DOI: 10.1002/adsc.200900016

Immobilisation of the Pyrphos Ligand on Soluble Hyperbranched Supports and Use in Rhodium-Catalysed Hydrogenation in Ionic Liquids

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Received: January 11, 2009; Published online: March 17, 2009

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900016.

Abstract: The immobilisation of the pyrphos ligand has been extended from highly symmetric dendrimers to less regular structured hyperbranched poly(ethylene imines). Cationic dendritic pyrphos-rhodium(norbornadiene) [pyrphos-Rh(NBD)] complexes have been synthesised using poly(propylene imine) (PPI) and poly(amido amine) (PAMAM) dendrimers as supports bearing between 4 and 64 potential catalytically active sites at their periphery as well as pyrphos-Rh(NBD) complexes tethered to hyperbranched poly(ethylene imines) carrying on average 9 to 139 functionalities located throughout the whole supporting structure. These immobilised systems have been used as catalysts for the hydrogenation of *Z*-methyl α-acetamidocinnamate. With the PPI, PAMAM, and hyperbranched poly(ethylene imine)-bound pyrphos-Rh(NBD) omplexes as catalysts, hydrogenations were carried out in methanol, and a decrease in activity and selectivity was observed with increasing size of the macromolecular support. Furthermore, the polycationic catalysts were tested in a liquid/liquid-biphasic system consisting of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate {[BMIM] [BF_4]} and isopropyl alcohol. Using the PPI-, PAMAM-, and PEI-immobilised systems, a strong negative "dendritic effect" with increasing molecular size was observed with respect to the catalytic activity, the stereoinduction, and the recyclability. The PPI-bound rhodium(I)-complexes of generations one and two showed good reusability; even after triple recycling, with no loss of activity or selectivity being noted. It has been demonstrated that in this case the catalytic behaviour of hyperbranched systems is essentially similar to that of the related dendritic model system.

Keywords: asymmetric catalysis; catalyst immobilization; catalyst recycling; hydrogenation; ionic liquids; pyrphos

Introduction

Homogeneous chiral catalysts are generally well defined systems, frequently affording high activity and selectivity in catalytic reactions as well as good reproducibility of the catalyst performance.[1] In contrast, most of the catalysts used in industry belong to the class of heterogeneous catalysts because they can be easily separated from reactants and products and reused several times.[2] To transfer this feature to homogeneous catalysts without some of the negative aspects of heterogeneous catalysts, dendrimers and other polymers have been used as soluble – but separable – supporting materials.[3] Dendrimers are highly branched macromolecules that combine a high level of structural regularity, molecular monodispersity, and a wide variety of modes of attachment of well-defined catalytic sites.[4]

In general, two different strategies are used to attach chiral catalysts to dendrimers.[5] One possibility is the fixation of catalysts at the dendrimer periphery. This type of attachment was first established by van Koten, van Leeuwen and co-workers, who used dendrimer tethered nickel(II) complexes containing NCN pincer ligands to study their catalytic properties in the Kharash reaction.[6]

The second possibility is the attachment of one or more dendritic wedges to the catalyst. In their extreme form these catalysts are located at the core of a complete dendrimer. The first example of such a system was reported by Brunner et al., who studied the influence of the chiral dendritic periphery on the performance of asymmetric cyclopropanation catalysts.[7]

The recycling of dendritic catalysts is achieved inter alia by using membrane reactors.[8] Unfortunately, in most cases the catalyst performance deteriorated with time. Another possibility is filtration after precipitation of the catalyst.[9]

When studying the activity and stereoinduction of chiral dendritic catalysts, two possible effects may be noticed.[10] A "positive dendritic effect" is referred to when the activity and/or selectivity of the dendritic catalyst increases in comparison to the mononuclear catalyst. This can be attributed to a cooperative interaction of two or more catalytic sites. On the other hand, the steric crowding caused by the dendritic wedges can lead to a diminished activity and/or stereoinduction ("negative dendritic effect") of the immobilised catalyst. Which of these effects is observed depends on the architecture of the dendritic structure as well as on the mechanism of the catalysed reaction.

In a previous study, a series of chiral phosphine-functionalised poly(propylene imine) (PPI) and poly(amido amine) (PAMAM) dendrimers was synthesised by reaction of the carboxyl-linked C_2-chiral pyrphos ligand with 0th to 5th generation PPI and 0th to 4th generation PAMAM dendrimers, respectively.[11] The relationship between the size/generation of the cationic cyclooctadiene-rhodium complexes of these ligands and their catalytic properties was established inter alia in the asymmetric hydrogenation of *Z*-methyl α-acetamidocinnamate and dimethyl itaconate. Generally, a slight decrease in activity and enantioselectivity of the catalysts was observed on going to higher dendrimer generations.

In addition to dendrimers, hyperbranched polymers have also been used as soluble supports for catalysts.[12] These supports are polydisperse and randomly branched and, since they are prepared in a single reaction step, are generally much cheaper materials. Nevertheless, it has been shown that catalysts immobilised on hyperbranched polymers may possess similar properties as dendritic systems.[13] Therefore, dendritic catalysts serve as ideal model systems for catalysts attached to hyperbranched polymers.

Results and Discussion

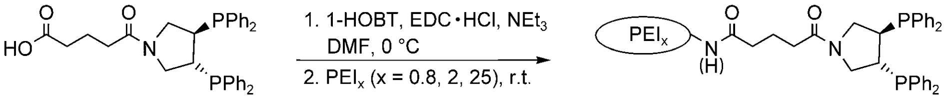
Synthesis of the PEI-Bound Pyrphos Ligands

The catalytic properties of phosphine ligands immobilised on dendrimers or hyperbranched polymers of related chemical structure can be similar but also completely different, depending on the mechanism of the catalytic reaction.[14] In order to further investigate this observation, pyrphos-functionalised hyperbranched poly(ethylene imines) were synthesised in addition to those attached to PPI and PAMAM dendrimers published previously. This was achieved following the same strategy that was developed for the hyperbranched BINAP ligands[14b] using glutaric acid as a linking unit. As coupling reagents ethyl-*N*,*N*-dimethylaminopropylcarbodiimide (EDC) and 1-hydroxybenzotriazole (1-HOBT) were used (Scheme 1). In analogy to dendrimers, hyperbranched polymers are also available in different molecular weights. For this study three supports provided by BASF SE with M_w of 800 ($PEI_{0.8}$), 2000 (PEI_2) and 25000 $g\,mol^{-1}$ (PEI_{25}) were used, giving the immobilised ligands **1**–**3** in yields of 88% and higher.

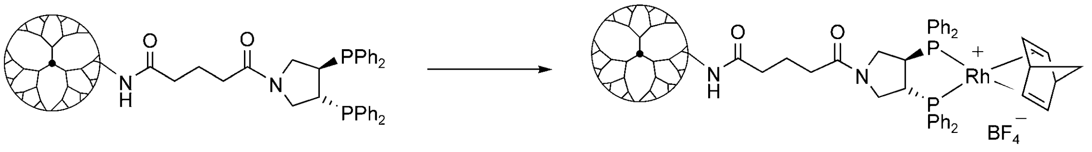
The degree of functionalisation (DF) of the supporting polymers was determined by elemental analysis. Both $PEI_{0.8}$ and PEI_2 have been functionalised completely (100%) and PEI_{25} still with 91% DF, resulting in systems bearing on average 9, 26 or 138 pyrphos ligands distributed throughout the whole supporting polymer backbone structure.

Synthesis of the Pyrphos Rh(I) Complexes

To date, the properties of the dendritic pyrphos ligands coordinated to Rh(1,5-cyclooctadiene) complexes have been tested in catalysis. These systems are characterised by long induction periods resulting from the hydrogenolytic elimination of the diolefin yielding the catalytically active species.[11a,15] Other diolefin-precursor complexes bearing, for example, norborna-2,5-diene (NBD) are much more active in hydrogenation reactions which is due to a more rapid formation of the active species without changes in enantioselectivity.[16] In order to enhance the catalytic activity of the immobilised pyrphos ligands cationic Rh(NBD) complexes have been synthesised by reaction of the dendritic and hyperbranched ligands with $[Rh(NBD)_2]\ BF_4$ in dichloromethane (Scheme 2). Ad-



Scheme 1. Functionalisation of poly(ethylene imines) with Glutaroyl-pyrphos ligands.



Scheme 2. Synthesis of the pyrphos-Rh(NBD) complexes **4–18**.

ditionally, a mononuclear complex [Pyrboc-Rh(NBD)] BF_4 (**4**) has been synthesised as reference system.

All complexes **4–18** have been obtained in excellent yields of between 88 and 99%. In Figure 1 the chemical structure of {G2}-PAMAM-{Glutaroyl-pyrphos-Rh(NBD) BF_4}$_{16}$ **13** is depicted, illustrating the high topological symmetry of the dendritic catalyst.

Although the symmetry of the hyperbranched catalysts is much lower due to their polydispersity, the individual catalytically active sites retain their local uniformity as can be readily seen in the ^{31}P NMR spectrum of PEI$_{0.8}$-{Glutaroyl-pyrphos-Rh(NBD) BF_4}$_n$ **16** shown in Figure 2.

The spectrum displays the AB multiplet of an ABX spin system with a resolution similar to that of the

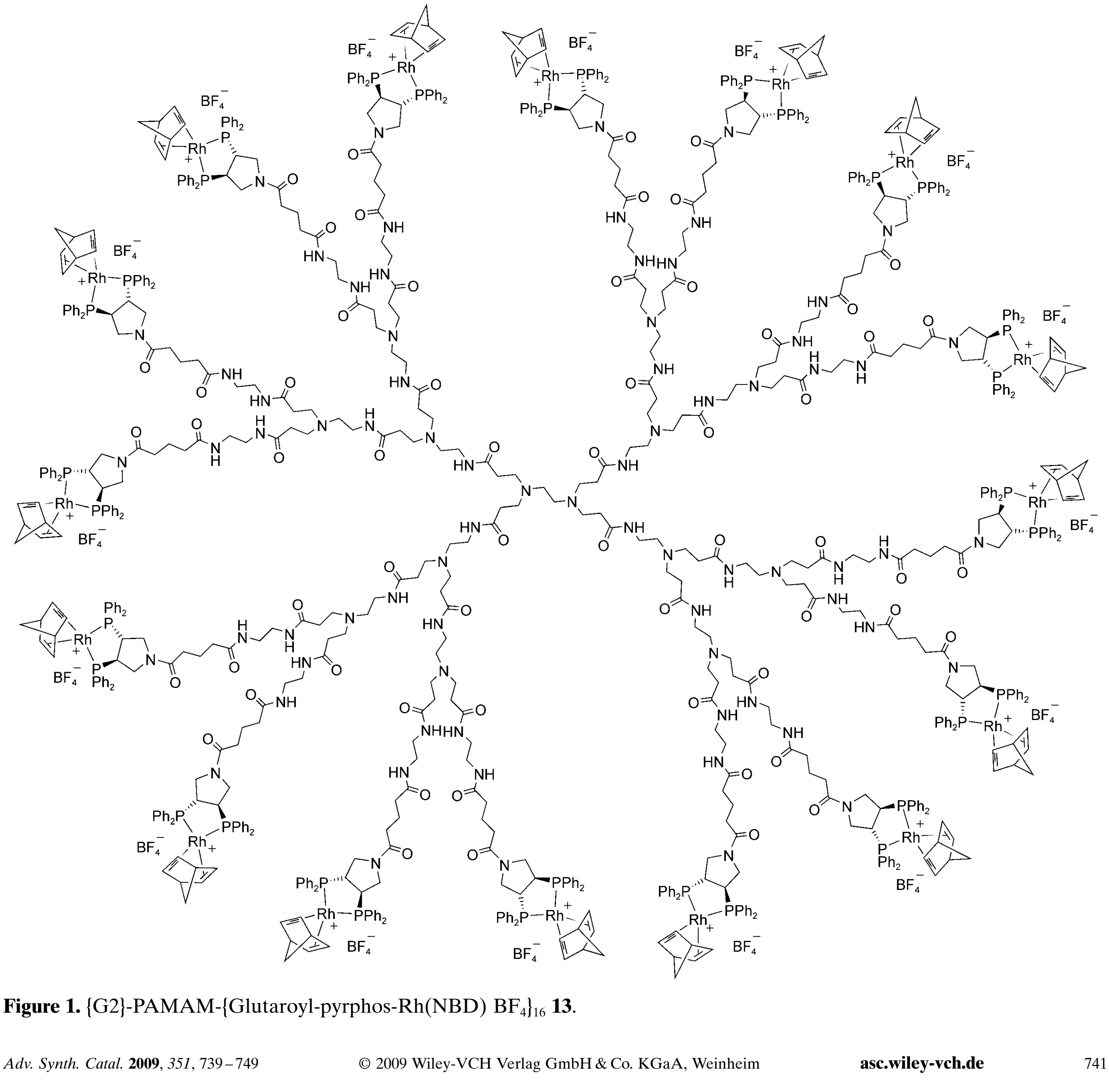


Figure 1. {G2}-PAMAM-{Glutaroyl-pyrphos-Rh(NBD) BF_4}$_{16}$ **13**.

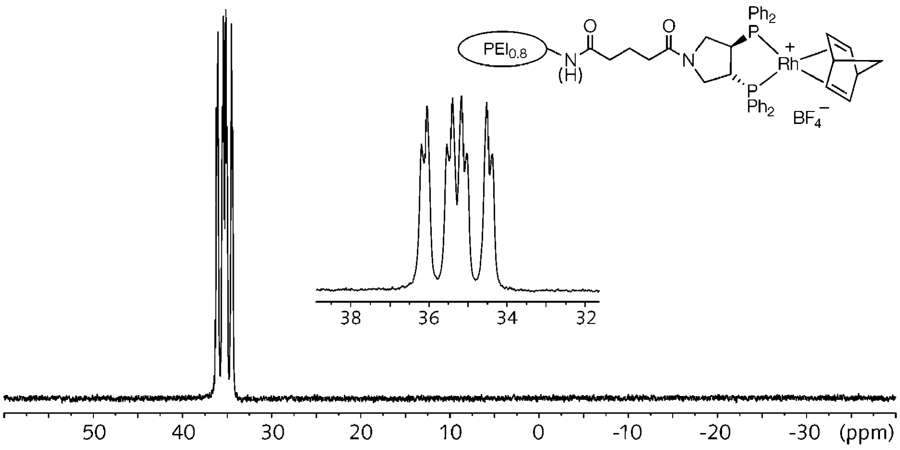


Figure 2. ^{31}P NMR spectrum of PEI$_{0.8}$-{Glutaroyl-pyrphos-Rh(NBD) BF$_4$}$_n$ **16**.

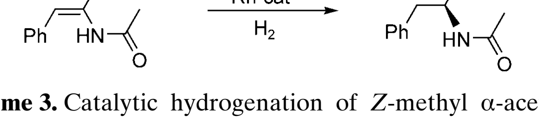
dendritic systems of comparable molecular size. The resonances at 35.8 and 34.8 ppm exhibit $^1J_{P,Rh}$ coupling constants of 159.3 and 156.8 Hz as well as a $^2J_{P,P'}$ coupling constant of 33.3 Hz The complete metallation of all of the diphosphine ligands can also be deduced from the ^{31}P NMR spectra of the complexes in which the resonance of the unmetallated ligands at *ca.* −12 ppm is absent.

In summary, cationic dendritic pyrphos-Rh(NBD) complexes have been synthesised using PPI and PAMAM dendrimers as supports bearing between 4 and 64 potential catalytically active sites at their periphery as well as hyperbranched pyrphos-Rh(NBD) complexes tethered to poly(ethylene imines) having on average 9 to 139 centres located throughout the whole polymeric supporting structure.

Catalytic Properties – Hydrogenations in Methanol

The immobilised pyrphos-Rh(NBD) complexes were studied as catalysts for asymmetric hydrogenations of functionalised olefins. In order to compare the catalyst properties with those obtained for related systems, *Z*-methyl α-acetamidocinnamate was chosen as benchmark substrate (Scheme 3).

Similar reaction conditions to those employed previously for immobilised pyrphos-Rh(COD) complexes[11] were initially chosen. Thus all hydrogenations were carried out using a rhodium/substrate ratio of 1:400 and a hydrogen pressure of 30 bar at 25 °C. Figure 3 displays the results obtained for the PAMAM-bound rhodium catalysts.



Scheme 3. Catalytic hydrogenation of *Z*-methyl α-acetamidocinnamate.

Generally, a decrease in activity was observed on going to higher dendrimer generations which may be due to an increase in steric crowding, the mononuclear catalyst **4** giving rise to the highest activity. A first qualitative indication for the higher activity of these catalysts compared to the corresponding Rh(COD) systems is the induction period at the beginning of the S-shaped curves which is much less pronounced. A more quantitative value to describe this observation is the turnover frequency (TOF) that has been calculated at 50% conversion. The results of this comparative study are listed in Table 1.

Comparison of the dendritic catalysts reveals that all systems display negative dendritic effects with respect to their activities but that the relative difference

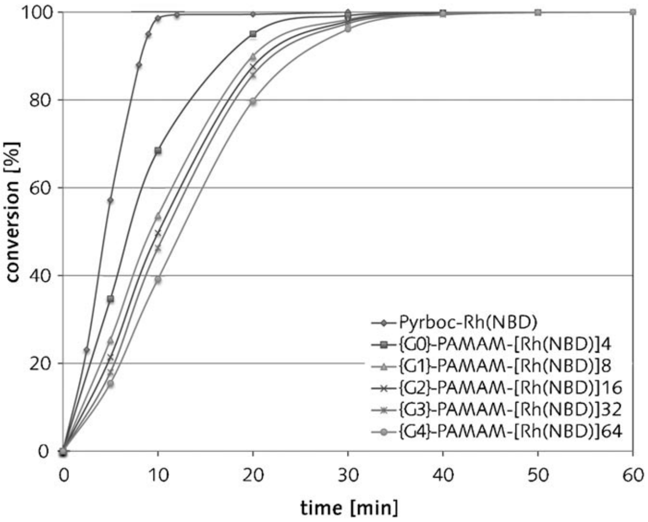


Figure 3. Comparison of the catalytic activities of the mononuclear Pyrboc-Rh(NBD) BF$_4$ **4** and the PAMAM-bound pyrphos-Rh(NBD) complexes **11**–**15**.

Table 1. Comparison of the the turnover frequencies (TOF) of the three families of dendritic pyrphos-Rh(I) complexes.

Catalyst	TOF [min^{-1}] PPI-{Rh(COD)}$_n$	TOF [min^{-1}] PPI-{Rh(NBD)}$_n$	TOF [min^{-1}] PAMAM-{Rh(NBD)}$_n$
Pyrboc-Rh	20	55	55
Dendr-(Rh)$_4$	11	46	29
Dendr-(Rh)$_8$	7	43	22
Dendr-(Rh)$_{16}$	6	18	20
Dendr-(Rh)$_{32}$	2	13	19
Dendr-(Rh)$_{64}$	n.d.	10	18

in activity between the largest and smallest system in each family of immobilised catalysts is different. The greatest variation in activity was found for the PPI-immobilised catalysts **6–10**, with TOFs between 46 and 10 min^{-1}. The activity of {G1}-DAB-*dendr*-{Glutaroyl-pyrphos-Rh(COD) BF_4}$_4$ of 11.0 min^{-1} is comparable to that of the PPI-bound Rh(NBD) complexes of generations four and five. This clearly indicates the higher activity of the norbornadiene precursor complexes when comparing catalysts attached to similar dendrimer generations. Comparison of the pyrphos-Rh(NBD) complexes tethered to PPI and PAMAM dendrimers reveals that the supporting backbone has an important impact on the catalytic properties: the decrease in activity is much less pronounced for the PAMAM systems. We note though that, for the latter, the catalytic activity of the smallest immobilised catalyst {G0}-PAMAM-{Glutaroyl-pyrphos-Rh(NBD) BF_4}$_4$ **11** is much lower than that of the comparable PPI-bound system **6**.

Figure 4 depicts the enantioselectivities obtained with the dendritic pyrphos-Rh(NBD) complexes **6–15**. The PPI- as well as the PAMAM-bound pyrphos-Rh complexes display a slight decrease in stereoinduction with increasing size of the supporting material, a trend which is more pronounced for the PPI tethered complexes. For the latter, a drop from 91% *ee* for the first generation system **6** to 86% *ee* for the fifth generation system **10** was observed. In comparison to the mononuclear catalyst **4**, which induces an enantioselectivity of 92% *ee*, the dendrimer fixation leads to a small negative effect in selectivity. When using the PAMAM-bound systems a decrease in enantioselectivity from 91% *ee* for the zeroth generation with four end groups **11** to 89% *ee* for the fourth generation **15** was found. The decrease may be due to a change in conformation of the diphenylphosphine units with increasing steric crowding at the periphery of the dendrimer in both cases.

In the following part of this study the pyrphos-Rh(NBD) complexes tethered to the hyperbranched poly(ethylene imines) **16–18** were employed as hydrogenation catalysts under analogous reaction conditions. Table 2 lists the results obtained with these systems.

The pyrphos-rhodium complexes bound to the hyperbranched polymers are active catalysts for the hydrogenation of *Z*-methyl α-acetamidocinnamate. The

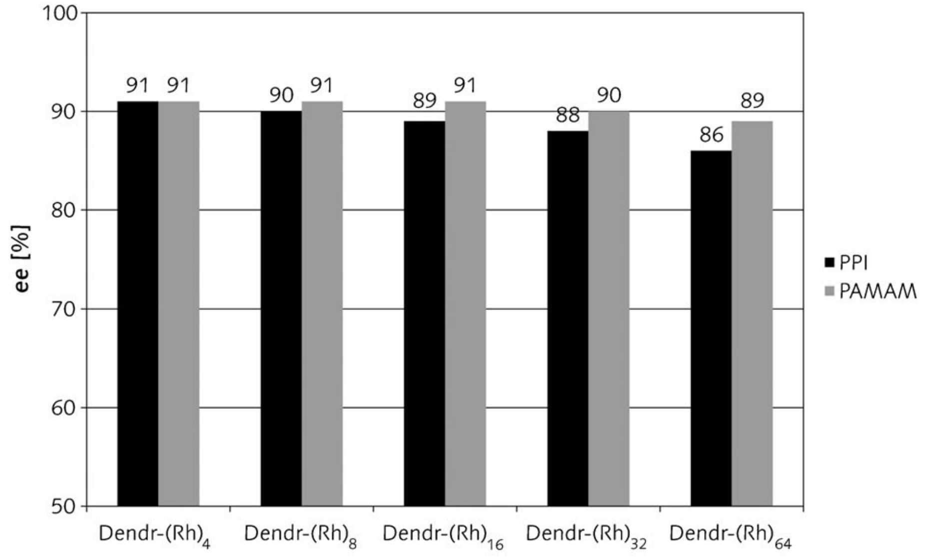


Figure 4. Comparison of the the enantioselectivities obtained with the PPI- and PAMAM-bound pyrphos-Rh(NBD) complexes **6–15**.

Table 2. Turnover frequencies (TOF) and enantioselectivities obtained with the hyperbranched catalysts **16–18**.

Catalyst	TOF [min^{-1}]	*ee* [%]
$PEI_{0.8}$-$(Rh)_n$ **16**	37	89
PEI_2-$(Rh)_n$ **17**	31	87
PEI_{25}-$(Rh)_n$ **18**	13	84

activity of these systems decreases with increasing size of the supporting material which is a very similar behaviour to that of the dendritic catalysts. The activity of $PEI_{0.8}$-{Glutaroyl-pyrphos-Rh(NBD)BF_4}$_n$ **16**, bearing on average 9 active sites, amounts to a TOF of 37 min^{-1} which is slightly less than that of {G2}-DAB-*dendr*-{Glutaroyl-pyrphos-Rh(NBD)BF_4}$_8$ **7**. PEI_2-{Glutaroyl-pyrphos-Rh(NBD)BF_4} **17** (26 end groups) exhibits a significantly higher activity (31 min^{-1}) than the dendritic system of comparable size, whereas PEI_{25}-{Glutaroyl-pyrphos-Rh-(NBD)BF_4}$_n$ **18** (on average 138 active sites) displays an activity (TOF of 12.5 min^{-1}) which is comparable to that of {G4}-DAB-*dendr*-(Glutaroyl-pyrphos-Rh-(NBD)BF_4)$_{32}$ **9**.

Thus it could be demonstrated that the catalysts bound to hyperbranched poly(ethylene imines) exhibit a decrease in activity similar to the regular dendrimers with increasing molecular weight, however, this decrease is much less pronounced. This observation may be attributed to the more open structure of these polymers which allows a good accessibility of the active sites. Not all of these are attached to the periphery of the supports because the secondary amino groups of the unfunctionalised polymers are located inside their core structure. The enantioselectivities are comparable to those observed with the dendritic systems and range from 88% *ee* for the smallest hyperbranched catalyst **16** to 84% *ee* for the largest supported catalyst **18**.

We therefore note that, in addition to the regular dendritic pyrphos-Rh(NBD) complexes, analogous catalysts based on hyperbranched poly(ethylene imines) have been obtained. They follow the behaviour established for the dendrimer model system very well, whilst generally displaying higher catalytic activity.

Catalytic Hydrogenations in the Biphasic System [BMIM] [BF_4]/*i*-PrOH

The aim of catalyst immobilisation is the possibility to recycle the catalytic system. It was therefore our goal to work out conditions for catalyst recycling in a biphasic solvent system by employing a suitable ionic liquid to trap the polycationic rhodium catalysts.

Depending on the dendrimer generation, the catalysts studied in this work are bearing 4 to 64 positive charges at their periphery or, depending on the size of the hyperbranched poly(ethylene imine), between 9 and 138 charges within the polymer structure as a whole. A biphasic reaction medium consisting of the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate {[BMIM] [BF_4]} and isopropyl alcohol[17] was thought to be suitable for such catalysts, the IL dissolving the catalyst and the isopropyl alcohol the substrate *Z*-methyl α-acetamidocinnamate as well as the corresponding amino acid as reaction product.

This was thought to allow for a facile separation of the phases after complete conversion with the possibility to reuse the ionic catalyst phase by simple addition of new substrate in *i*-PrOH. Each catalyst was tested in three successive catalytic runs of 2 h. The reaction temperature was raised to 55 °C in order to take advantage of the *thermomorphic* behaviour of the solvent mixture. This allows the actual catalytic conversion to take place in a homogeneous reaction medium under these conditions, with the phases separating again upon cooling to ambient temperature at the end of the reaction. The conversions obtained when using the mononuclear and the PAMAM-bound complexes as catalysts are depicted in Figure 5.

Using the mononuclear catalyst **4**, complete conversion was obtained in the first two runs, while decreasing to 79% in the third run. The principal reason for this is the leaching of the catalyst into the isopropyl alcohol phase which could be easily identified by its orange colour. In contrast, for none of the immobilised pyrphos systems was leaching into the alcohol phase found. The loss of activity for the higher dendrimer generations must therefore be attributed to the partial degradation of the catalyst. The enantioselectivities observed with these catalysts are summarised in Figure 6.

A negative “dendritic effect” with regard to the reusability as well as the stereoinduction, which is more pronounced than under monophasic reaction conditions, was observed. Compared to the reactions carried out in methanol all enantioselectivities are lower in the biphasic mixture as a result of the use of isopropyl alcohol as solvent.

Employing these reaction conditions, the reusability of the PPI-fixed catalysts was also tested in the hydrogenation of *Z*-methyl α-acetamidocinnamate (Figure 7). In this case a negative dendritic activity effect has even been observed in the first catalytic run. Similar to the homogeneous reaction in methanol, the PPI-bound catalysts display greater variation in activity. This leads to an incomplete conversion of the fourth and fifth generation systems already in the first catalytic run. In addition, a decrease in activity in successive catalytic runs was detected. As in the case of the mononuclear catalyst **4** the dimer {G0}-DAB-

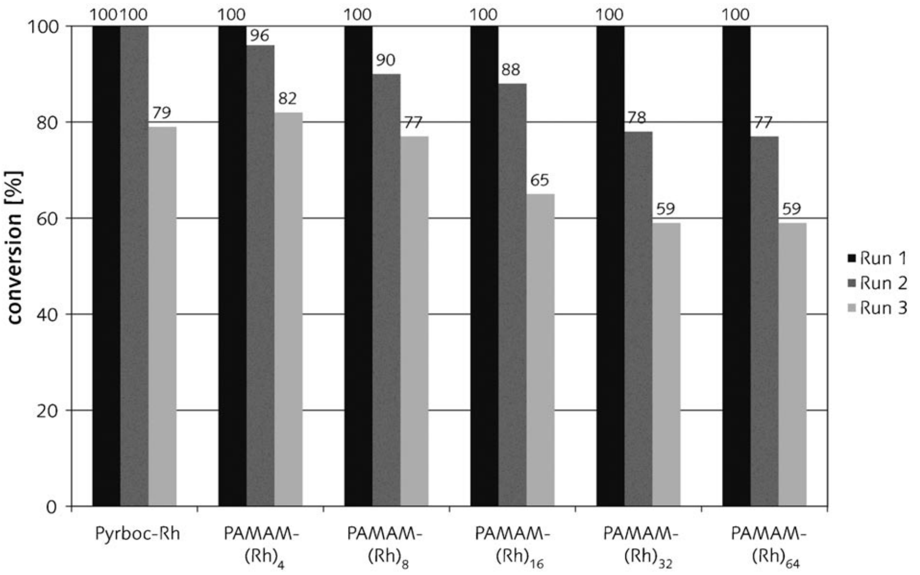


Figure 5. Conversions obtained when using Pyrboc-Rh(NBD) BF_4 **4** and the PAMAM-bound pyrphos-Rh(NBD) complexes **11–15** as catalysts.

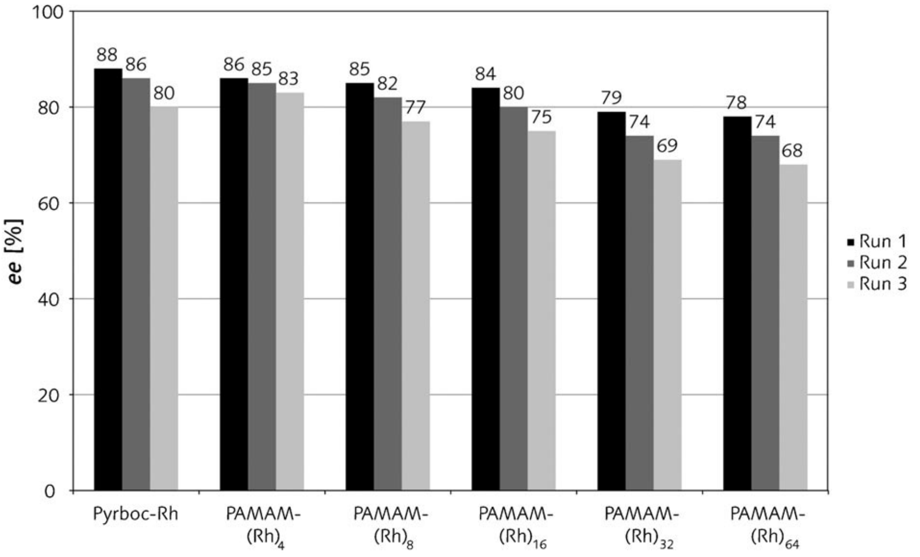


Figure 6. Stereoinductions obtained when using Pyrboc-Rh(NBD) BF_4 **4** and the PAMAM-bound pyrphos-Rh(NBD) complexes **11–15** as catalysts.

dendr-{Glutaroyl-pyrphos-Rh(NBD) $BF_4\}_2$ **5** leaches into the *i*-PrOH phase whereas the activity decay observed with the dendritic systems **6–10** must be due to the partial decomposition of the active sites. Nevertheless, the decrease in activity of the PPI bound systems of generations one (**6**) and two (**7**) is rather small, a trend which can also be seen from the stereoinduction data listed in Figure 8.

The catalysts tethered to the hyperbranched poly(ethylene imines) **16–18** were also tested under similar reaction conditions and the results obtained are represented in Figure 9.

Similar to the regular dendritic systems, the hyperbranched catalysts also show a decrease in activity and enantioselectivity with increasing size of the macromolecular support. However, this decrease is less pronounced! The conversions and stereoselectivities of $PEI_{0.8}$-{Glutaroyl-pyrphos-Rh(NBD) $BF_4\}_n$ **16** and PEI_2-{Glutaroyl-pyrphos-Rh(NBD) $BF_4\}_n$ **17** lie between those of PPI generations two and three where-

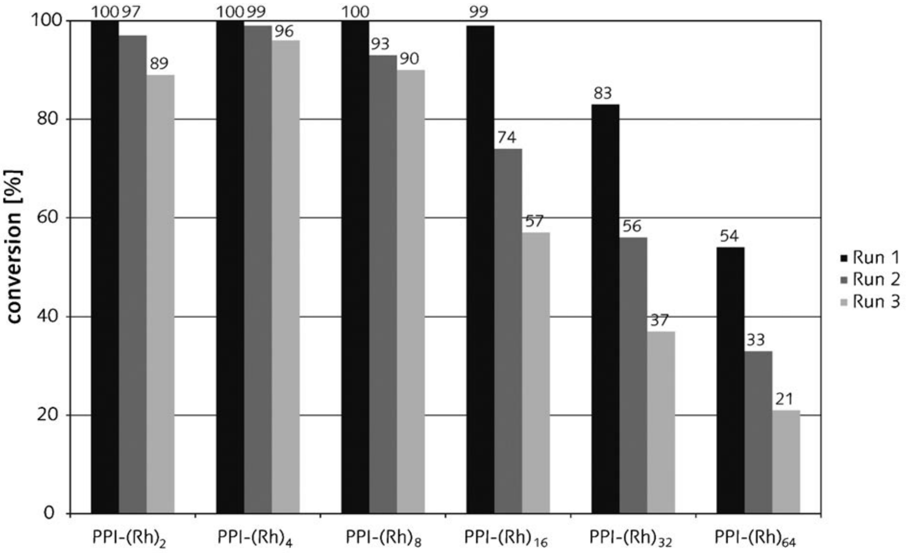


Figure 7. Conversions after a reaction time of 2 h at 55 °C using the PPI-tethered pyrphos-Rh(NBD) complexes **5**–**10** as catalysts.

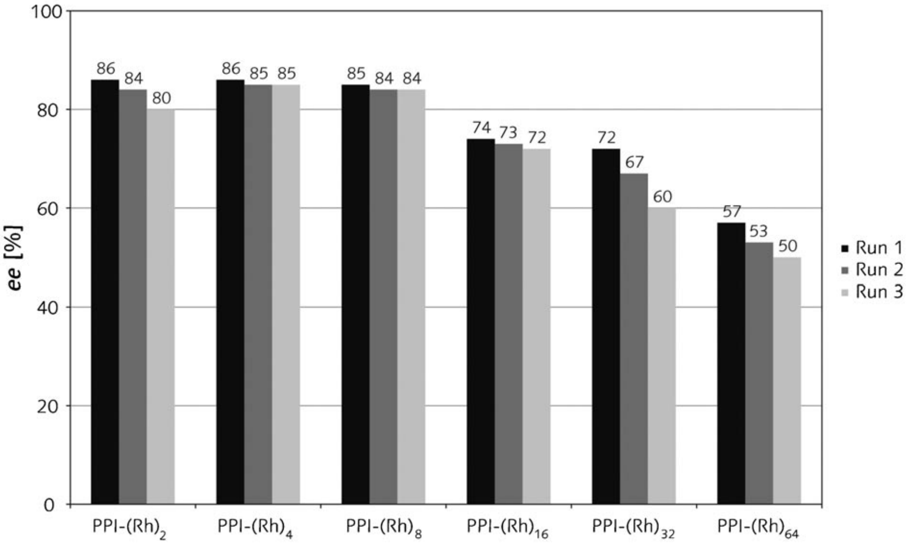


Figure 8. Enantioselectivities obtained when using the PPI-fixed pyrphos-Rh(NBD) complexes **5**–**10** as catalysts.

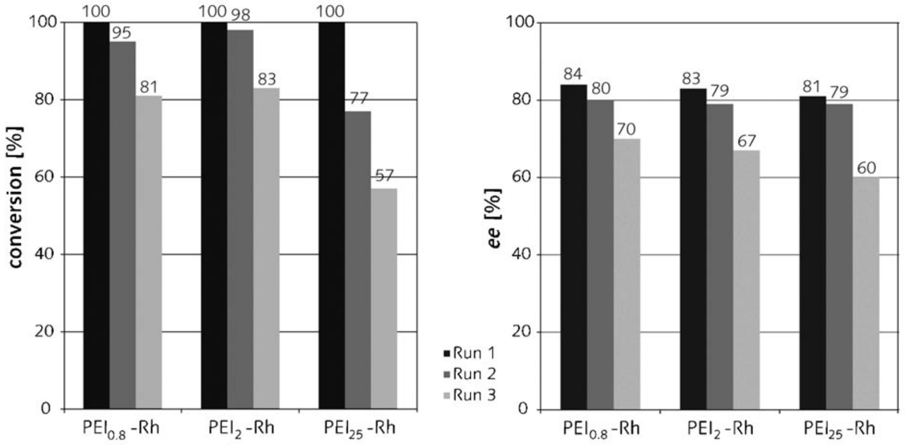


Figure 9. Conversions and enantioselectivities obtained when using the hyperbranched systems **16**–**18** as catalysts.

as the largest catalyst PEI_{25}-{Glutaroyl-pyrphos-Rh-(NBD) BF_4}$_n$ **18** exhibits an activity which is comparable to that of {G3}-DAB-*dendr*-{Glutaroyl-pyrphos-Rh(NBD) BF_4}$_{16}$ **8** in combination with a higher selectivity in the first two catalytic runs.

Conclusions

In conclusion, it has been shown that the immobilisation of the pyrphos ligand could be extended to less regular structured hyperbranched poly(ethylene imines). Cationic dendritic pyrphos-Rh(NBD) complexes have been synthesised using PPI and PAMAM dendrimers as supports, bearing between 4 and 64 potential catalytically active sites at their periphery as well as hyperbranched pyrphos-Rh(NBD) complexes tethered to poly(ethylene imines) having on average 9 to 139 centres distributed throughout the whole supporting structure.

These immobilised systems have been used as catalysts for the hydrogenation of Z-methyl α-acetamidocinnamate. With the PPI-, PAMAM-, and hyperbranched poly(ethylene imine)-bound pyrphos-Rh-(NBD) complexes as catalysts, hydrogenations were carried out in methanol, and a decrease in activity and selectivity was observed with increasing molecular size. Furthermore, the polycationic catalysts were tested in a liquid/liquid biphasic system consisting of [BMIM] [BF_4] and isopropyl alcohol. Using the PPI-, PAMAM- and PEI-fixed systems, a strong negative “dendritic effect” with increasing molecular size was observed for the catalytic activity, stereoinduction, and reusability. Nevertheless, the PPI-bound pyrphos-rhodium(I) complexes of generations one and two displayed good reusability, and even after recycling twice, no loss of activity or selectivity was observed.

It could be demonstrated that in this case the catalytic behaviour of the hyperbranched systems is similar to that of the dendritic model systems. Whilst hyperbranched polymers are available in a broader mass range as well as with greater variations in the reactive end groups in comparison to regular dendrimers, catalysts tethered to them usually do display similar properties in catalysis.

Experimental Section

General information about equipment and methods employed in this work along with the complete spectroscopic and analytical data of all new compounds is provided in the Supporting Information.

General Procedure for the Synthesis of the Hyperbranched Pyrphos Ligands (1–3)

A mixture of *N*-((4′-carboxyl)butanoyl)-pyrphos (HO-Glutaroyl-pyrphos, 1.30 equiv.), EDC·HCl (1.43 equiv.), 1-HOBT (1.95 equiv.) and triethylamine (2.09 equiv.) was stirred in DMF at 0 °C for 40 min. To this suspension was added the respective amino-terminated hyperbranched poly(ethylene imine) dissolved in DMF. The resulting solution was warmed to room temperature and stirred for 90 h. All volatiles were completely removed under vacuum. The residue was taken up in 20 mL CH_2Cl_2 and thoroughly extracted with KOH (0.2 M, 2×15 mL), H_2O (2×15 mL), hydrochloric acid (0.2 M, 2×15 mL), KOH (0.2 M, 2×15 mL) and again H_2O (2×15 mL). Finally, the solvent was removed under vacuum. The resulting solid was washed several times with *n*-pentane and dried under vacuum yielding the Glutaroyl-pyrphos-functionalised hyperbranched poly(ethylene imines) as white powders.

General Procedure for the Synthesis of the Rh(I)-Norbornadiene Complexes (4–18)

To a solution of [Rh(NBD)$_2$] BF_4 (1.05 equiv. per diphosphine) in CH_2Cl_2 the dendritic or hyperbranched phosphine (1.00 equiv.) dissolved in CH_2Cl_2 was added. The resulting orange solution was stirred for 18 h at room temperature, then passed through Celite (3 cm) and concentrated to 0.5 mL under vacuum. Upon addition of diethyl ether (20 mL) an orange solid precipitated which was separated from the supernatant liquid by centrifugation, washed with diethyl ether and twice with *n*-pentane and dried under vacuum.

General Procedure for the Catalytic Hydrogenation of *Z*-Methyl α-Acetamidocinnamate in Methanol

The rhodium/substrate ratio was chosen to be 1:400 in all cases. About 10 mg of the catalyst precursor were weighed under an inert atmosphere, the calculated amount of *Z*-methyl α-acetamidocinnamate was added and the solids were transferred to a laboratory autoclave (Büchi miniclave drive) under argon. The mixture was dissolved in absolute methanol (60 mL) and the inert gas was displaced with hydrogen. The pressure was set to 30 bar and the reaction started upon stirring. The temperature was kept constant at 25 °C ± 1 °C with a cryostat. For sampling, a small quantity (*ca.* 100 μL) of the solution was taken with a dipping tube. The sample was dissolved in CH_2Cl_2 and analysed by GC.

Work-up of the hydrogenated solution: The solution was reduced to dryness and the residue was purified by column chromatography (silica gel, diethyl ether). After removal of the solvent the product was dried under vacuum and analysed by HPLC.

General Procedure for the Hydrogenation of *Z*-Methyl α-Acetamidocinnamate in [BMIM] [BF_4]/*i*-PrOH

The rhodium/substrate ratio was 1:400 in all cases. The catalyst (2.03 μmol per catalytically active site) was dissolved in 1 mL of [BMIM] [BF_4] and *Z*-methyl α-acetamidocinnamate (0.81 mmol) was dissolved in 4 mL of *i*-PrOH. Both phases were transferred into a laboratory autoclave (Büchi miniclave drive) under argon. The inert gas was displaced with hydrogen. The pressure was set to 30 bar and the temperature was kept constant at 55 °C with a cryostat. After two hours, the pressure was released and the autoclave was cooled to room temperature. Both phases were decanted. The *i*-PrOH phase was analysed by chiral GC. The catalytic phase was reused without further washing for a new catalytic experiment by addition of a fresh solution of substrate.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 623, C8) and the Fonds der Chemischen Industrie (Ph.D. scholarship to J.K.K.) for support. We are also grateful to Dr. Bernd Bruchmann (BASF SE) for providing the hyperbranched poly(ethylene imines).

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