

Silica-Supported Dendrimer-Palladium Complex-Catalyzed Selective Hydrogenation of Dienes to Monoolefins

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Abstract: The selective hydrogenation of cyclic and acyclic dienes to monoolefins occurs under very mild conditions, in the presence of silica-supported PAMAM-Pd complexes. The activity and selectivity of this reaction is sensitive to the dendrimer structure.

These dendritic complexes display excellent recycle properties, retaining activity for up to eight recycles.

Keywords: alkenes; dienes; hydrogen; palladium; silica-supported PAMAM dendrimers.

Introduction

Recent publications have demonstrated that silica-supported polyamidoamine (PAMAM) dendrimer-metal complexes can catalyze a variety of reactions. For example, dendrimer-rhodium complexes on silica or a resin, display excellent activity and recyclability for the hydroformylation of alkenes.^[1–3] Dendrimer-palladium complexes have been used to catalyze the Heck coupling reaction of bromoarenes,^[4] the carbonylation of haloarenes,^[5] as well as the hydroesterification,^[6] and oxidation^[7] of alkenes. It was anticipated that, under appropriate conditions, the dendritic Pd complexes could effect selective reduction reactions. A particularly fascinating transformation would be to attain the semi-hydrogenation of dienes to monoolefins in fine selectivities.

The catalytic selective hydrogenation of multiple unsaturated hydrocarbons can be used for synthetic and non-synthetic purposes. For instance, the production of flavour components including hexen-1-ol and methyl *trans*-2-hexenoate, from their parent diene compounds was effected by hydrogenation.^[8] For non-synthetic purposes, selective hydrogenation is used to remove dienes and other polyunsaturated hydrocarbons from alkene feedstocks. van Leeuwen showed that the presence of impurities such as alkynes, dienes and enones in alkene feedstocks can bring about deactivation in certain catalytic reactions.^[9,10] The challenge in this area is that, in general, the insertion of dienes to metal complexes is faster than the insertion of alkenes. Dienes tend to deactivate the catalyst by forming π -allyl species that are often inactive as catalysts for hydroformylation. For the same reaction, catalyzed by rhodium complexes, the

presence of alkynes in the reaction medium can result in irreversible deactivation, while dienes simply slow down the reaction, and enones cause temporary inactivity. The removal of these impurities from alkene feedstocks is crucial for extending the catalyst lifetime. Moreover, as the alkene is often hydrogenated as well, the challenge is to find a catalytic system that can remove these minute impurities without affecting the alkene feedstocks.

There are few examples of the homogeneously catalyzed selective hydrogenation of dienes. Work by Dupont and co-workers^[11] using $\text{Pd}(\text{acac})_2$ dissolved in the ionic liquid 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIM.BF₄) resulted in the hydrogenation of simple and functionalized dienes to their corresponding monoolefins at 50 °C and 5–20 atm in selectivities ranging from 93 to 100%. Kaneda and co-workers demonstrated that the dendrimer-bound palladium complex of phosphonated poly(propyleneimine) can selectively hydrogenate conjugated cyclic dienes to monoolefins.^[12] The dendrimer complex gave better results than the monomeric catalyst $[\text{PhN}(\text{CH}_2\text{PPh}_2)_2\text{PdCl}_2]$. The proposed reaction mechanism involves a Pd–H species. The equation of the reaction rate indicated that the presence of bases should speed up the reaction. Superior results obtained with the dendrimer complex were attributed to the fact that the large number of basic amino groups present in the dendrimer accelerated the reaction.

In a different strategy, dendrimers have been utilized as templates to prepare nanoparticles with well-controlled size, stability and solubility. Crooks^[13] and co-workers have used generations G4, G6 and G8 of hydroxy-terminated PAMAM to prepare Pd nanoparticles which

were studied as catalysts for the hydrogenation of allyl alcohol and *N*-isopropylacrylamide. For the latter substrate, there was a strong dependency between the hydrogenation activity and the dendrimer generation. G6 and G8 gave TOFs that were 10 and 5% that of G4. Allyl alcohols with substituents of different sizes on the α -position were catalyzed with the G4-Pd nanoparticles. The activity diminished with the increase in the size of the α -substituent. Kaneda^[14] et al. functionalized third to fifth generation PPI dendrimers with triethoxybenzamide, prior to using them as templates for the synthesis of Pd nanoparticles. The catalytic performance of these nanocatalysts was investigated towards the hydrogenation of various olefins. The hydrogenation rates were lower than those obtained with Pd/C and they decreased in the order G3 > G4 > G5 for all substrates. The Pd nanoparticles encapsulated with G5 dendrimer showed interesting molecular recognition properties. For example, this system allowed the selective hydrogenation of certain substances. Polar substrates reacted faster than non-polar substrates when they were simultaneously present in the reaction mixture.

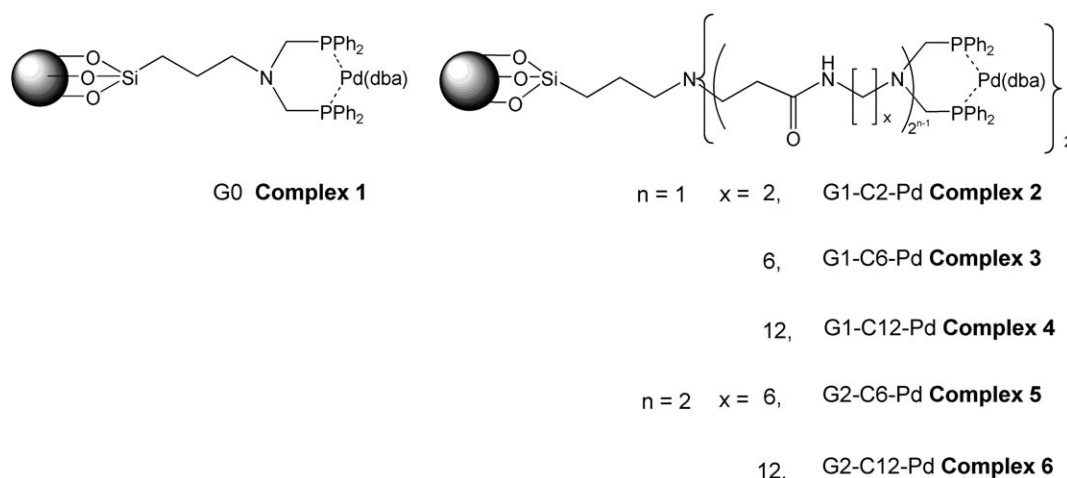
The need for more selective hydrogenation catalysts coupled with the successful application of supported Pd catalysts in hydrogenation reactions prompted us to investigate the catalytic performance of our silica-supported, palladium-based dendrimers **1–6** (Scheme 1) for the selective hydrogenation of dienes to monoolefins. We wanted to determine if these catalysts would display a positive or negative dendritic effect in activity and selectivity. It was our hope to transform the dienes to monoolefins without any deleterious effect on the monoolefins formed during the reaction. The potential to recycle the dendrimer–palladium catalysts for the reaction is an important additional feature, should this be possible.

Results and Discussion

The dendrimer-Pd complexes **1–6** were synthesized following the procedures reported in an earlier publication.^[17] Our goal was to carry out the hydrogenation reactions under mild conditions. 1,3-Cyclohexadiene and complex **1** were used to determine the optimum conditions for the reaction. Since the solvent usually has an effect on the selectivity of hydrogenation reactions, we began our investigation by testing different solvents (Table 1). Three alcohols were screened, methanol, ethanol and isopropyl alcohol. The highest selectivity was observed using methanol, with isopropyl alcohol being the least selective. Activity was highest for isopropyl alcohol and lowest for methanol. Reasonable selectivity and good activity was obtained in dichloromethane, while in acetonitrile and ethyl acetate, lower activities and selectivities were found. Since selectivity took priority over activity, methanol was used for subsequent reactions. Parameters such as temperature, pressure and catalyst loading were also examined.

After establishing the optimum conditions, we proceeded to examine the catalytic performance of the various dendrimer complexes **2–6**. Various spacer lengths were used within the dendrimer structure with the hope that the resulting catalysts would effect different activities. Cyclohexene was the major product for the hydrogenation of the 1,3-cyclohexadiene (Table 2). Cyclohexane and benzene were minor products using some of these complexes. 1,3-Cyclohexadiene is known to disproportionate to cyclohexene and benzene in the presence of Pd particles. Therefore, the presence of benzene in the product mixture may be an indication of traces of Pd particles within the catalyst matrix.

The G0 complex, **1** showed the highest activity with 76% selectivity to cyclohexene (Table 2, entry 1). The second generation C12 catalyst, **6** gave complete conversion after 5 hours (Table 2, entry 11), while the other cat-



Scheme 1. Dendritic catalyst.

Table 1. Effect of solvent on the hydrogenation of 1,3-cyclohexadiene.

Entry	Solvent	Time [min]	Conv. [%]	%	
					
1	Methanol	30	20	>99	-
2		150	>99	76	24
3	Ethanol	30	57	75	25
4		60	>99	68	32
5	Isopropyl alcohol	30	83	68	32
6		35	>99	62	38
7	Dichloromethane	30	38	80	20
8		70	>99	73	27

Reaction conditions: 5.25 mmol 1,3-cyclohexadiene, 10 μ mol Pd catalyst **1**, 5 mL MeOH, pressurized glass autoclave to 14 psi H₂, 25 °C. GC and NMR were used to monitor the reaction.

Table 2. Hydrogenation of cyclohexadiene.

Entry	Catalyst	Time [h]	Conv. [%]	%		
						
1	G0, 1	1.75	>99	76	24	-
2	G1-C2, 2	0.5	21	>99	-	-
3		20	>99	88	10	2
4	G1-C6, 3	0.5	11	>99	-	0
5		20	72	97	1.5	1.5
6	G1-C12, 4	0.5	15	>99	-	-
7		20	20	>99	-	-
8	G2-C6, 5	0.5	N.R	-	-	-
9		20	>99	73	11	6
10	G2-C12, 6	0.5	24	>99	-	-
11		5	>99	80	14	6

Reaction conditions: 5.25 mmol 1,3-cyclohexadiene, 10 μ mol Pd catalyst, 5 mL MeOH, pressurized glass autoclave to 14 psi H₂, 25 °C. GC and NMR were used to monitor the reaction.

Table 3. Hydrogenation of ethyl sorbate.

Entry	Catalyst	Time [min]	Conv. [%]	Distribution [%]			
				a	b	c	d
1	G0, 1	60	>99	86	4	3	7
2	G1-C2, 2	150	>99	82	10	7	1
3	G1-C6, 3	90	>99	77	15	5	3
4	G1-C12, 4	420	N.R	-	-	-	-
5	G2-C6, 5	90	>99	81	11	5	3
6	G2-C12, 6	90	>99	80	10	7	3

Reaction conditions: 5.4 mol ethyl sorbate, 10 μ mol Pd catalyst, 5 mL MeOH, pressurized glass autoclave to 14 psi H₂, 25°C. GC and NMR were used to monitor the reaction.

Table 4. Recycling of complex **1** (G0).

			Distribution [%]			
			a	b	c	d
G0	Run 1	60	86	4	3	7
	Run 2	90	79	11	7	3
	Run 3	90	75	14	8	3
	Run 4	105	77	11	7	5
	Run 5	160	63	17	10	10
	Time [min]					

Reaction conditions: 5.4 mol ethyl sorbate, 10 μ mol Pd catalyst **1**, 5 mL MeOH, pressurized glass autoclave to 14 psi H₂, 25°C. GC and NMR were used to monitor the reaction.

alysts required 20 hours (Table 2, entries 3, 5, 7 and 9). Cyclohexene was the only product for all of the catalysts at conversions below 30%. At higher conversions, the alkene formed began to compete with the diene for the active site. Complexes **3** and **5** of the C6 series gave similar activity, but the former afforded better selectivity. For the C12 series, the first generation catalyst is less active than the second generation. The question as to what is responsible for this difference in activity and selectivity is not easy to answer. Nevertheless, from

a reaction perspective, one can achieve excellent results.

The hydrogenation of ethyl sorbate catalyzed by $\{[(t\text{-Bu})_2\text{PH}]\text{Pd}[\text{P}(t\text{-Bu})_2]\}_2$ pre-activated with O₂ gave 70% methyl 2-hexenoate and 30% methyl hexanoate.^[15] The dendrimer complex **4** was ineffective in catalyzing the hydrogenation of ethyl sorbate. All the other dendrimer-Pd complex catalysts displayed comparable selectivity, i.e., there was no significant sensitivity to catalyst structure for this substrate (Table 3).

Table 5. Recycling of complex **6** (G2-C12).

			Distribution [%]			
			a	b	c	d
Time [min]						
G2-C12	Run 1	90	80	10	7	3
	Run 2	90	81	10	7	1
	Run 3	90	79	10	7	4
	Run 4	90	81	9	5	5
	Run 5	90	82	9	4	5
	Run 6	90	81	10	7	2
	Run 7	90	75	11	6	8
	Run 8	90	73	16	9	2

Reaction conditions: 5.4 mol ethyl sorbate, 10 μmol Pd catalyst, 5 mL MeOH, pressurized glass autoclave to 14 psi H_2 , 25 °C. GC and NMR were used to monitor the reaction.

Table 6. Hydrogenation of acyclic dienes.

Time [h] Conv. [%]			Product Distribution [%]			
Complex 1	4	>99	3	26	19	52
Complex 3	6	>99	3	33	17 (1)	46
Complex 5	9	88	10	10	13	67

Time [h] Conv. [%]			Product Distribution [%]			
Complex 1	1.5	>99	39	59	2	
Complex 3	1.5	>99	48	52		
Complex 5	4	>99	43	57		

Time [h] Conv. [%]			Product Distribution [%]			
Complex 1	1.5	>99	68 (1.3)	21	11	
Complex 3	3	>99	81 (1.2)	6	13	
Complex 5	9	>99	69 (1.2)	7	24	

Standard reaction conditions: 5.5 mmol substrate, 10 μmol Pd, 5 mL methanol. Pressurized glass autoclave to 14 psi H_2 , 25 °C. GC and NMR were used to monitor the reaction. Number in parenthesis refers to *trans* to *cis* ratio.

Table 7. Hydrogenation of cyclic dienes.

	Time [mins]	Conv. [%]	Product Distribution		
	90	92	 83 %	 13 %	 4 %
	40	>99	 78 %		 22 %
	135	>99	 68 %		 32 %
	90	43	 95 %		 5 %
	135	>99	 92 %		 8 %
	90	92	 >99 %		-
	120	>99	 98 %		 2 %

Standard reaction conditions: 5.25 mmol substrate, 10 μ mol Pd complex **1**, 5 mL methanol. Pressurized glass autoclave to 14 psi H₂, 25 °C. GC and NMR were used to monitor the reaction.

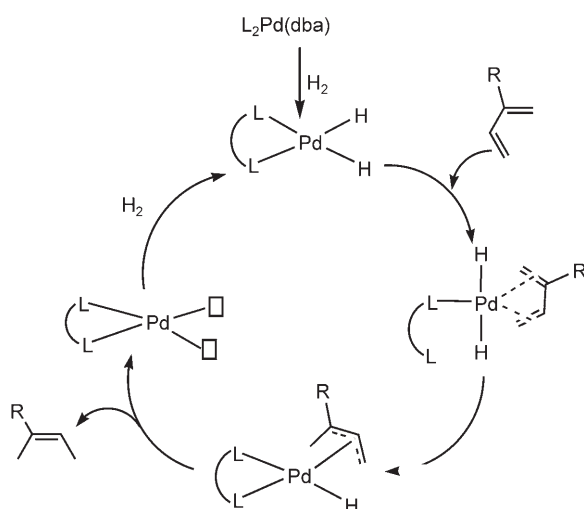
Since complex **6** showed better activity than the other complexes for the hydrogenation of cyclohexadiene, it was chosen for an experiment where the recycle properties of the catalyst were tested for the hydrogenation of ethyl sorbate. When compared to the G0 catalyst **1**, the G2 complex **6** retained activity and selectivity for up to eight runs while **1** began to show a decrease after three runs (Tables 4 and 5). Complex **6** was therefore shown to be an excellent catalyst for the hydrogenation of ethyl sorbate, with good selectivity for the γ,δ -double bond.

For the partial reduction of acyclic dienes, the catalytic activity decreased with the augmentation of the generation number (Table 6). The least substituted double bond was selectively reduced during the hydrogenation, e.g., 2-methyl-1-phenyl-1,3-butadiene afforded 2-methyl-1-phenyl-1-butene in 52–67% selectivity using complexes **1**, **3**, and **5**. 2,4-Dimethyl-1,3-pentadiene gave almost equal amounts of the two monoene isomers, 2,4-dimethyl-1-pentene and 2,4-dimethyl-2-pentene. For the partial hydrogenation of 3-methyl-1,3-hexadiene, the least substituted double bond was reduced in preference

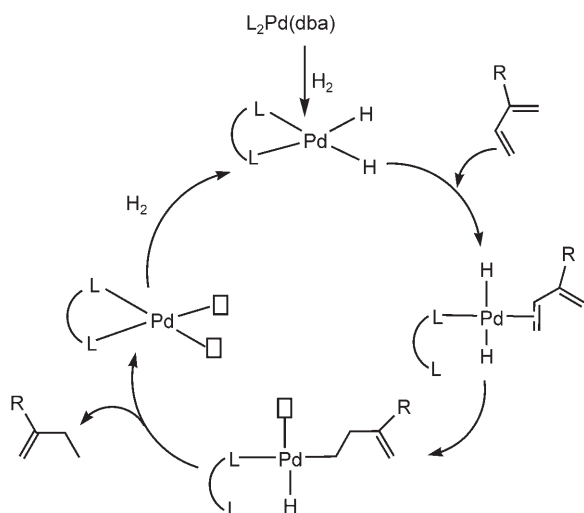
to the more substituted double bond. Up to 81% selectivity was obtained with complex **3**.

In Table 7 are shown the results for the hydrogenation of cyclic dienes using the complex **1**. 1-Methyl-1,4-cyclohexadiene and 1,2,3,4,5-pentamethyl-1,3-pentadiene were transformed to their corresponding monoolefins in selectivities of 83% and 78%, respectively. Non-conjugated 1,4-cyclohexadiene was converted to cyclohexene in 68% selectivity.

1,3-Cycloheptadiene has been selectively reduced to cycloheptene using SmI₂/H₂O/amine mixtures in THF in >99% yield.^[16] At least 2.5 equivalents of SmI₂ were required with the reaction operating through a radical mechanism. When complex **1** was used, 92% of cycloheptene along with 8% of cycloheptane was obtained. 1,3-Cyclooctadiene was reduced with 98% selectivity towards the monoolefin, which is comparable to the result obtained using $\{[(t\text{-Bu})_2\text{PH}] \text{Pd}[\text{P}(t\text{-Bu})_2]\}_2$ pre-activated with O₂.^[15] The cyclic conjugated dienes showed an increase in selectivity in the order C₆ < C₇ < C₈ with the complex **1**.



Scheme 2. Proposed mechanism 1.



Scheme 3. Proposed mechanism 2.

Proposed Mechanism

Two mechanisms are proposed for this reaction. Both involve the initial generation of a Pd–H species from the reaction of the dendrimer complex with H₂ through oxidative addition. In the first mechanism (Scheme 2), the diene coordinates to the metal complex in a η^4 -fashion. After the transfer of hydrogen, a Pd-allyl species is formed. It is at this stage that different alkene isomers can be formed because the allyl-Pd species can lead to double bond isomerization. The elimination of the monoene is accompanied by the formation of Pd(0), which upon reaction with H₂ regenerates the active Pd–H species. In the second mechanism (Scheme 3), the diene coordinates to the metal complex in an η^2 -mode. Here the steric bulk of the diene is a major factor in determining which double bond should coordinate to the metal centre. Generally, the less substituted or least bulky unsatu-

ration will preferentially bind to the metal. After monoene expulsion, the Pd–H species can be regenerated.

Conclusions

The results described herein show that silica-supported PAMAM-palladium complexes can catalyze the hydrogenation of conjugated dienes to olefins in good to excellent selectivity. The higher generation catalysts also display good recycle properties; they could be reused up to eight times without loss in selectivity. This method is superior than the one reported by Dupont as it employs milder reaction conditions.

Experimental Section

General Procedure for the Selective Hydrogenation of Dienes

The diene substrate (5.5 mmol) in methanol (5 ml) was added to 10 μ mol (referred to Pd) of the dendrimer-Pd complex in a glass autoclave. The reaction mixture was purged three times with H₂ before pressurizing to 14 psig with H₂. The autoclave was stirred at 25 °C for the amount of time specified in the Results and Discussion section. The liquid phase was passed through a pad of silica and then analyzed. Catalyst recycle was done after the catalyst was washed with methanol and ether.

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