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Hydroformylation Reactions Using Recyclable Rhodium-Complexed Dendrimers on Silica

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In recent years, considerable attention has been directed toward the attachment of homogeneous catalysts to insoluble supports in an attempt to combine the practical advantages of a heterogeneous catalyst with the efficiency of a homogeneous system.[1] Heterogenization allows for easy separation of the reaction products from the catalyst, which opens up the possibility of recycling, while homogenization offers excellent specificity and high catalytic activity. Typically, immobilization of a catalyst on a solid support results in a significant decrease in the activity of the catalyst.[1a,b]

Dendrimers, a relatively new class of compounds introduced about 20 years ago, have already found numerous applications[2] including metal complexation[2d] and occasional use as catalysts.[3] Previously we reported that a silica-supported polyamidoamine dendrimer ligand for rhodium ($Rh-PPh_2-PAMAM-SiO_2$) is a highly active and regioselective catalyst for the hydroformylation[4] of aryl olefins and vinyl esters.[5] However, the third- and fourth-generation catalysts displayed low activity compared to the lower generations. This was believed to be due to incomplete phosphonation reactions arising from steric crowding and ultimately resulting in the threshold of dendrimer growth being reached.[6] It was perceived that extending the chain length of each generation would relieve the steric crowding and allow for increased catalyst loading at higher generations. To extend the chain length, the ethylenediamine linker was substituted by 1,4-diaminobutane, 1,6-diaminohexane, and 1,12-diaminododecane. The lengthening of the monomeric unit of the dendrimer should decrease the congestion at the surface. This can easily be observed by comparing the theoretical amine content (Table 1 in the Supporting Information) for the various chain lengths and generations. For example, the C12 G-4 (1.84 mmol of NH_2/g of SiO_2) dendrimer has approximately half the amine content of the C2 G-4 (3.55 mmol NH_2/g SiO_2) dendrimer.

Table 1. Hydroformylation of Styrene with $Rh-PPh_2-PAMAM-SiO_2$ Catalysts[a]

entry	catalyst	cycle[b]	temp (°C)	conversion[c] (%)	selectivity[d] B:L ratio
1[e]	**11a**(C2−G3)	1	75	99	8:1
2	**11a**(C2−G3)	2	75	5	nd[f]
3	**11b**(C4−G3)	1	65	99	9:1
4	**11b**(C4−G3)	2	65	90	7:1
5	**11b**(C4−G3)	3	65	65	7:1
6	**11b**(C4−G3)	4	65	6	nd
7	**11c**(C6−G3)	1	65	99	10:1
8	**11c**(C6−G3)	2	65	92	12:1
9	**11c**(C6−G3)	3	65	84	13:1
10	**11c**(C6−G3)	4	65	80	11:1
11	**11d**(C12−G3)	1	65	99	8:1
12	**11d**(C12−G3)	2	65	99	11:1
13	**11d**(C12−G3)	3	65	88	12:1
14	**11d**(C12	4	65	76	10:1
15	**12a**(C2−G4)	1	75	99	8:1
16	**12a**(C2−G4)	2	75	12	nd
17	**12b**(C4−G4)	1	65	99	10:1
18	**12b**(C4−G4)	2	65	90	12:1
19	**12b**(C4−G4)	3	65	63	11:1
20	**12b**(C4−G4)	4	65	13	12:1
21	**12c**(C6−G4)	1	65	99	8:1
22	**12c**(C6−G4)	2	65	99	9:1
23	**12c**(C6−G4)	3	65	99	12:1
24	**12c**(C6−G4)	4	65	90	11:1
25	**12d**(C12−G4)	1	65	99	12:1
26	**12d**(C12−G4)	2	65	99	7:1
27	**12d**(C12−G4)	3	65	99	9:1
28	**12d**(C12−G4)	4	65	99	9:1

[a] 10.0 mmol of styrene, 10 mL of CH_2Cl_2, 22 h, 1000 psi of a 1:1 ratio of CO:H_2, 25 mg of catalyst. [b] Catalyst was recovered by microporous filtration after the first cycle, washed with CH_2Cl_2, and reused in the next cycle. [c] Determined by ^{1}H NMR and GC. [d] Determined by ^{1}H NMR. [e] 2.0 mmol of styrene. [f] Not determined.

Polyamidoamino (PAMAM) dendrimers up to generation 4 (**1**−**4**) were constructed on the surface of aminopropylsilica employing a standard divergent growth strategy.[7,8] The isolation of the dendrimers under construction proved to be extremely time-consuming, as the filters generally became clogged with precipitated diamine. In the case of the diaminedodecane linkers, filtration and washing took up to 3 days. Figures 1−3 (see Supporting Information for Figures 2 and 3) show the gradual

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(6) A communication, which was received following submission of the manuscript, concerns the synthesis of phosphine-functionalized carbosilane dendrimers (G0−G2) and the use of their palladium complexes for allylic alkylation. The authors note that, “The dendrimer with seventy-two phosphine groups could not be prepared, probably because of surface congestion.” See: de Groot, D.; Eggeling, E. B.; de Wilde, J. C.; Kooijman, H.; van Haaren, R. J.; van der Made, A. W.; Spek, A. L.; Voget, D.; Reek, J. N. H.; Kanier, P. C. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1999**, 1623−1624.

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(8) See Supporting Information for procedure, Figure 2, and the hydroformylation results of vinyl acetate.

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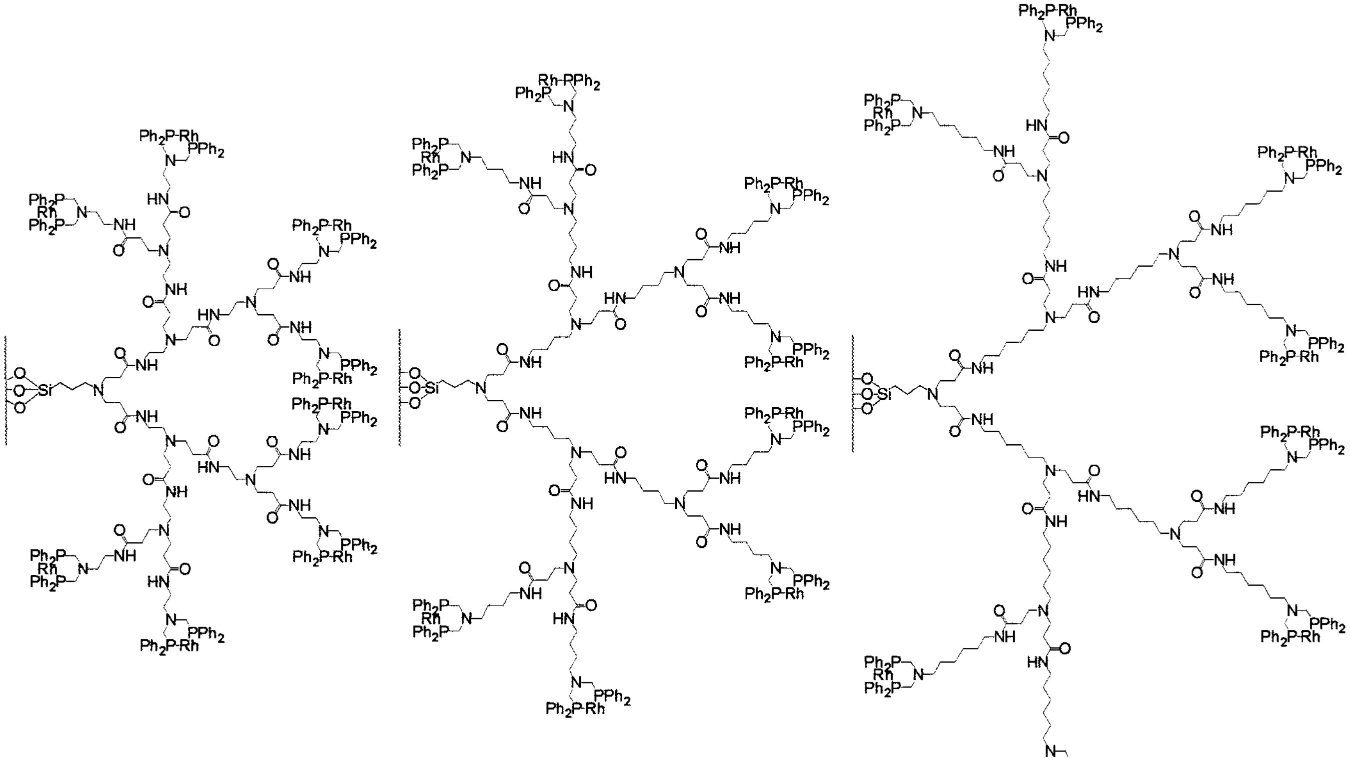


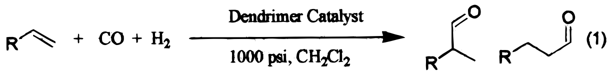
11a 11b 11c

Figure 1. Proposed structures of the third generation C2, C4, and C6 Rh$-$PPh$_2-$PAMAM$-$SiO$_2$ dendrimers, displaying the gradual decongestion of the terminal groups as the diamine linker increases.

decongestion of the terminal groups on the third- and fourth-generation dendrimers as the diamine linker increases from 2 to 12 carbons.

The dendrimers on silica were phosphonated prior to complexation with rhodium.[3b,5,8] Each terminal amine was phosphonated by reaction with diphenylphosphinomethanol, prepared *in situ* from paraformaldehyde and diphenylphosphine. The phosphonated dendrimers (**5**$-$**8**) on silica were easily complexed to chloro(dicarbonyl)rhodium(I) dimer in distilled and degassed hexanes at 40 °C for 12 h under argon to give G-1(**9a**$-$**9d**), G-2(**10a**$-$**10d**), G-3(**11a**$-$**11d**), and G-4(**12a**$-$**12d**) complexes.

The hydroformylation of styrene and vinyl acetate was examined using a 1:1 carbon monoxide and hydrogen gas mixture (total pressure = 1000 psi) in dichloromethane (eq 1).[8] The hydroformylation results for styrene are summarized in Table 1, and the results obtained for vinyl acetate are provided in Table 2 of the Supporting Information.



The hydroformylation of either styrene or vinyl acetate proceeds in up to quantitative yields, and in fine regioselectivity. These silica-supported catalysts are easily recovered by microporous filtration using a 0.45-μm membrane filter and are reusable for at least three more cycles. Generally, as the chain length is increased from 2 (Table 1 , entries 1, 2, 15, and 16) to 4 carbons (Table 1, entries 3$-$6 and 17$-$20), the catalytic activity and recyclablity increases dramatically as shown. There is another increase of activity going from 4 to 6 carbons (Table 1, entries 7$-$10 and 21$-$24). However, there is not a significant activity difference between the 6- and 12-carbon dendrimers.

After the hydroformylation reaction, the product solution is orange or yellow. There is evidently a slow leaching of rhodium from the silica. Soxhlet extraction does not remove this excess rhodium. Pressurizing the catalyst in dichloromethane with hydrogen gas (1000 psi) does not promote the leaching of the catalyst from the solid support; however, pressurizing the catalyst with either carbon monoxide or mixtures of carbon monoxide and hydrogen (1000 psi total pressure) does promote the leaching of rhodium. Preleaching of the catalyst was attempted by pressurizing the catalyst in dichloromethane with carbon monoxide and rinsing away the leached rhodium for several cycles until no rhodium was observed to leach from the silica. However, addition of substrate to the preleached catalyst in dichloromethane promotes further leaching of rhodium under hydroformylation conditions.

In conclusion, this investigation demonstrates the importance of the length of the spacer chain on the activity and recyclability of the dendrimer rhodium complex.

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Supporting Information Available: General procedures, the proposed structures of the third- (C12) fourth-generation Rh$-$PPh$_2-$PAMAM$-$SiO$_2$ dendrimers, and the hydroformylation results of vinyl acetate with Rh$-$PPh$_2-$PAMAM$-$SiO$_2$ catalysts (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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