Macromol. Symp. **2004**, *209,* 97-118

Metallodendritic Materials for Heterogenized Homogeneous Catalysis

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Summary: Design of supports containing a hyperbranched backbone and active transition metal centers at the periphery is described. Such nanoarchitectures can be easily assembled from 3,5-dihydroxybenzyl alcohol and dimethylsilylamine using a divergent synthetic methodology. Following a controlled reaction pathway, construction of dendrimers of up to generation 5 is achieved, while a simple mix of reagents in one-pot or with sequential additions yields analogous hyperbranched polymers. Subsequent functionalization at the periphery with phosphine followed by Rh(I) centers yields the desired metallodendritic materials. The efficiency of the latter in catalytic hydrogenation of decene under varied conditions is surveyed.

Keywords: dendrimers; hyperbranched polymers; organometallic dendrimers; supported metal catalysis

Introduction

Ideally, a catalytic system should be well defined, enable rapid and selective chemical transformations, and its complete separation from the reaction mixture should easily be achieved.[1-4] Catalysts fall into two classes based on their physical behaviour in solution. They are referred to as "homogeneous" when they are solvated with the reactants. Homogeneous catalysis offers an easy access to all catalytic moieties, and reactions can be done in a high metal-to-substrate ratio.[5] However, their separation from the products is difficult and remains a major issue. Common methods of separation include distillation, liquid-liquid extraction, crystallization or even destruction of the catalyst.[5] "Heterogeneous" catalysts are insoluble materials by definition. They offer the advantages such as high thermal and mechanical stability, a loading potential far superior than the homogeneous catalysts, and of course an inherent ability to be easily separated from the product.[6] However, their nonuniformity and ill-defined structures tend to limit

DOI: 10.1002/masy.200450507

the accessibility to the catalytic sites. Other problems encountered with heterogeneous catalysts are related to slow diffusion and metal leaching, hence a lower catalytic activity when compared to their homogeneous analogs.

Dendrimers appear to offer a good compromise between the homogeneous and heterogeneous catalysts. Dendrimers are well defined materials with structure and size that can be tuned to support or host transition metal catalysts, and the location as well as number of catalytic sites can be regulated.[7,8] The globular shapes they adopt in higher generations seem particularly suited to new means of catalyst-product separation such as the nanofiltration using a membrane.[1] Seminal work on the first examples of metallodendrimers used in catalysis is attributed to van Koten's group with the preparation of a dodeca(aryl bromide) terminated carbosilane dendrimers.[4] In this study, peripheries of carbosilane dendrimers were functionalized by oxidative addition of [$Ni(PPh_3)_4$] to afford diaminoarylnickel(II) terminated dendrimer. The resulting metallodendrimers were used to catalyze the Kharasch addition of tetrachloromethane to C=C bonds. Turnover frequencies were found to be 30% lower than the monomeric or polymer-bound analogs.

The design and topology of metallodendrimers can define the activity and selectivity of the resulting catalyst.[7-10] The catalytically active metal centers could be present at the periphery of hyperbranched dendrimers, or of star branch dendrimers. Transition metals can also be part of the backbone, or found at the center, acting as a core. They can be coordinated throughout the backbone, as host. Also, periphery metal supported dendritic wedge can be grafted on a polymeric support.

The majority of supported metal dendrimer catalysts are the result of the peripheral modification of pre-existing dendritic macromolecules. Although an attractive route, this can lead to a decrease in catalytic activity by steric congestion if the concentration of metal centers becomes too high. For example, van Koten and co-workers[11] reported the preparation of periphery palladated dendrimer using the same carbosilane backbone as that of his Ni metallodendrimers.[4] Catalytic activity of the supported Pd dendrimers decreased as the steric congestion increased, as observed for the Ni metallodendrimers. Other examples of catalytically active metallodendrimers can be found in the literature.

Peripheral functionalization with varied transition metal centers has been achieved in star branched dendrimers[12] as well as hyperbranched dendrimers.[13-18]

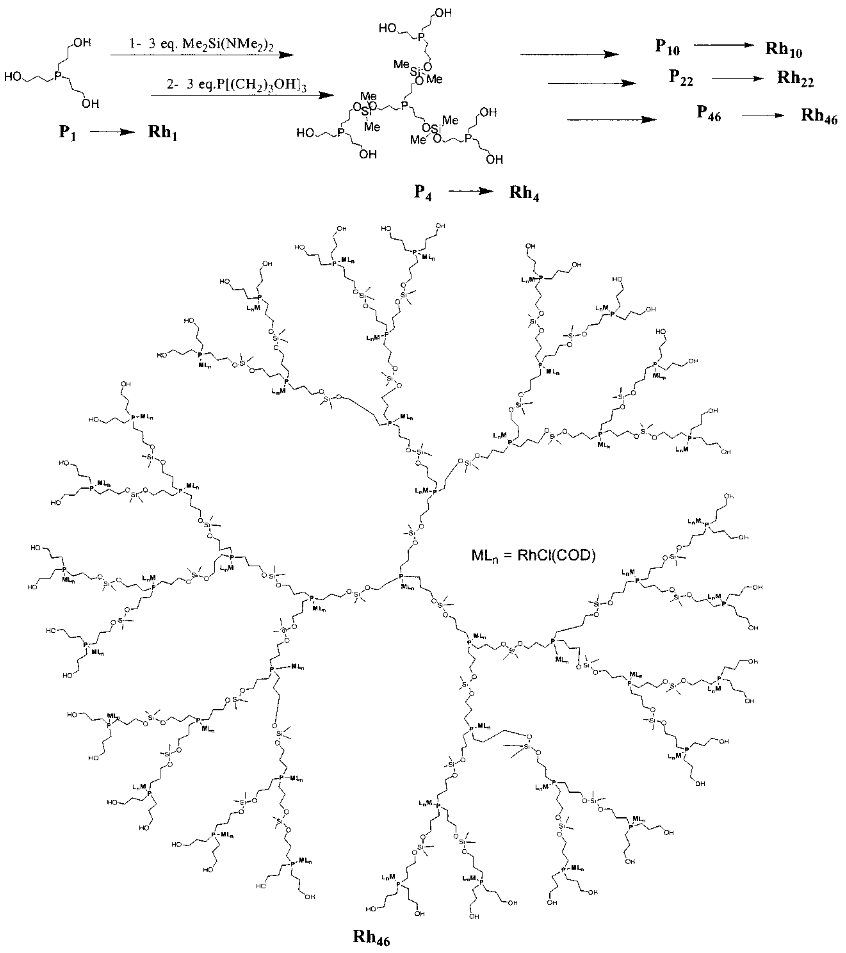
Hoveyda et al.[12] reported the preparation of recyclable poly(organoruthenium) metathesis star carbosilane catalysts. Ring closing metathesis of bis(allyl)-*N*-tosylamide to the corresponding cyclopentane was reported using the latter dendrimers with yields exceeding 90%, and only a slight loss of Ru upon recovery.

P-branched dendrimers synthesized by Majoral et al.[13] have been functionalized with a variety of transition metals coordinated to terminal phosphine ligands.[14,15] $PdCl_2$ terminated dendrimers were used to catalyze the Stille coupling reaction whereas the $RuH_2(PPh_3)_2$ terminated dendrimers catalyzed the Knoevenagel condensation and the Michael addition reactions.[16]

Also, phosphanyl-terminated dendrimers have been prepared by Reetz et al.[17] from third generation poly(propylene imine) dendrimer treated with Ph_2PCH_2OH. Treatment with $[PdCl_2(PhCN_2)]$, $[Pd(CH_3)_2(TMEDA)]$, $[Ir(COD)_2BF_4]$, $[Rh(COD)_2BF_4]$ and a 1:1 mixture of $[PdCl_2(PhCN)_2]$ and $[Ni(CH_3)_2(TMEDA)]$ afforded the related metallodendrimers. The Rh(I) supported dendritic catalyst was used for the hydroformylation of 1-octene with a turnover number comparable to the monomer, and with the possibility to recover the catalyst by membrane separation techniques.[17] Hydrogenation of conjugated dienes using the $PdCl_2$ supported catalyst has been reported by Mizugaki et al.[18] The selectivity was found to be excellent with the conversion of cyclopentadiene into cyclopentene with a catalytic activity higher than the corresponding monomer $[PdCl_2\{PhN(CH_3PPH_2)_2\}]$.

Dendrimer supported transition metal complexes have also been used for the hydrogenation of olefins.[9,10,18,19-23] “Nanoreactors” were prepared by Crooks et al.[19] using dendrimers as templates for the inclusion of metal nanoclusters within the branched framework. Both independent studies led by Crooks[19] and Tomalia[20] were based on the internal functionalization of the PAMAM dendrimer and showed the formation of colloids by reduction of metal ions coordinated to the nitrogen ligands forming the dendrimer. Crooks assessed the catalytic efficiency of such a system with the hydrogenation of allylic alcohol into 1-propanol by Pd particles encapsulated in OH-terminated dendrimers in water.[21] The turnover frequency was found to be 218 $mol_{H2}/mol_{Pd}/h$ at 20 °C.

Rh(I) based catalysts are often used in hydrogenation of olefins due to the high affinity of Rh(I) towards H_2 oxidative addition.[6] Dendrimers have also served as supports for these Rh(I) transition metal complexes. For example, we reported the preparation of organophosphine dendrimers in which phosphine moieties were distributed throughout the backbone of the resulting macromolecule.[9] A divergent acid-base hydrolytic methodology was employed using $Me_2Si(NMe_2)_2$ and tri(hydroxypropyl)phosphine as reaction partners (Scheme 1). One strategy leading to the preparation of related metallodendrimers was to react the organophosphine dendrimers with $[Rh(COD)Cl]_2$ by a bridge splitting reaction. The other strategy directly started with the preparation of the complex $[Rh(COD)ClP\{(CH_2)_3OH\}_3]$ before building the dendritic backbone. In very few synthetic steps, dendrimer "**Rh$_{46}$**" was prepared, featuring easy accessible 46 Rh(I) centers. Hydrogenation of 1-decene was carried out at T = 25°C, with 20 bar H_2 pressure in benzene for a reaction time of 30 min in a 1:200 dendrimer-to-substrate ratio. The catalytic activities (turnover frequency = 400 $mol_{prod}/mol_{dendrimer}/h$) of the Rh(I) dendrimers (**Rh$_4$**, **Rh$_{10}$**, **Rh$_{22}$**, **Rh$_{46}$**) were found to be similar to that of the monomeric complex **Rh$_1$**. The catalytic efficiency of these metallodendrimers was assessed upon recycling **Rh$_{46}$** cascade under the same reaction conditions. A slight decrease of about 5% conversion was observed after the second cycle.



Scheme 1. Preparation of Rh(I) supported organophosphine dendrimers.[9]

The asymmetric hydrogenation by chiral centers located at the periphery of the dendrimer, has been studied by Togni et al.[22] Rh (I) complexes were prepared from ferrocenyldiphosphine ligand terminated dendrimers. The hydrogenation of dimethyl itaconate was performed with ee of 98%. Asymmetric hydrogenation by chiral centers located at the core[24, 25] and on the branches[26] of the dendrimer have also been reported. Rhodium catalyzed hydroformylation reaction of 1-octene was studied by Reek and van Leeuwen's group.[26] Functionalization of the diphenylphosphine terminated carbosilane dendrimers $Si\{(CH_2)_nSi(CH_3)_2(CH_2PPh_2)\}_4$ and $Si\{(CH_2)_nSi(CH_3)(CH_2PPh_2)_2\}_4$ (n = 2, 3) with Rh(I) catalysts afforded the related metallodendrimers. Selectivity was comparable to their monomer analogs and activities depended on the size and flexibility of the metallodendrimers. Diphenylphosphine functionalized dendrimer featuring a polyhedral oligomeric silsesquioxane core was reported by the Cole-Hamilton's group.[27] Functionalized with Rh(I) complexes, the resulting metallodendrimer catalyzed the hydroformylation of 1-octene and showed a higher selectivity than their small molecule analogs.

Hyperbranched Polymers as Supports for Catalysis

Though the use of dendrimers as supports for transition metal complexes is considered to bridge the gap between homogeneous and heterogenized catalysis, their synthesis can involve expensive, labour-intensive multistep procedures which limit the amount of available material. The preparation of hyperbranched polymers circumvents these synthetic difficulties but often results in materials with high polydispersity. Studies related to their use as supports for catalysts are seminal but remain promising. The van Koten's group has reported the preparation of Pd-supported hyperbranched polytriallylsilane.[28] The hyperbranched carbosilane support (HCS) was synthesized by polymerization of triallylsilane with platinum catalysis. Hydrosilylation of the poly(triallylsilane) with $HSiMe_2Cl$ was followed by the addition of 3,5-bis[(dimethylamino)methyl]phenyl lithium (Li-NCN) to afford the coordinating ligand NCN-terminated hyperbranched polymer. After lithiation, the addition of the Pd(II) complex afforded the corresponding Pd(II) supported hyperbranched carbosilane. This new catalytic hyperbranched system was used for the catalytic aldol condensation of benzaldehyde and methyl isocyanate with $[Pd(OH_2)]OTf$ replacing the PdCl complexes. The turnover number per Pd site was shown to be slightly lower when using the hyperbranched catalyst compared with the monomer analog.

Search for catalysts featuring advantageous properties of both homogeneous and heterogeneous systems remains a topical area of research. The use of dendrimers in which transition metal catalytic centres can be distributed throughout the backbone or at the periphery, seems to offer a good compromise in this regard. In addition, the loading capacity increases exponentially as the dendrimers increase in size (generation number). Peripheral functionalization of 3,5-dihydroxybenzyl alcohol based dendrimers and hyperbranched polymers with Rh(I) catalysts is an attractive route to synthesize organometallic dendritic polymers,[10] since the supports are easily prepared in large amounts by following a simple acid-base hydrolytic methodology[30-35] using commercially available reagents 3,5-dihydroxybenzyl alcohol and $Me_2Si(NMe_2)_2$.[36] The catalytic activity of the resulting materials in hydrogenation of 1-decene was examined, and the influence of the distribution of the Rh(I) centers, at the periphery or throughout the backbone, was assessed by comparing the results obtained using the DHBA-based metallodendrimers with the ones containing Rh(I) sites distributed throughout the backbone reported previously by our research group.[9,10,36,37]

Results and Discussion

3,5-Dihydroxybenzyl Alcohol Based Dendrimers and Hyperbranched Polymers Functionalized with Rh(I) Metal Catalysts at Their Periphery

The 3,5-dihydroxybenzyl alcohol based dendrimers were prepared using an iterative sequential divergent acid base hydrolytic protocol involving the reaction of 3,5-dihydroxybenzyl alcohol and bis(dimethylamino)dimethylsilane.[10, 36] By controlling each reaction through a slow addition process, we were able to prepare hydroxyl group terminated dendrimers up to the fifth generation (Figure 1).

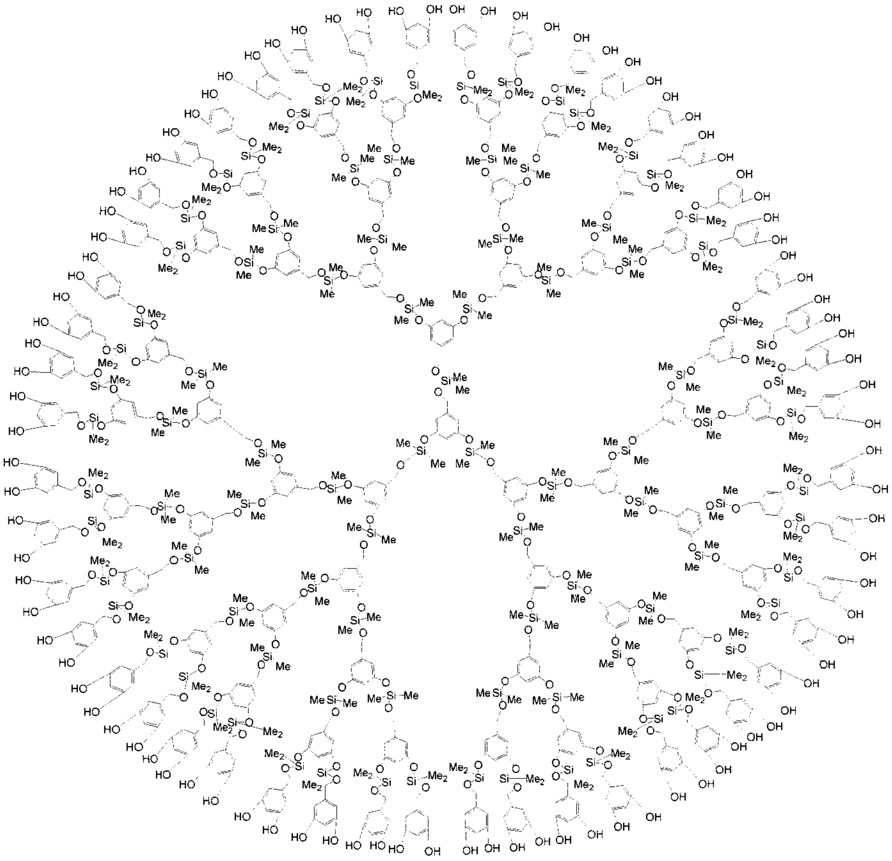
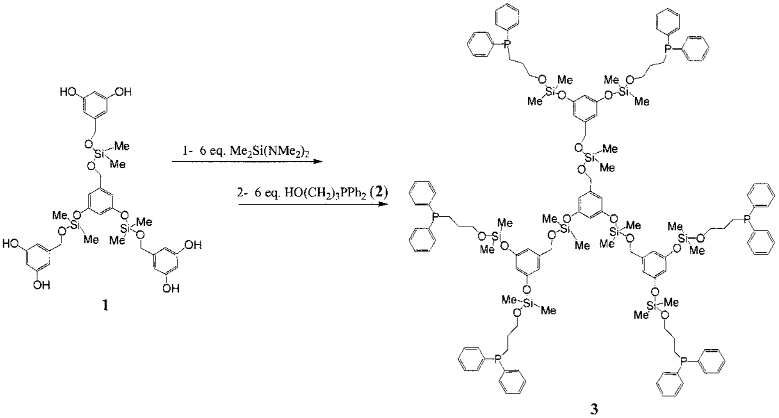


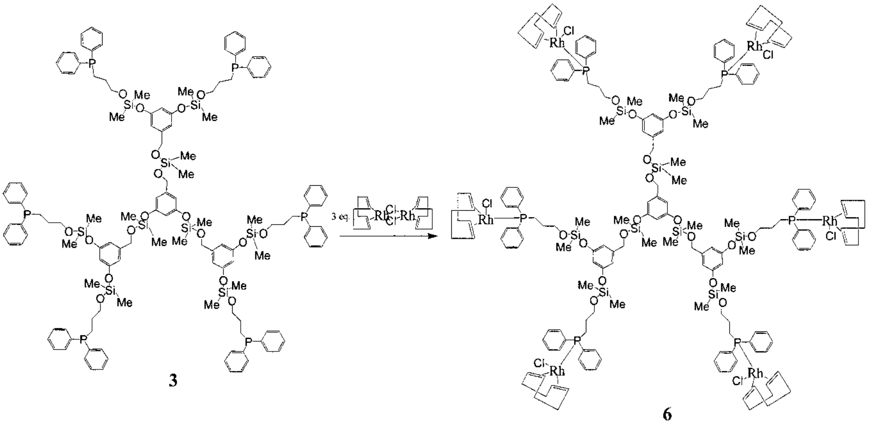
Figure 1. 3,5-dihydroxybenzylalcohol based 5th generation dendrimer.[36]

Because of their design as well as the flexibility of the acid-base hydrolysis synthetic methodology, the functionalization of the periphery with donor phosphine ligands that would coordinate with rhodium metal centers was easily achieved. A typical procedure used for this synthesis involved reacting 6 equivalents of $Me_2Si(NMe_2)_2$ with 1 equivalent of the first-generation dendrimer (**1**) in THF, followed by the addition of 6 equivalents of 3-hydroxypropyldiphenylphosphine ($HO(CH_2)_3PPh_2$, **2**) in THF.[10,36] The solution mixture was stirred at room temperature overnight, and the solvent was then removed under vacuum to yield the diphenylphosphine terminated first generation dendrimer (**3**) (Scheme 2).[10, 36] This procedure was repeated for dendrimer generations 2 and 3 using 12 and 24 equivalents of $HO(CH_2)_3PPh_2$ respectively resulting in diphenylphosphine-terminated second and third generation dendrimers (**4** and **5**). However, completion of the reaction of 3-hydroxypropyldiphenylphosphine with the peripheral aminosilane groups of the dendrimers required heat as well as additional time of reaction, as the steric congestion at the surface increased: 24 h at 55 °C to yield compound **4**, and 7 days at 55 °C to yield compound **5**.[36] This study focuses on functionalizing dendrimer generations 1-3 with phosphines followed by complexation with Rh(I) metal centers, as the steric congestion at the periphery of dendrimer generations 4 and 5 would prevent complete functionalization with the phosphine ligands.[10] $^{31}P\{^1H\}$NMR proved to be particularly useful to determine if the functionalization with the terminal phosphine units was complete. In the original mixture of aminosilane-terminated dendrimers and 3-hydroxypropyldiphenylphosphine, two peaks could be observed in the $^{31}P\{^1H\}$NMR spectra, one at -15.7 ppm for the $HO(CH_2)_3PPh_2$ reagent and the other at -16.0 ppm for the grafted $-O(CH_2)_3PPh_2$ moiety. Reaction completion was determined when the only peak at -16 ppm remained in the spectrum.[10, 36] MALDI-TOF mass spectroscopy was also very useful to characterize these metallodendrimers.



Scheme 2. Functionalization of first generation DHBA-based dendrimer with terminal 3-hydroxypropyldiphenylphosphine units.[10,36]

The related metallodendrimers were prepared by reacting phosphinated first-generation dendrimer (**3**) with $[RhCl(COD)]_2$ in a bridge-splitting reaction (Scheme 3).[10, 36] No residual free phosphine units at the periphery (**6**) were observed, as indicated by the complete disappearance of the singlet at -16.0 ppm and the appearance of a doublet at 27.3 ppm due to Rh-P coupling (J_{Rh-P} = 150 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Metallodendrimers **7** and **8** were prepared using similar procedure of reacting dendrimer generations 2 and 3 with 6 and 12 equivalents of the rhodium dimer respectively.[10, 36] Metallodendrimers **6-8** were recovered as yellow solids once the solvent was removed under vacuum.



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Scheme 3. Preparation of metallodendrimers by bridge splitting reaction of $[Rh(COD)Cl]_2$.[10,36]

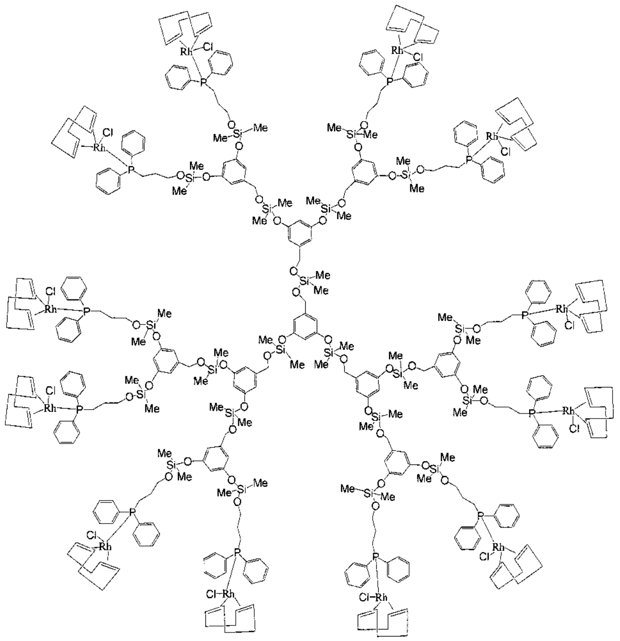

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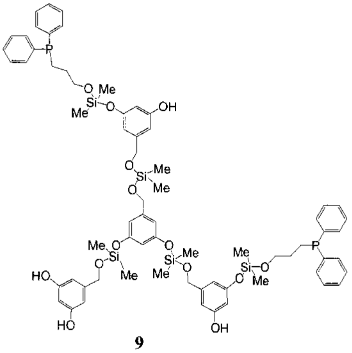
Figure 2

Functionalization of Hyperbranched Polymers

Preparation of DHBA-based hyperbranched polymers using a similar methodology as the one used for dendrimers,[36] led to the formation of a mixture of hyperbranched macromolecules. We were interested to know if their functionalization with Rh(I) complexes was possible, and how their results in hydrogenation of 1-decene would compare with that of metallodendrimers. The general synthetic strategy leading to the functionalization of the DHBA-based hyperbranched polymers[10, 36, 38] was the same as the one adopted for dendrimers. However, we had to take into consideration the fact that the synthesis of hyperbranched polymers leads to the formation different structural species. The preparation of hyperbranched polymers through 2 step-, 4 step- as well as 6 step-procedures resulted in multi-species mixtures with structures ranging from that of dendrimer generation 1 to the dendrimer generation 2. Hence, HP-2 step, HP-4 step and

HP-6 step were reacted with 6, 12 and 24 equivalents of $Me_2Si(NMe_2)_2$ and then 3-hydroxypropyldiphenylphosphine, respectively as in the case of their dendrimer analogs.[38] The number of moles of hyperbranched polymers used for the reaction was related to the initial molar quantity of DHBA involved during the first step of the preparation of the hyperbranched polymers. Reaction completion of the phosphine needed 3 days of stirring at 55°C for all of them. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The completion of the reaction was assumed when a single peak was obtained at -16.0 ppm. The different mass fractions observed by MALDI-TOF mass spectroscopy were also indicative of diphenylphosphine units grafted on the hyperbranched backbone. For **[HP-2]-(PPh$_2$)**, masses ranged from 1315 amu with a probable structure depicted in compound **9**, to 3 475 amu (**10** as the possible structure) and including the diphenylphosphine-terminated dendrimer generation one (**3**) (2 530 amu).[38]



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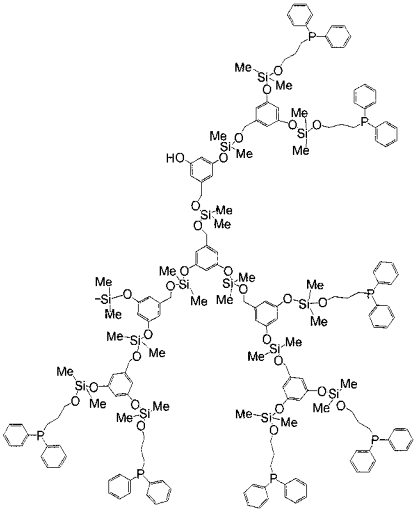

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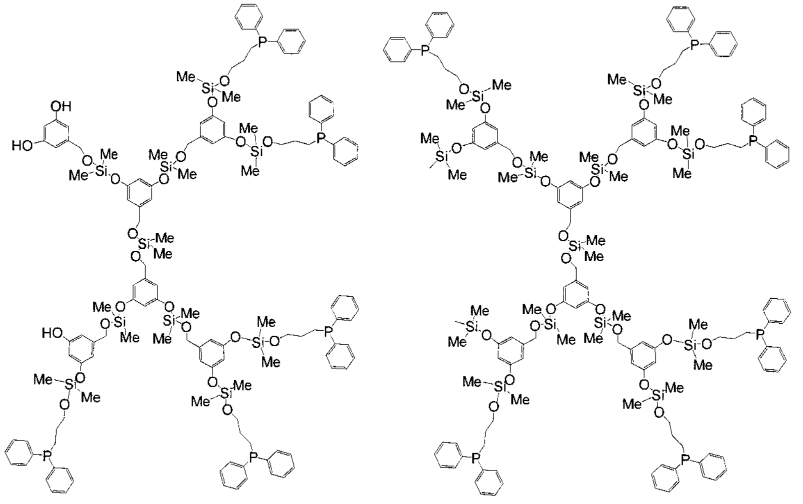
Figure 3

The main fractions observed for **[HP-4]-(PPh$_2$)** ranged from 1 315 (**9**), to 2 673 amu (**11**) also including compound **3**. The one for **[HP-6]-(PPh$_2$)** ranged from 1 315 (**9**) to 3 045 amu (**12**), again including compound **3**.[36, 38]



11 **12**

Figure 4

Reaction with the metal complexes was carried out using 3, 6 and 12 equivalents of Rh dimer with the phosphine functionalised HP-2 step, HP-4 step and HP-6 step respectively. Coordination to the rhodium center was monitored by $^{31}P\{^1H\}$ NMR with the appearance of a doublet at 27.3 ppm ($J_{Rh\text{-}P}$ = 150 Hz).[38] In the case of the **[HP-2]-(Rh)**, MALDI fractions could be observed from 1 524 (**13**) to 5 289 (**14**) including Rh-functionalized first generation dendrimer (**6**). The mass fractions for **[HP-4]-(Rh)** from 1 848 (**15**) to 7 463 amu (**16**) and from 1162 (**17**) to 8 464 amu (**4**) for **[HP-6]-(Rh)**.[38]

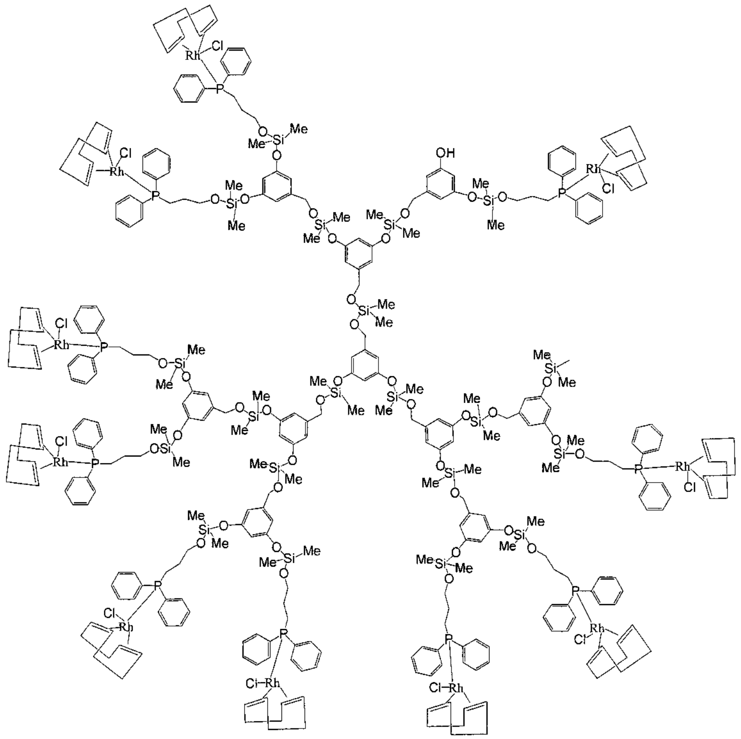


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Figure 5

Hydrogenation of 1-Decene

Using Metallodendrimers Based on 3,5-Dihydroxybenzyl Alcohol Dendrimers[36,38]

The hydrogen pressure reactor was loaded with the organometallic dendrimer and decene (1:200 molar ratio) dissolved in benzene. Hydrogenation of decene was carried out at room temperature at 20 bars H_2 pressure for periods of 0.5 to 5 h, and these reaction conditions were used as standard throughout the study.[36,38] Distillation of the reaction mixture after catalysis afforded the recovery of the Rh(I) dendritic material as a residue.

The % conversion rates of 1-decene into decane are summarized in Table 1, and show dependence on two distinct factors, the time of reaction and the generation number.

Table 1. Conversion rates (in %) of 1-decene into decane.[10, 36, 38]

Dendrimer	Time of Reaction h					
	0.5	**1**	**2**		**5**	
			1st cycle	2nd cycle	1st cycle	2nd cycle
[G-1]-(Rh)$_6$	19	47	48	85	97	93
[G-2]-(Rh)$_{12}$	23	65	71	93	98	97
[G-3]-(Rh)$_{24}$	26	65	93	98	93	91

The catalytic activity increased with an increase of time of reaction. For example, with organometallic dendrimer of generation 1, only 19% of decene was found to be converted to decane after 0.5 h of the reaction which gradually increased to 97% at 5 h of the reaction time. The reactivity of organometallic dendrimer of generation 2 followed a similar pattern of an increase in activity with time. Dendrimer generation 3 showed a maximum conversion after 2 h of contact time.

If we compare the differences in catalytic activity between all three metallodendrimers for 0.5 h reaction time, results are similar (19, 23 and 26%), and do not show a significant increase when the generation number increases. A roughly similar trend can be observed for 1 h reaction time as **[G-1]-(Rh)$_6$** converted 47% of decene into decane and both **[G-2]-(Rh)$_{12}$** and **[G-3]-(Rh)$_{24}$** showed 65% conversion. However, for a reaction time of 2 h, conversion rates of **[G-1]-(Rh)$_6$**, **[G-2]-(Rh)$_{12}$** and **[G-3]-(Rh)$_{24}$** are 48, 71 and 93% respectively.[10, 36, 38] Results for 5 h reaction time show maximum conversion rates for all three metallodendrimers. The results at lower time of contact suggest that the catalytic conversions of decene into decane are slower. It should be noted that increasing the generation number increases the number of Rh(I) centers at the periphery of the DHBA-based metallodendrimer. More decene is then likely to be converted into decane using higher generation number metallodendrimers.

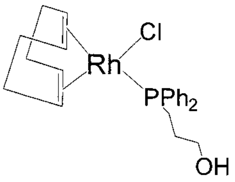
By reloading the catalyst with fresh decene for another 2 h, we expected, at best, a conversion rate similar to that obtained at the end of the first cycle of 2 h. However, an increase in catalytic activity was observed for **[G-1]-(Rh)$_6$** (48% to 85%) and **[G-2]-(Rh)$_{12}$** (71% to 93%).[36,38] This increase in conversion rates suggests that the catalyst was activated in the first cycle of 2 h reaction.[38] This activation can be caused by having decene already bound to the Rh center. Displacement of COD by decene is one of the steps involved in the catalytic reaction, and having it taken care of in the first 2 h of the cycle will accelerate the reaction in the second cycle of 2 h. One can also consider the fact that the recycling reaction started with the active Rh(III) dihydride species. Results upon recycling of the catalysts after a period of 5 h did not lead to an increase in conversion rates that were already at their maximum after one cycle. They are actually comparable to that of the first cycle of 5 h.[36, 38]

The monomeric species [$HO(CH_2)_3PPh_2Rh(COD)Cl$] **18** showed a catalytic conversion of decene to decane at 49% for 1 h reaction time. By determining the turnover frequency (TOF) of the metallodendrimers and that of the monomeric species (**18**), we could compare their catalytic activity with that of the Rh(I)-supported tri(alkyl)phosphine dendrimers in which the active catalytic centers are distributed throughout the backbone.[9] TOFs after 1h reaction time for monomer **18**, **[G-1]-(Rh)$_6$**, **[G-2]-(Rh)$_{12}$** and **[G-3]-(Rh)$_{24}$** were found to be 98, 94, 130 and 130 $mol_{prod}/mol_{cat}/h$ respectively.[10,36,38] However, TOFs per molecule of tri(alkyl)phosphine-based metallodendrimer were found to be 400 $mol_{prod}/mol_{cat}/h$ for **Rh$_1$**, **Rh$_4$**, **Rh$_{10}$**, **Rh$_{22}$** and **Rh$_{46}$** for a reaction time of 0.5 h.[9] By considering the number of catalytic sites supported on each species, TOFs of **18**, **[G-1]-(Rh)$_6$**, **[G-2]-(Rh)$_{12}$** and **[G-3]-(Rh)$_{24}$** can be compared to that of **Rh$_1$**, **Rh$_4$**, **Rh$_{10}$** and **Rh$_{22}$** respectively. The catalytic activities are lower for compound **18** as well as DHBA-based metallodendrimers (**[G-1]-(Rh)$_6$**, **[G-2]-(Rh)$_{12}$** and **[G-3]-(Rh)$_{24}$**), in which phosphine ligand features substituents of both aryl and alkyl nature. In addition, in the latter metallodendrimers, the catalytic sites are situated at the periphery. Such differences in catalytic efficiency can be explained by steric arguments as well as by difference of electron density at the metal center.

In DHBA-based and tri(alkyl)phosphine-based[9] metallodendrimers, distribution of the catalytic sites is different. For the tri(alkyl)phosphine-based dendrimers, the phosphine ligands are distributed throughout the entire backbone of the dendrimer whereas the phosphine ligands are only periphery situated in the case of the DHBA-based dendrimers. Coordination with Rh(I) complexes throughout the backbone reduces the steric congestion that can occur around the metal centers when they are located at the periphery only. Nevertheless, one could argue that distribution of Rh(I) centers throughout the backbone would lead to an increase in steric hindrance around them. However, it should be noted that there is inherent flexibility of the structural backbone of these dendrimers imparted by the alkyl branches. If one considers the schematic representation of **Rh_{46}** (Scheme 1), each Rh centre is far away from its neighbours, and there is less steric congestion around the metal center.

It is also known that steric congestion at the phosphine ligand can influence the rate of catalysis.[29] For example, it is known that triphenylphosphine ligand shields the metal.[29] The steric bulkiness of a phosphine ligand is generally measured by its cone angle.[39] Although undetermined, we can assume that the cone angle of the propyldiphenylphosphine ligand used in DHBA-based dendrimers will be in between 132° (for PEt_3) and 145° (for PPh_3).[29,39] It is safe to assume then that it is higher than tri(hydroxypropyl)phosphine. Higher cone angle will reflect higher congestion at the metal center, and the latter will reduce the accessibility of the substrate to the metal centre. This will lead to slower rates of olefin hydrogenation.[38]

Substituents at the phosphine ligand can also influence the conversion rates in hydrogenation of olefins.[5b,29] It is known that alkyl groups are more electron donating than aryl groups. Phosphines in which substituents are of alkyl nature are more electron rich, and when bound to a metal, will increase the electron density at the transition metal center. Kinetic studies led by Halpern[40] related to olefin hydrogenation have shown that the oxidative addition of H_2 occurred before binding of the olefin for Wilkinson-type Rh(I) catalysts.[5a,5b,29] If the Rh complexes, coordinated to tri(hydroxypropyl)-phosphine,[9] follow a similar reaction path, the oxidative addition should be enhanced in a more electron rich Rh(I) center. Because the Rh(I) centers are coordinated to hydroxylpropyldiphenylphosphine in the case of the DHBA-based metallodendrimers, the electron density at the Rh centre is expected to be lower than those in tri(alkyl)phosphine bound Rh centers. Hence, a slower addition of H_2 is expected. This is reflected in catalytic hydrogenation of decene to decane using model complexes (**18** and **Rh$_1$**).[36, 38] Tri(alkyl)phosphine monomeric species **Rh$_1$** shows a TOF of 400 $mol_{prod}/mol_{cat}/h$ whereas that for the monomeric species **18** is 98 $mol_{prod}/mol_{cat}/h$.[36] This argument can be extended to dendrimers as DHBA-based metallodendrimers show TOFs of 94, 130 and 130 $mol_{prod}/mol_{cat}/h$ for **[G-1]-(Rh)$_6$**, **[G-2]-(Rh)$_{12}$** and **[G-3]-(Rh)$_{24}$** respectively, that is much lower than tri(alkyl)phosphine metallodendrimers (400 $mol_{prod}/mol_{cat}/h$ for **Rh$_4$**, **Rh$_{10}$** and **Rh$_{22}$**).



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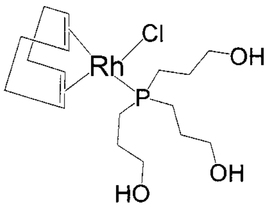

Rh$_1$

Figure 6

Using 3,5-Dihydroxybenzyl Alcohol Based Hyperbranched Polymers

The hydrogenation of 1-decene was also examined using Rh(I)-supported hyperbranched polymers. Reaction conditions were kept identical (RT, P = 20 bar H_2) to those used for the DHBA-based metallodendrimers. Conversion rates obtained from the hydrogenation reactions were intriguing (Table 2),[36, 38] and did not follow the trends observed in the case of metallodendrimers. **[HP-2]-(Rh)** and **[HP-4]-(Rh)** showed similar results (~ 80% conversion) for reaction times ranging from 0.5 to 2 h. Maximum conversion rates were obtained after 5 h reaction time as in the case of DHBA-based metallodendrimers (Table 1). Recycling of the catalyst for a 2 h reaction time did not increase the conversion rate as observed for the metallodendrimers. % conversion rates obtained using **[HP-6]-(Rh)** were comparable to those obtained using **[G-3]-(Rh)$_{24}$**. The catalytic activity increased gradually as the time of reaction was increased (26% after 0.5 h to 99% after 5 h). This difference in catalytic activity between **[HP-2]-(Rh)** and **[HP-4]-(Rh)**, and **[HP-6]-(Rh)** is intriguing, and some explanation may be obtained by analyzing the

MALDI-TOF MS data. Spectra obtained for **[HP-2]-(Rh)** and **[HP-4]-(Rh)** showed a multitude of peaks of different masses with similar peak heights. This suggests that both **[HP-2]-(Rh)** and **[HP-4]-(Rh)** are mixtures with a composition of organometallic macromolecules of similar ratio. MALDI-TOF spectrum for **[HP-6]-(Rh)** also showed a mixture of organometallic macromolecules, but revealed the dominance of one particular peak (compound **16**) for which peak height was much higher than the others. This may explain the differences in trend of the catalytic activity between **[HP-2]-(Rh)** and **[HP-4]-(Rh)**, and **[HP-6]-(Rh)**. The latter, if it could be considered as an almost single species organometallic hyperbranched polymer, would behave like a metallodendrimer. This might explain its catalytic activity, that is comparable to **[G-3]-(Rh)$_{24}$**. **[HP-2]-(Rh)** and **[HP-4]-(Rh)** polymers contain a mixture of organometallic hyperbranched species, and follow a different trend than **[HP-6]-(Rh)**.

Table 2. Conversion rates (in %) of 1-decene into decane for hyperbranched polymers.[36, 38]

Hyperbranched Polymer	Time of Reaction h					
	0.5	**1**	**2**		**5**	
			1st cycle	2nd cycle	1st cycle	2nd cycle
[HP-2]-(Rh)	78	79	82	81	93	95
[HP-4]-(Rh)	86	83	84	80	100	99
[HP-6]-(Rh)	26	60	91	92	99	95

Conclusions

The search for the ideal catalytic system is a topic of continued high interest. Dendrimers are attractive supports since they can be tailored to host transition metal complexes at varied locations. The preparation of Rh(I) catalyst-supported dendrimers was rendered possible via the peripheral functionalization of the DHBA-based dendrimers with a tertiary phosphine by continuation of the divergent acid base hydrolytic procedure. Reaction of the dendrimers with $Me_2Si(NMe_2)_2$ resulted in peripheral aminosilane groups, needed to graft the 3-hydroxypropyldiphenylphosphine molecules. Reaction completion was found to require heat and supplemental time of reaction as the steric congestion increased in higher generations. Coordination of these phosphine ligands to transition metal centers was achieved by bridge splitting reaction with $[Rh(COD)Cl]_2$ resulting in dendrimers of generations 1-3 featuring 6, 12 and 24 Rh(I) catalytic sites respectively on their surface. A similar procedure was applied to functionalize the DHBA-based hyperbranched polymers with similar Rh(I) catalytic moieties.

The hydrogenation of 1-decene was studied using these DHBA-based organometallic dendritic materials under standard conditions (RT, P = 20 bar H_2) over different periods of reaction time ranging from 0.5 to 5 h. In the case of organometallic dendrimers, the catalytic activity was found to be dependent upon two distinct factors. An increase in time of reaction led to an increase in catalytic activity, as well as upon an increase in the generation number. Upon recycling the catalyst after a period of 2 h, a significant increase in % conversion rate was observed. Maximum conversion was observed for a reaction time of 5 h.

Comparing these results to previous study on the hydrogenation of 1-decene using dendrimers in which Rh(I) centers were distributed throughout the backbone,[9] indicated much slower conversion rates in periphery situated metallodendrimers. Steric arguments around the Rh centers, differences in bulkiness, and electron donating abilities between the tri(alkyl)phosphine[9] and the propyldiphenylphosphine can partly explain these differences in conversion rates. The nature of the substituents on the phosphine ligand is known to influence the sterics and electron density at the metal center. Oxidative addition of H_2 may be facilitated when the Rh center is more electron rich, as in the case of the tri(alkyl) substituted phosphine,[9] leading to higher catalytic activity than when the phosphine contains one alkyl group and two aryl groups. This may explain higher catalytic efficiency of tri(alkyl)phosphine-based metallodendrimers than DHBA-based metallodendrimers.

The hydrogenation of 1-decene using the Rh(I)-supported hyperbranched polymers led to good conversion rates with a reaction time as low as 0.5 h in the case of the **[HP-2]-(Rh)** and **[HP-4]-(Rh)**, whereas the catalytic activity increased gradually in the case of **[HP-6]-(Rh)**. This difference in behaviour can be related to the inherent composition of each hyperbranched polymer mixture. **[HP-2]-(Rh)** and **[HP-4]-(Rh)** are both mixtures of organometallic macromolecules of equal ratio, and **[HP-6]-(Rh)** mixture showed the presence of a single dominant species, from which the trend in catalytic activity can be compared to that of metallodendrimers.

Acknowledgements

We would like to thank NSERC (Canada) and FQRNT (Quebec, Canada) for financial support.

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