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Hydroesterification Reactions with Palladium-Complexed PAMAM Dendrimers Immobilized on Silica

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Highly active, recyclable catalytic systems for the hydroesterification reaction of olefins with methanol and carbon monoxide were prepared by complexing various palladium species to generation zero through four PAMAM dendrimers immobilized on silica. The silica−dendrimer−$Pd(PPh_3)_2$ complexes were the most facile recyclable catalysts and could be recycled four to six times by filtration under air. These catalysts show selectivity for the linear reaction product.

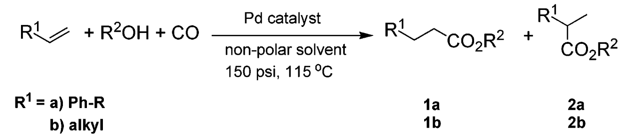
Introduction

From the outset, the aim of this research was to find an effective recyclable catalyst for the hydroesterification of olefins. Metal-complexed dendrimers immobilized on silica have been used previously as catalysts for the hydroformylation of olefins,[1] for the Heck reaction,[2] and for the carbonylation of aryl iodides.[3] It was thought that modification of these systems could lead to effective recyclable catalysts for the hydroesterification reaction.

The hydroesterification reaction (Scheme 1) is a valuable transformation as it is atom efficient, and the ester products (**1**, **2**, Scheme 1) are attractive for numerous industrial and pharmaceutical applications. For instance, branched esters derived from the hydroesterification of functionalized styrene molecules (**2a**, Scheme 1) can be hydrolyzed to the corresponding acids that are potent nonsteroidal anti-inflammatory agents[4] and terminal long-chain esters (**1b**, Scheme 1) are excellent industrial lubricants and surfactants.[5] Palladium-based catalysts are preferred, but these have not found widespread application industrially due to the challenges involved with catalyst and product separation and the high cost associated with palladium-based systems.[6] An effective recyclable catalyst for this reaction is therefore highly desirable.

Only two examples of palladium-based recyclable catalysts for hydroesterification reactions have been reported previously. One example was based on a polymer support,[7] and the other, based on modified montmorillonite clay,[8] was prepared in this laboratory. Both these catalysts could not be recycled satisfactorily.

SCHEME 1. Hydroesterification Reaction



This paper describes the identification, optimization, and evaluation of effective recyclable palladium-complexed dendrimer-based catalysts immobilized on silica. Considerable effort was also spent on developing characterization methods for the dendrimers both in the normal and phosphonated state.

Results and Discussion

As with any catalytic system, the complex loaded into the reactor usually represents only the precatalyst. The active catalyst can be significantly different. After normal deactivation, the active catalyst is transformed into a resting state, which can be reactivated under the right conditions to regenerate the active species. With supported dendrimer catalysts the situation becomes more complicated. In conventional heterogeneous catalysis the deactivated catalyst must be reactivated by some external process like calcination, reduction, or oxidation. Some catalysts must be treated with an activating substance before the reaction.[9] In the case of the supported dendrimer catalyst with highly active metals such as rhodium, this problem does not seem to be a significant factor. But as soon as more complex reactions with less active metals are attempted, like the hydroesterification reaction with palladium, for instance, the resting state becomes very important. It is essential that the resting state of the catalyst be reactivated under the reaction conditions to ensure high catalytic activity in subsequent cycles.

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Palladium catalysts are difficult to characterize due in part to the fact that palladium is not NMR active. Previous attempts to elucidate the mechanism of this reaction have been hindered by this fact. However by studying the accepted proposed mechanisms it is possible to predict what possible resting states the catalyst would form.[6,10,11,21] The greater part of this research was devoted to the search for a pre-catalyst and reaction conditions, under which a resting state that could be reactivated in subsequent cycles is generated.

Preparation and Characterization of Palladium-Complexed PAMAM−SiO_2 Dendrimers. Polyamidoamine (PAMAM) dendrimers, up to the fourth generation (Figure 1), on commercial aminopropyl silica gel (0.9 mmol ±0.1 amine groups/g), were prepared using literature methods (aminopropyl silica gel obtained from Fluka).[1] The dendrimers were phosphonated using diphenylphosphine and paraformaldehyde by modification of literature methods.[12] The double phosphinomethylation of the terminal amine groups of the dendrimers was achieved by reacting the dendrimers with diphenylphosphinomethanol prepared in situ from diphenylphosphine and paraformaldehyde in toluene (110 °C, 48 h). The resulting phosphonated dendrimers were characterized by solid-state ^{31}P and ^{13}C NMR; e.g., a chemical shift of −27 ppm in the ^{31}P NMR spectrum compares well with previously reported systems.[1] The phosphonated dendrimers were readily complexed on treatment with the appropriate palladium complexes in toluene (rt, 1−2 h under argon). The silica would turn deep orange to blood red, and decolorization of the supernatant solvent was used as an indication of the extent of complexation.

Due to the heterogeneous nature of the catalysts, usual dendrimer characterization methods such as MS and GPC could not be employed, but ^{13}C and ^{31}P NMR were used to elucidate the structure, and palladium and phosphorus ICP analysis was done to quantify the amount of palladium and the extent of phosphonation of the catalysts. A solid-state NMR internal standard method (methyltriphenylphosphonium bromide as the internal standard) for the rapid quantification of the extent of phosphonation was also developed. The phosphorus NMR method was used as a quick estimation to determine the amount of palladium required during the complexation step, and the ICP analyses (carried out externally) was done to improve the level of accuracy (Table 1).

It is clear from Table 1 that the extent of phosphonation differed from the theoretical expectations, and several reasons for this are plausible: (1) Some of the amino groups on the aminopropyl silica gel used for the synthesis of the dendrimers might reside in the pores of the support and would therefore lead to ineffective growth of the dendrimers due to steric hindrance and would then result in ineffective phosphonation. (2) It is statistically probable that the growth of the dendrimers (whether inside the pores or outside) is not complete,[13] and therefore, more than likely they resemble highly branched polymers instead of dendrimers. This in turn leads to a smaller amount of free amines available for phosphonation. (3) Higher generations of dendrimers grafted to the silica surface should be subject to crowding at the periphery leading to further steric congestion and possible back-folding, making fewer free amines available for phosphonation.[14]

A solid-state ^{13}C NMR method was developed to assess the extent of growth of the dendrimers. The process is quite straightforward and is derived from a method developed by Mayoral[18] for his phosphorus-containing dendrimers. If the dendrimer grows perfectly, the ratio of the integral of the aliphatic carbons to the integral of the carbonyl carbon in the PAMAM backbone will be a function of the generation, with the ratio declining over the generations. As we cannot determine the absolute value of the aliphatic carbons associated with the aminopropyl silica gel alone (there is no carbonyl carbon in the structure of aminopropyl silica gel), we have to correct the theoretical value for G(1), with the experimental values of G(1). The method indicates a trend for the growth of the G(2)−G(4) dendrimers. The correction factor was determined to be 13.6. This is most likely due to the methyl capping of the aminopropylsilica gel. Data for the higher generations was then calculated with this value as a correction in the G(1) theoretical value.

To clarify the results further, we also calculated a 50% growth column based on the assumption that only one branch grows for each branching point (and not two as in the perfect dendrimer). The results are reported in Table 2.

As the growth of the dendrimers was not complete, another characterization method was required to verify the ICP and NMR results.

To quantitatively determine the degree of growth of the dendrimer, a function D, defined as follows, is proposed:

$$D = M(\mathrm{d})/M_t(\mathrm{d})$$

where D is the degree of growth of the dendrimer, M(d) is the mass of the dendrimer per gram, and M_t(d) is the theoretical mass of the dendrimer per gram.

To assess D, a thermal gravimetric analyses (TGA) study was undertaken. The results are summarized in Table 3.

As can be seen in Table 3, the degree of growth of the dendrimers is about 0.3−0.6 for the different generations. Therefore, about 30% growth is detected for the higher generations of the dendrimers. This is in accordance with

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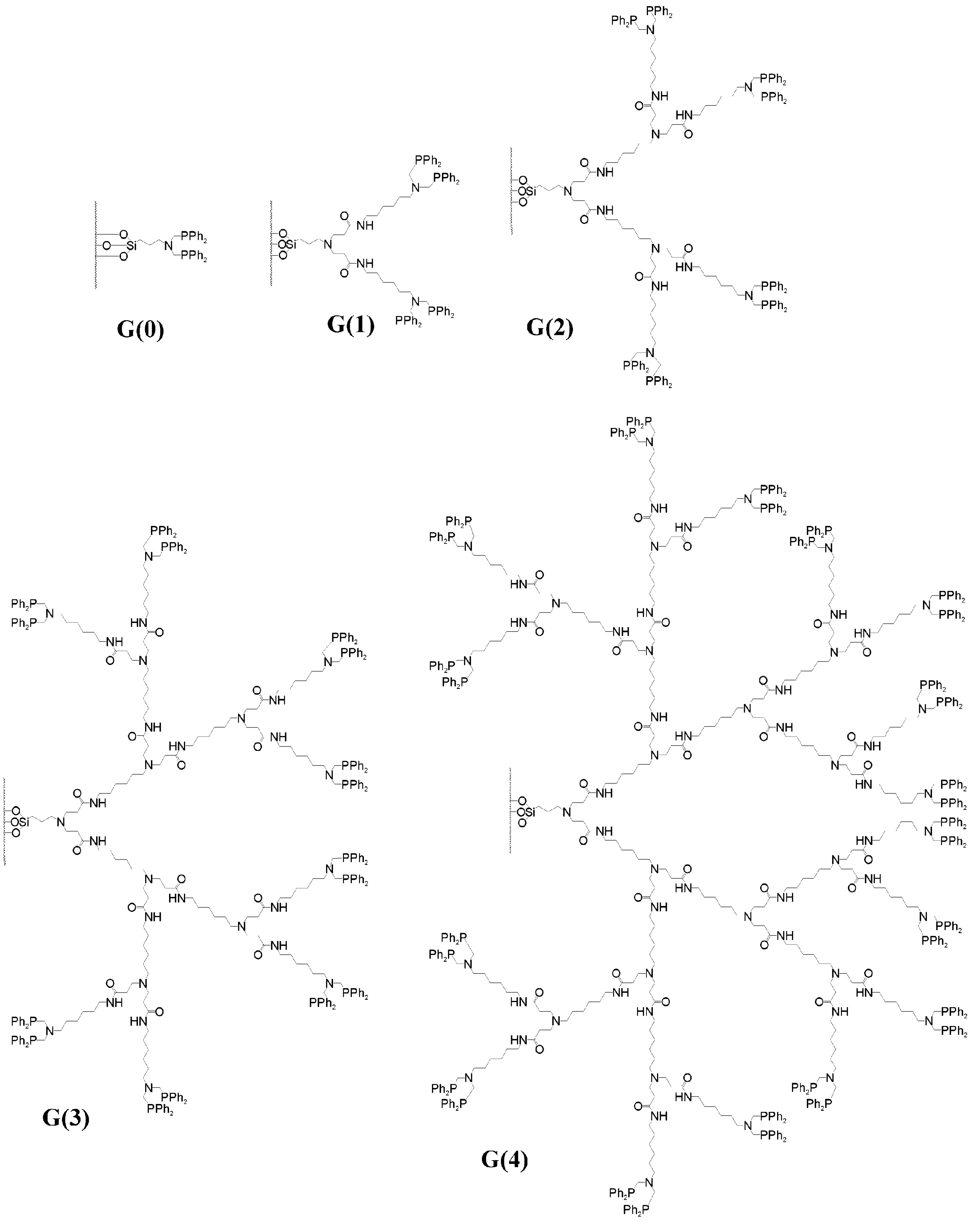

FIGURE 1. Proposed structure of the phosphonated generation zero through four (G(0)−G(4)) PAMMAM-silica dendrimer ligands (C6-linker).

the NMR and ICP analyses. It is well documented that the divergent growth approach to the synthesis of dendrimers can lead to flawed dendrimer species. Statistically, only a small fraction of the higher generations will

TABLE 1. ICP and Quantatative ^{31}P NMR Analysis of the Different Generations of the $Pd(PPh_3)_2$–PAMAM–Silica Catalysts

entry	generation[b]	P_{ICP} (mass %)	P_{NMR} (mass %)	P_{theory} (mass %)	P_{ICP}/P_{theory}	Pd_{ICP} (mass %)	Pd_{used} (mass %)
1	G(0)	1.11	1.19−1.44	4.1	0.27		
2	$G(0)_c$					0.96	1.29
3	G(1)	1.57	0.69−0.99	5.5	0.28		
4	$G(1)_c$					0.74	0.79
5	G(2)	1.38	1.13−1.25	4.15	0.33		
6	$G(2)_c$					0.96	1.32
7	G(3)	1.96	0.56−0.87	4.43	0.44		
8	$G(3)_c$					0.99	1.31
9	G(4)	1.90	0.75	4.59	0.41		
10	$G(4)_c$					0.88	1.29
11[a]	G(0)	1.74	1.70−2.00	4.10	0.42		
12[a]	G(4)	1.37	0.95−1.43	4.59	0.30		

[a] Previously prepared dendrimer samples. [b] Subscript c refers to Pd-complexed dendrimers.

TABLE 2. Quantatative ^{13}C NMR Study of the PAMAM–Silica Dendrimers

generation	integral (aliphatic)	integral (carbonyl)	ratio	theoretical ratio	difference[a]	corrected theoretical	50% growth[b]
1	23.1	1	23.1	9.5	13.6	23.1	23.1
2	14.9	1	14.9	8.5		10.8	13.6
3	14.2	1	14.2	8.2		9.2	11.3
4	10.9	1	10.9	8.1		8.6	9.8

[a] Excess carbon due to methyl capping of the silanol groups on the surface of the support. [b] Determined on the basis of the assumption that only one branch, instead of two, grows at each branching point (thus 50% growth).

TABLE 3. Degree of Growth As Determined by TGA Analyses

entry	generation	organic mass (TGA) (%)	mass theoretical $M_t(d)$ (%)	difference (correction factor)[a]	corrected TGA mass $M(d)$ (%)	degree of growth $M(d)/M_td$
1	0	7.03	5.22	1.81	5.22	N/A
2	1	18.36	27.40	1.81	16.55	0.60
3	2	19.24	50.58	1.81	17.43	0.35
4	3	23.84	69.80	1.81	22.03	0.32
5	4	26.05	83.04	1.81	24.24	0.30

[a] Excess carbon due to methyl capping of the silanol groups on the surface of the support; adsorbed water was excluded as a cause by only using the part of the TGA associated with the organic mass.

TABLE 4. Surface Area and Pore Volume Data for the Different Generations)

entry	generation	surface area (m^2/g)	total pore volume (cm^3/g)	average pore diameter (nm)
1	0[a]	305.59	0.70	7.68
2	1	248.06	0.51	7.04
3	2	225.16	0.46	7.05
4	3	190.32	0.39	6.90
5	4	147.92	0.33	6.98

[a] Determined for commercial aminopropyl silica gel.

be perfect.[16] In this instance, a further complication results due to the fact that we are working on a solid support, and therefore separation of imperfect dendrimers is not feasible. Furthermore, some dendrimers might reside inside the pores and, therefore, not grow perfectly, also leading to lower *D* values. To test this hypothesis, BET surface areas, pore volumes, and pore diameters of the different generations were also determined. The results are presented in Table 4. It is interesting to note that the surface area of the support decreases with increasing generation of the dendrimer and that the pore volume and pore diameter also decrease with increasing generation. This would support our first assumption that some of the dendrimer growth takes place within the pores of the support. Therefore, the steric interference becomes pronounced in the higher generations (especially as we are using the hexamethylenediamine linker).

Although the characterization results would suggest a highly branched polymeric species as opposed to a perfect dendrimer on the surface, the different generations could still influence the catalytic activity and selectivity, with the higher generations having a more pronounced influence. An evaluation of the catalytic activity was undertaken.

Evaluation of Catalyst Precursors. The generation zero complexes were first synthesized and tested to find appropriate precatalysts and to optimize the reaction conditions, both for catalytic activity and recyclability (Figure 2.)

$G(0)PdCl_2$ (**3**, Figure 2) was synthesized and tested with an acidic solution. The complex showed no activity without added phosphine. Although this is unusual, the montmorillonite catalyst prepared earlier also showed this behavior.[7] It could be that a “release and capture” mechanism is at work. This observation was consistent with all the other catalysts tested. An initial crude optimization showed strong temperature, pressure, and acid concentration dependence, but a full optimization was postponed until recyclability could be afforded. The $G(0)PdCl_2$ (**3**, Figure 2) and $G(4)PdCl_2$ systems were evaluated for recyclability, but the catalysts showed little

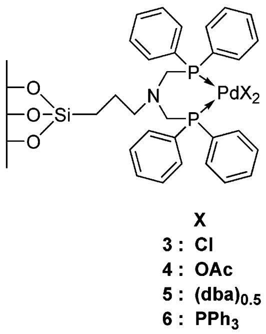

FIGURE 2. Generation zero palladium catalysts.

TABLE 5. Effect of Various Acids on the Hydroesterification of 1-Decene[a]

entry	acid	conversion (%)	L/B
1	*p*-TsOH	77	1.36
2	HCO_2H	0	
3	F_3CCO_2H	0	
4	HI	0	
5	HCl	73	3.6
6	$MeSO_3H$	82	1.3

[a] Conditions: 30 mg of catalyst (4 μmol of Pd), PPh_3 (25 equiv), acid (35 equiv), 0.150 mL of 1-decene (0.8 mmol), THF/MeOH (1:1 mixture, 5 mL), P_{CO} = 150 psi, 22 h.

or no activity in subsequent cycles with some leaching observed for the $PdCl_2$ systems. Initial trials with the G(0)Pd(OAc)$_2$ analogue (**4**, Figure 2) gave comparable activity to the G(0)PdCl$_2$ catalysts (**3**, Figure 2), and these could be recycled under very specific conditions. The G(0)Pd(dba) (**5**, Figure 2)[16] analogue also was very active, and this showed that a Pd(II) species as pre-catalyst is not essential for the reaction. As the G(0)Pd(OAc)$_2$ complex (**4**, Figure 2) showed the most promise in initial trials, this catalyst was chosen as the test catalyst of choice for the optimization reactions. To understand the reaction parameters better a full optimization of the reaction conditions were undertaken

Optimization of the Reaction Conditions. In the preliminary runs, several parameters were identified that affect the activity of the catalyst, and these were optimized separately. Thirty milligrams of the catalyst (**4**, Figure 2, 4.0 μmol of Pd), was used at 115 °C, with 160 equiv of 1-decene in the optimization reactions.

Pressure Optimization. Optimization reactions were conducted at pressures ranging from 100 to 1000 psi of CO. The 1-decene conversion increases linearly with the pressure up to a pressure of 150 psi, after which the change in conversion is less sensitive to pressure with a maximum conversion reached at 250 psi. At pressures higher than 250 psi the 1-decene conversion decreases linearly with increasing pressure. It is important to note that although the highest conversion was obtained at 250 psi, the catalyst gives more than 90% of the optimum conversion between 150 and 480 psi, thus enabling a window of operation of more than 300 psi over the preferred pressure (150 psi). The optimum pressure was accordingly chosen as 150 psi.

Optimization of Acid Additive. Various acid additives were tested in an effort to improve the selectivity and conversion. It is clear from the results in Table 5 that methanesulfonic and *p*-toluenesulfonic acid give the highest conversions but that hydrochloric acid gives the best selectivity. Also, strongly coordinating anions such as iodide (from HI) form very stable Pd complexes and all catalytic activity is lost immediately (Entry 4, Table 5). For the G(0)Pd(OAc)$_2$ catalyst (**4**, Figure 2), formic acid and trifluoroacetic acid do not activate the catalyst, although these acids will activate the $PdCl_2$ systems but give lower activity than the Pd(OAc)$_2$ $MeSO_2H$/*p*-TsOH systems.

TABLE 6. Effect of *p*-Toluenesulfonic Acid/Pd Ratio on the Conversion of 1-Decene[a]

entry	acid/Pd	conversion (%)
1	3	0
2	4	0
3	10	17
4	14	23
5	26	39
6	37	71
7	51	36

[a] Conditions: 30 mg of catalyst (4 μmol of Pd), PPh_3 (25 equiv), 0.150 mL of 1-decene (0.8 mmol), THF/MeOH (1:1 mixture, 5 mL), P_{CO} = 150 psi, 22 h.

The molar ratio of the acid to palladium is of great importance, and an effort was made to optimize this ratio. The acid optimization shows that no catalyst activity can be detected at ratios of acid/palladium of less than 5. Above ratios of 5 there exists a linear relationship between acid concentration and conversion up to about a ratio of 35, after which the acid concentration is high enough to lead to detrimental side-reactions such as isomerization. A ratio of acid to palladium of 35 was selected for subsequent studies (Table 6)

Optimization of the Amount of Added Phosphine. The amount of added phosphine was also optimized by varying the ratio of P to Pd between 2 and 100. The catalyst shows no activity up to a P/Pd ratio of 10, and then the optimum is reached at a ratio of 25. At ratios of more than 25 the activity decreases, suggesting that stable Pd complexes are formed, inhibiting catalytic activity. It is common for the activity of hydroesterification catalysts to be highly sensitive to acid and phosphine concentrations. In a related patent, Reman et al. reported that for the homogeneous Pd(OAc)$_2$(PPh$_3$)$_2$−acid system, the catalyst requires high acid and phosphine ratios for optimum activity.[17]

Up to this point, only PPh_3 was tested as an added phosphine ligand, and so other phosphine ligands were tested, to assess the effect of the added phosphine on the catalyst. Of the ligands tested, only PPh_3 gave any activity.

Solvent Optimization. Solvents with different polarities were employed, and the catalyst performed best in solvents with low polarity although intermediate polarity solvents also gave acceptable results. Almost no activity is observed with very polar solvents such as NMP (entry 6, Table 7). It became apparent that lower polarity solvents are superior in recycle reactions (Tables 9−11).

Temperature Optimization. The catalyst activity was evaluated between 60 and 150 °C, and although activity was observed over the whole temperature range, the optimum conversion was observed between 100 and 120 °C with 115 °C chosen as the temperature of choice in subsequent recycle tests.

TABLE 7. Solvent Optimization for the Hydroesterification of 1-Decene[a]

entry	solvent	dielectric constant	conversion (%)
1	hexane	1.9	90
2	toluene	2.379	89
3	dimethyl ether	4.335	86
4	THF	7.6	78
5	CH_2Cl_2	9.08	81
6	NMP	32	0

[a] Conditions: 30 mg of catalyst (4 μmol of Pd), ligand (25 equiv), *p*-TsOH (35 equiv), 0.150 mL of 1-decene (0.8 mmol), solvent/MeOH (1:1 mixture, 5 mL), P_{CO} = 150 psi, 22 h.

Recycle Studies. From the first attempts at recycling with the $PdCl_2$ functionalized dendrimers it was apparent that these could not be recycled without pretreatment with carbon monoxide and PPh_3. Therefore, the $Pd(OAc)_2$ functionalized dendrimers were tested. As with the $PdCl_2$-functionalized catalysts, the optimum recyclability was achieved after the catalyst was pretreated. After pretreatment, the catalyst could be used for six consecutive runs. Because the palladium is effectively reduced during the pretreatment step, it was thought that starting off with a palladium(0) precursor could eliminate the necessity of a pretreatment step, and a Pd(dba)-functionalized catalyst (**5**, Figure 2) was prepared and tested. Although this catalyst was highly active, it could not be satisfactorily recycled.

We purposefully exposed a large quantity of the catalyst to the reducing environment of the reaction, without the addition of substrate. In this manner, we were able to generate a sample (200 mg) for solid-state NMR analyses. A peak at 3.6−5 ppm in the ^{31}P NMR was attributed to PPh_3 bound to a palladium(0) species attached to the dendrimer.

$Pd(PPh_3)_4$ as Complexation Agent. It is clear from previous results that PPh_3 stabilizes the catalyst and is crucial for catalytic activity. It is therefore likely that the resting state of the catalyst would be a complex where two coordination sites are occupied by the phosphines of the bidentate moiety on the dendrimer and two by PPh_3. The $G(0)Pd(PPh_3)_2$ catalyst (**6**, Figure 2) was then synthesized and characterized by ^{31}P and ^{13}C NMR (entry 4, Table 8).

The first test showed comparable activity to the $Pd(OAc)_2$-complexed catalyst, and for the first time the complex could be recycled effectively without pretreatment. The catalyst could be recycled for three runs at 135 °C in THF (low yields observed during second and third cycles). By changing the solvent to toluene and effecting the reactions at 115 °C, the catalyst showed good activity for up to 5 cycles and 11% conversion in the sixth (Table 9). The ratio of linear to branched products improved during the recycle runs. This could be due to a different reactivity of the complexes grafted on the inside surface as opposed to the outside surface. One would expect from the crowding inside the pores that the catalysts residing there would favor the linear products. It is also conceivable that the outside complexes would be more susceptible to leaching when compared to the complexes residing inside the pores. The catalyst therefore evolves by the leaching of outside grafted palladium molecules to a more selective system where the catalyst sites are protected inside the pores. Johnson et al. prepared grafted homogeneous catalysts in MCM-41 and Carbosil to study the effect of the pore walls on the selectivity of the catalyst. They found that the catalyst supported inside the pores of MCM-41 showed completely different selectivity than both the carbosil-supported catalyst and the homogeneous catalyst.[20] We are currently attempting to secure evidence in support of this hypothesis. The catalyst was also tested for activity without added phosphine or acid. In both cases the catalyst showed no activity, but the catalyst could be activated by adding acid (*p*-TsOH) and phosphine (PPh_3) to the reactor after the preliminary tests were done.

The ability of the catalyst to be recycled was very promising, and the next step was to synthesize the generation one through four analogues of this complex (Figure 1). The G(1)−G(4) analogues of complex **6** were tested for activity without added phosphine, but like the G(0) catalyst no activity was detected. The catalysts were then used for recycle tests under the same conditions as the G(0) catalyst but leaching was observed, and the catalysts showed little or no activity in subsequent runs (Table 10). However, by changing the solvent system to a mixture of hexane and methanol, activity could be afforded up to at least the third cycle and in most of the cases up to five cycles (Table 11). Lower initial activity was observed here, possibly due to the low solubility of methanol in hexane. The G(1)−G(4) catalysts were also evaluated with the addition of a small amount of toluene to afford mixing of the two main solvents. This improved the initial activity without changing the recycling significantly (entries 3, 4, 5, 8, Table 11).

An interesting observation is that the higher generations, although having higher activity initially, do not recycle as well as the G(0) catalysts (Table 11).

Various generations of the $Pd(PPh_3)_2$-complexed dendrimers were selected for representative tests to determine the scope of the reaction, and the ratio of substrate to palladium was increased to at least 1000 to gauge the activity of the catalysts. The results are shown in Table 12.

Internal olefins were not catalytically active (entries 10 and 13, Table 12). To determine if the internal olefins deactivate the catalyst, or if the catalyst is just inactive toward internal olefins, premixed 1-decene and 2-decene were exposed to the catalyst. The catalyst was able to react with the 1-decene selectively without any discernible reaction with 2-decene. Also, styrene containing an electron-withdrawing group shows completely different activity, favoring oligomerization and polymerization at the reaction temperature (entries 3, 5, and 6, Table 12). The reaction with *p*-chlorostyrene was repeated at 85 °C in an effort to eliminate polymerization, but the conversion was substantially lower (entry 3b, Table 12). The most surprising observation, however, was that even for styrene, the linear product is favored. This is a unique observation as the branched product is usually formed in a highly regioselective manner. For *o*-methylstyrene (entry 2, Table 12), remarkable selectivity was observed for the linear product with the ratio of linear to branched

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TABLE 8. ^{13}C and ^{31}P NMR Characterization of the Catalysts

entry	complex	catalyst	^{13}C (ppm)	^{31}P (ppm)	ratio P/Pd
1	3	G(0) $PdCl_2$		28, 13.0	2
2	4	G(0) $Pd(OAc)_2$		28.0, 15.8, −27.6	2
3	5	G(0) Pd(dba)	131.1	28.0	2
4	6	G(0) $Pd(PPh_3)_2$	130	27.7, 7.5, −26.1	3
5		G(1) $Pd(PPh_3)_2$	130.5	26.23, 10.29, −26.22	3
6		G(2) $Pd(PPh_3)_2$	129.6	25.9, 8.7, −27.4	3
7		G(3) $Pd(PPh_3)_2$	128.33	27.7, 13.62, −25.3	3
8		G(4) $Pd(PPh_3)_2$	127.8	28.51, 11.32, −28.97	3

TABLE 9. Recycle Test of G(0)$Pd(PPh_3)_2$-Catalyzed Hydroesterification of 1-Decene[a]

entry	run no.	conversion (%)	L/B
1	1	78	1.35
2	2	52	2.60
3	3	62	2.36
4	4	71	3.20
5	5	36	4.50
6	6	11	

[a] Conditions: 50 mg of catalyst (4.5 μmol of Pd), PPh_3 (25 equiv), *p*-TsOH (35 equiv), 1-decene (160 equiv), toluene/MeOH (1:1 mixture, 5 mL), $P_{CO} = 150$ psi, $T = 115$ °C, 22 h.

TABLE 10. Recycle Test of G(1)$Pd(PPh_3)_2$ and G(2)$Pd(PPh_3)_2$ in Toluene/MeOH[a]

entry	generation	run no.	conversion (%)	L/B
1	1	1	76	3.41
2	1	2	30	
3	2	1	86	2.23
4	2	2	trace	

[a] Conditions: 50 mg of catalyst (4.5 μmol of Pd), PPh_3 (25 equiv), *p*-TsOH (35 equiv), 1-decene (160 equiv), toluene/MeOH (1:1 mixture, 5 mL), $P_{CO} = 150$ psi, $T = 115$ °C, 22 h.

TABLE 11. Recycle Test of G(1)−G(4) $Pd(PPh_3)$ Catalysts in Hexane/MeOH[a]

		conversion (%)				
entry	generation	run 1	run 2	run 3	run 4	run 5
1	1	87	73	61	55	44
2	2	87	78	55	26	
3[b]	1	>99	53	33		
4[b]	2	>99	83	57	35	
5[b]	3	>99	86	29		
6	3	83	84	36		
7	4	89	72	53	37	
8[b]	4	92	75	73	45	

[a] Conditions: 50 mg of catalyst (4.5 μmol of Pd), $PO{=}Ph_3$ (25 equiv), *p*-TsOH (35 equiv), 1-decene (160 equiv), hexane/MeOH (1:1 mixture, 5 mL), $P_{CO} = 150$ psi, $T = 115$ °C, 22 h. [b] Hexane/MeOH (1:1 mixture, 5 mL), 1 drop of toluene.

isomers being 12.5:1. This large difference between the selectivity of styrene and *o*-methylstyrene is mainly due to the presence of a methyl group in the 2-position on the ring. This shows the sensitivity of the catalyst system to steric factors. *p*-*tert*-Butylstyrene (entry 4, Table 12) also afforded full conversion, with 56% selectivity for the ester products (L/B ratio of 2). The other 44% was converted to ether-type products formed by the direct addition of methanol to the double bond. (A side reaction that was also observed due to the acid.) 1-Octene and 1-hexene (entries 8 and 9, Table 12) showed lower activity than 1-decene. Carbonyl-containing substrates such as vinyl benzoate and vinyl acetate (entries 11 and 12, Table 12) proved to be completely unreactive under the reaction conditions. The catalysts do, however, show high activity (TON of up to 1200) especially as 1−2 mol % of palladium (TON of 50−100) is usually employed in homogeneous reactions of higher olefins.

Proposed Mechanism. To understand the different parameters involved, it is important to look at a proposed mechanism for this reaction. This mechanism has been deduced from literature data and observations. It illustrates the different parameters that were optimized to afford maximum activity.

From literature considerations, there exist two possible initial steps, paths A and B. Most likely, a combination of the two initiates the cycle, but neither has been confirmed experimentally.[6,8,10,11,21] For clarity, the ligands L refers to either phosphine or CO ligands, but at least one phosphine is assumed to be present during the entire catalytic cycle (Figure 3).

After the initial reaction, following path A, the cationic−hydride complex I is formed. This is followed by an attack by the olefin, most likely forming a five-coordinate square-pyramidal intermediate that rearranges to complex II. This attack is believed to proceed by an associative mechanism, as the concentration of the olefin affects the rate of this step. Complex III is generated from II in much the same fashion, but by attack of CO. The CO inserts into the palladium−carbon bond, and after attack by the alcohol (in this case methanol), reductive elimination occurs to generate the Pd(0) species (IV). The cycle is completed by oxidative addition (simple protonation) of the acid to complex IV regenerating species I.

It is clear that the overall reaction rate will depend on the olefin concentration, the acid concentration, and the methanol concentration. The rate will also depend on the electrophilic nature of the metal center, and the nucleophilic nature of the alcohol. Based on the assumption that a cationic palladium species is the key intermediate, it follows that the solvent polarity would also have a significant effect on the overall rate. The CO pressure will also affect the rate of the reaction. The CO pressure was optimized, and as predicted by the proposed mechanism, the reaction rate increases with pressure until a threshold pressure is reached, at which point the CO starts to block the vacant sites, and consequently reduces the reaction rate. The same relationship, although more pronounced, is observed for the acid concentration. At higher acid ratios, side reactions such as isomerization and ether formation are favored. The phosphine ligand concentration, although not directly evident from the mechanism, is also pivotal to the effectiveness of the catalyst. This is due to the electronic interaction of the

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(21) Cavinato, G.; Vavasori, A.; Tonolio, L.; Benetollo, F. *Inorg. Chim. Acta* **2003**, *343*, 183−188.

TABLE 12. Other Substrates Tested with G(0)−G(4)Pd(PPh$_3$)$_2$^{a}

entry	generation	substrate	conversion (%)	TON	TOF (h^{-1})	L/B
1	1	styrene	>99	1100	50	2.4
2	2	*o*-methylstyrene	>99	1200	53	12.5
3a	4	*p*-chlorostyrene	>99 (73)	829	38	2.2
3b^b	2		20	232	10	-
4	1	*p*-^{t}Bu-styrene	>99 (56% esters)	1478	67	2
5	2	*p*-vinylbenzoic acid	polymerized			
6	2	*p*-methoxystyrene	oligomerized			
7	4	1-decene	>99	1243	56	1.9
8	1	1-octene	75%	1108	50	3.2
9^c	1	1-hexene	63%	931	42	2.47
10	4	2-decene	no reaction			
11	1	vinyl acetate	no reaction			
12	2	vinyl benzoate	no reaction			
13	2	cyclohexane	no reaction			

^{a} Conditions: 20 mg of catalyst (1.8 μ mol of Pd), PPh$_3$ (25 equiv), pTsOH (35 equiv), olefin (2 mmol, 1000 equiv), toluene/MeOH (1:1 mixture, 5 mL), PCO = 150 psi, T = 115 °C, 22 h. ^{b} 85 °C. ^{c} 300 psi.

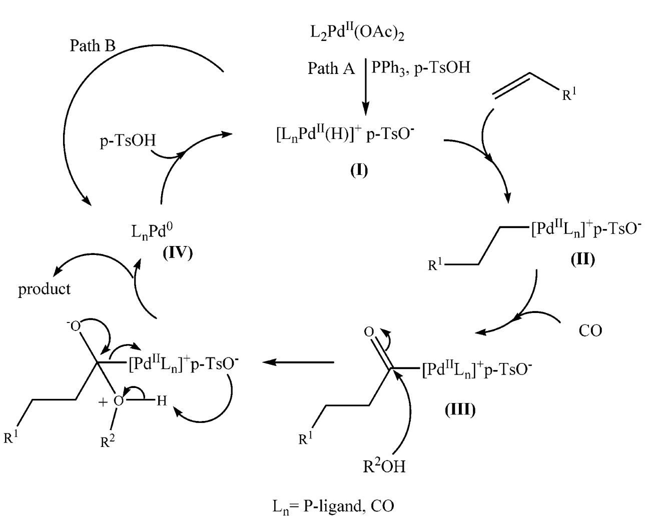

FIGURE 3. Proposed mechanism for the hydroesterification reaction.

phosphine and the metal center. At low concentrations, the phosphine does not effectively stabilize the intermediates such as the palladium(0) species. Higher concentrations of the phosphine block the activity by stabilizing the intermediates too much and thereby slowing down the cycle. It appears that the other phosphorus ligands do not possess the right electronic characteristics to stabilize both the cationic palladium species and the other intermediates.

Experimental Section

Materials. All olefins were used as received or percolated through a short column of activated alumina. All solvents were dried, distilled, and in some cases degassed before use. All other chemicals were used as received without further purification.

Instruments. Gas chromatography was used for the quantification of conversions (a direct retention factor quantification method was used). A 300 MHz NMR instrument was used for the ^{1}H, and ^{13}C, analyses of reagents and products. A 200 MHz solid-state NMR instrument was used to characterize the supported dendrimers. A Fourier transform infrared spectrometer was used to verify the IR spectra of the products. GC−MS was used to determine the molecular masses of the products. Phosphorus and palladium ICP along with TGA and BET surface characterization were determined by commercial laboratories.

General Experimental Procedure for the Hydroesterification of Olefins with Methanol. To a 50 mL stainless steel autoclave equipped with a pressure gauge, a glass liner, and a stirring bar were added 20 mg of a palladium containing catalyst (4.0 μmol Pd), a toluene/methanol mixture (1:1 v/v, 5 mL), 25 equiv of PPh$_3$, 35 equiv of acid, and 1000 equiv of olefin. The autoclave was flushed three times with carbon monoxide, pressurized to 150 psi, and placed in a preheated oil bath at 115 °C. The reaction was left for 22 h under vigorous stirring, and after cooling, ether (2 mL) was added and the contents were filtered through 0.45 μm membrane filter and washed with ether. The conversion and the branched-to-linear ratio was determined by GC (filtration for recycle studies was done both under inert atmosphere and under air, with no discernible difference).

Conclusions

We have developed a new recyclable catalyst for the hydroesterification of olefins, based on palladium-complexed dendrimers immobilized on silica. The catalysts show high activity for styrene derivatives and linear long-chain olefins (TON of up to 1200) and favor the linear product of the reaction even for styrene. The catalysts can be recycled up to six times by simple filtration in air. We have also found through the characterization of the dendrimers that some of the growth takes place within the pores of the silica support, and therefore, a function *D* (for degree of growth) was defined and determined to be around 0.6 (60%) for the lower generations and around 0.3 (30%) for the higher generations.

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