesis of metal carbonyl clusters within dendrimers.<sup>8</sup> The high stability of the  $[Rh_5(CO)_{15}]^$ provided by the PPI dendrimer promotes selectivity for nitro groups that cannot be achieved by the Rh clusters reported previously.

The PPI dendrimer possesses an internal nanovoid consisting of regularly arranged tertiary amino groups. A series of thirdgeneration PPI dendrimers ( $G_3$ ) with several functional groups on the surface were synthesized, such as a  $G_3$  with a  $C_{16}$  long alkyl chain ( $G_3$ - $C_{16}$ ), a  $G_3$  with a  $C_5$  short alkyl chain ( $G_3$ - $C_5$ ), and a  $G_3$ containing a dimethylamino surface group ( $G_3$ -**NMe**<sub>2</sub>) (Fig. 1).<sup>11</sup>

When  $G_3$ - $C_{16}$  was added to toluene with  $H_2O$  in the presence of  $Rh_6(CO)_{16}$  at 353 K under 10 atm of CO pressure,  $Rh_6(CO)_{16}$ gradually dissolved and the color of the solution became reddish purple. Infrared (IR) spectrum of the solution revealed that the CO stretching peak near 2075 cm<sup>-1</sup> derived from  $Rh_6(CO)_{16}$  disappeared and new peaks attributed to CO stretching



Fig. 1 Structures of a series of surface-modified  $G_3$  poly(propylene imine) (PPI) dendrimers.

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<sup>&</sup>lt;sup>13</sup>C NMR, and ESI-MS spectra. See DOI: 10.1039/c4cc00976b



Fig. 2 IR spectrum of the reaction mixture of Rh<sub>6</sub>(CO)<sub>16</sub> and **G<sub>3</sub>-C<sub>16</sub>** {[PPN][Rh<sub>5</sub>(CO)<sub>15</sub>], IR  $\nu_{CO}$ : 2045, 2010, 1868, 1838, 1785 cm<sup>-1</sup>; see ref. 6a}.

appeared at 2044, 2010, 1870, 1840, and 1785 cm<sup>-1</sup> (Fig. 2).<sup>12,13</sup> These peaks are consistent with a  $[Rh_5(CO)_{15}]^-$  cluster<sup>6</sup> (referred to as  $G_3$ - $C_{16}$ - $Rh_5(CO)_{15}$ ). Besides, this spectrum showed no peaks derived from Rh(I)-carbonyl complexes around 2100 and 1993 cm<sup>-1</sup>.<sup>13</sup> The negative ESI-MS spectrum of G<sub>3</sub>-C<sub>16</sub>-Rh<sub>5</sub>(CO)<sub>15</sub> also contained a signal at m/z = 934, which corresponds to  $[Rh_5(CO)_{15}]^-$  (Fig. S3, ESI<sup>†</sup>). The <sup>13</sup>C NMR spectrum of  $G_3$ - $C_{16}$ - $Rh_5(CO)_{15}$  contained a signal for the  $\alpha$ -carbon atoms of inner tertiary amino groups of G<sub>3</sub>-C<sub>16</sub> upfield from that of free  $G_3$ - $C_{16}$  (Fig. S2, ESI<sup>+</sup>), suggesting protonation of the internal tertiary amino groups of  $G_3$ - $C_{16}$ .<sup>14</sup> In addition, DLS measurements confirmed that G<sub>3</sub>-C<sub>16</sub>-Rh<sub>5</sub>(CO)<sub>15</sub> was a unimolecular micelle with an average diameter of 6.2  $\pm$  1.2 nm.<sup>15</sup> These combined results strongly support the formation of the  $[Rh_5(CO)_{15}]^$ cluster within the nanovoid of G<sub>3</sub>-C<sub>16</sub> and stabilization through electrostatic interactions between the  $[Rh_5(CO)_{15}]^-$  anion and a quaternary ammonium cation of the branch units.

In contrast, synthesis attempted using  $G_3$ - $C_5$  with a short alkyl chain or  $G_3$ -**NMe**<sub>2</sub> without an alkyl chain failed to yield the  $[Rh_5(CO)_{15}]^-$  cluster; instead, Rh carbonyl species such as  $[Rh_{12}(CO)_{30}]^{2-}$  and  $[Rh_{13}H_2(CO)_{24}]^{3-}$  were formed together with unidentified carbonyl species (Fig. S1, ESI†). These phenomena demonstrate that  $G_3$ - $C_{16}$  plays a key role in selective synthesis of the  $[Rh_5(CO)_{15}]^-$  cluster. Adding  $C_{16}$  alkyl chains to the surface of the  $G_3$  dendrimer enables the internal nanovoid to act as a suitable basic nanoreactor for the transformation of  $Rh_6(CO)_{16}$  into  $[Rh_5(CO)_{15}]^-$ .<sup>13,16</sup>

Next, the catalytic performance of  $G_3$ - $C_{16}$ - $Rh_5(CO)_{15}$  was investigated in the chemoselective reduction of *o*-nitrobenzaldehyde (1) to *o*-aminobenzaldehyde (2) using CO/H<sub>2</sub>O as a reductant (Table 1).<sup>17</sup> Interestingly, **1** was converted successfully to the desired product **2** in 99% yield in 4 h without the occurrence of any side reactions, such as reduction of **2** to *o*-aminobenzyl alcohol (3) or reductive cyclization of **1** to 2,1-benzoxazole (4) (entry 1). Even upon a prolonged reaction time after full conversion of **1**, the formyl group of **2** was completely retained (entry 2). These results demonstrate that  $G_3$ - $C_{16}$ - $Rh_5(CO)_{15}$  actively reduces the aromatic nitro group, but is inactive toward reduction of the formyl group. This fact is also supported by the

Table 1Reduction of o-nitrobenzaldehyde (1) using  $CO/H_2O$  as a reductant catalyzed by various Rh carbonyl cluster catalysts<sup>a</sup>

$\begin{array}{c} \begin{array}{c} \begin{array}{c} CHO \\ \\ \end{array} \\ \begin{array}{c} NO_2 \end{array} \\ \begin{array}{c} CO/H_2O, \text{ toluene, } 80 \ ^{\circ}C \end{array} \end{array} \xrightarrow{} \begin{array}{c} \begin{array}{c} \begin{array}{c} CHO \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ $									
Rh carbonyl				Yield <sup>b</sup> [%]					
Entry	cluster catalyst	Time [h]	Conv. <sup>b</sup> [%]	2	3	4			
1	$G_3-C_{16}-Rh_5(CO)_{15}$	4	>99	99	0	0			
2	$G_3-C_{16}-Rh_5(CO)_{15}$	12	>99	99	0	0			
3	DMAPS-Rh	4	>99	77	10	12			
4	DMAPS-Rh	12	>99	60	15	0			
5	[PPN][Rh <sub>5</sub> (CO) <sub>15</sub> ]	4	2	2	0	0			
6	$Rh_6(CO)_{16}$	4	0	—	_	—			

<sup>&</sup>lt;sup>*a*</sup> Reaction conditions: Rh carbonyl cluster catalyst (Rh: 60 μmol), 1 (1.0 mmol), toluene (2 mL),  $H_2O$  (0.72 mL), CO (10 atm). <sup>*b*</sup> Determined by GC internal standard technique.

control experiment using benzaldehyde (5) as a starting material under the same reaction conditions, which resulted in the complete recovery of 5 after the treatment.

To examine the catalytic activity of  $G_3$ - $C_{16}$ - $Rh_5(CO)_{15}$ , it was compared with that of other Rh clusters, such as dimethylaminated polystyrene-bound [Rh<sub>6</sub>H(CO)<sub>15</sub>]<sup>-</sup> (DMAPS-Rh)<sup>18</sup> and  $[PPN][Rh_5(CO)_{15}]$  (PPN =  $(Ph_3P)_2N^+$ ),<sup>6a</sup> which were synthesized according to previously reported procedures. Chemoselective reduction of 1 to 2 was conducted using these Rh clusters. In contrast to G<sub>3</sub>-C<sub>16</sub>-Rh<sub>5</sub>(CO)<sub>15</sub>, the use of DMAPS-Rh resulted in non-selective production of 2 with 77% selectivity along with the formation of 3 and 4 (entry 3). Extending the reaction time further decreased selectivity of 2 (entry 4). The [PPN][Rh<sub>5</sub>(CO)<sub>15</sub>] decomposed during the reduction and possessed extremely low catalytic activity (entry 5). In addition,  $Rh_6(CO)_{16}$ , which is a precursor to G<sub>3</sub>-C<sub>16</sub>-Rh<sub>5</sub>(CO)<sub>15</sub>, did not exhibit any catalytic activity (entry 6). These results demonstrate that  $G_3$ - $C_{16}$ -Rh<sub>5</sub>(CO)<sub>15</sub> acts as an efficient catalytic nanoreactor for the selective transformation of 1 into 2.

With the G3-C16-Rh5(CO)15 catalyst in hand, the chemoselective reduction of functionalized aromatic nitro compounds was investigated extensively. The results are summarized in Table 2. The G<sub>3</sub>-C<sub>16</sub>-Rh<sub>5</sub>(CO)<sub>15</sub> was applicable to a wide range of functionalized nitro aromatics. Aromatic nitro compounds containing other carbonyl groups such as ketones, esters, and amides were converted to the corresponding anilines in excellent yields (entries 2-4). The sulfonamide, methyl, halogen, cyano, and ether groups were resistant to reaction during the reduction (entries 5-10). 3-Nitrostyrene also was selectively reduced to 3-aminostyrene in 98% yield while the olefinic moiety remained intact (entry 11). Furthermore, G<sub>3</sub>-C<sub>16</sub>-Rh<sub>5</sub>(CO)<sub>15</sub> was capable of working under the gram-scale reactions of o-nitrobenzaldehyde (1) and 2'-nitroacetophenone (Scheme 1). The excellent chemoselectivity for nitro groups over both formyl and olefinic groups indicated that the reduction path might involve a Rh-nitrene species formed through deoxygenation of nitro groups by a Rh-CO species.<sup>19,20</sup> The original [Rh<sub>5</sub>(CO)<sub>15</sub>]<sup>-</sup> remained unchanged during the reductions, which was confirmed by IR spectroscopy,<sup>21</sup> and indicated that the [Rh<sub>5</sub>(CO)<sub>15</sub>]<sup>-</sup> cluster was strongly stabilized

Table 2 Substrate scope of reduction of aromatic nitro compounds using  $G_3-C_{16}-Rh_5(CO)_{15}{}^a$ 

		G <sub>3</sub> -C <sub>16</sub> -Rh <sub>5</sub> (CO CO/H <sub>2</sub> O	$R_{i}$	`NH <sub>2</sub>
Entry	Substrate	Time [h]	Conv. <sup>b</sup> [%]	Yield <sup>b</sup> [%]
1	2-CHO	4	>99	99
2	2-COCH <sub>3</sub>	6	>99	99
3	2-COOCH <sub>3</sub>	10	>99	99
$4^c$	2-CONH <sub>2</sub>	10	>99	99
5 <sup>c</sup>	$2-SO_2NH_2$	8	98	98
6	$2-CH_3$	6	>99	99
7	4-Cl	4	>99	99
8	4-Br	4	>99	99
9	4-CN	16	>99	99
10	3-OCH <sub>3</sub>	6	>99	99
$11^{c}$	$3-CH = CH_2$	24	98	98

<sup>*a*</sup> Reaction conditions: Rh<sub>6</sub>(CO)<sub>16</sub> (10  $\mu$ mol), **G**<sub>3</sub>-**C**<sub>16</sub> (12  $\mu$ mol), substrate (1.0 mmol), toluene (2 mL), H<sub>2</sub>O (0.72 mL), 80 °C, CO (10 atm). <sup>*b*</sup> Determined by GC using internal standard technique. <sup>*c*</sup> Substrate (0.5 mmol).



Scheme 1 Gram-scale reactions of  $G_3-C_{16}-Rh_5(CO)_{15}$ -catalyzed chemoselective reduction of 1 and 2'-nitroacetophenone.

within  $G_3$ - $C_{16}$  through ionic interactions between the  $[Rh_5(CO)_{15}]^-$  cluster anion and the quaternary ammonium cation of the branch units.

In conclusion, the selective synthesis of a  $[Rh_5(CO)_{15}]^-$  cluster within a PPI dendrimer was accomplished and this dendrimerencapsulated  $[Rh_5(CO)_{15}]^-$  promoted highly chemoselective reduction of nitro aromatics. The **G**<sub>3</sub>-**C**<sub>16</sub> PPI dendrimer not only acted as an efficient nanoreactor for the selective synthesis of the  $[Rh_5(CO)_{15}]^-$  cluster in one step, but also transformed into a catalytic nanoreactor by encapsulation of the  $[Rh_5(CO)_{15}]^-$  cluster within the nanovoid. The **G**<sub>3</sub>-**C**<sub>16</sub>-encapsulated  $[Rh_5(CO)_{15}]^-$  promoted chemoselective reduction of aromatic nitro groups containing reducible functional groups. The **G**<sub>3</sub>-**C**<sub>16</sub> can function as a basic nanoreactor for direct transformation of Rh<sub>6</sub>(CO)<sub>16</sub> to  $[Rh_5(CO)_{15}]^-$ , a cation stabilizer for the  $[Rh_5(CO)_{15}]^-$  anion generated, and a macroligand that suppresses decomposition of the  $[Rh_5(CO)_{15}]^-$  carbonyl cluster during catalytic reactions.

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