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Immobilisation of the BINAP Ligand on Dendrimers and Hyperbranched Polymers: Dependence of the Catalytic Properties on the Linker Unit

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Abstract: A series of immobilised Carbo-BINAP ligands has been synthesised using poly(propylene imine) (PPI) dendrimers as soluble supports. They contain up to 64 BINAP ligands at their periphery without an additional linking unit. Despite the high steric requirements of the ligand, all dendrimers could be completely functionalised, resulting in the immobilised systems in good yields. Furthermore, the immobilisation strategy that worked out for the fixation of AMINAP ligands with additional linking units as well as of Carbo-BINAP ligands without additional linking units on dendrimers has thus been extended to less regularly hyperbranched poly(ethylene imines) (PEI) as soluble supports. In that way it has been possible to attach on average 9, 26, and 138 Glutaroyl-AMINAP or Carbo-BINAP ligands to PEIs of different molecular weights. The catalytic properties of these systems in the copper-catalysed hydrosilylation of acetophenone were investigated. The dendritic PPI-bound Carbo-BINAP ligands displayed a strong dependence of enantioselectivity and activity on the generation of the dendrimer. For the Carbo-BINAP and Glutaroyl-AMINAP ligands immobilised on the hyperbranched polymers, however, activities and enantioselectivities comparable to those of the mononuclear catalysts were found. The macromolecular, immobilised BINAP ligands could be recycled several times without any observable loss of activity or enantioselectivity.

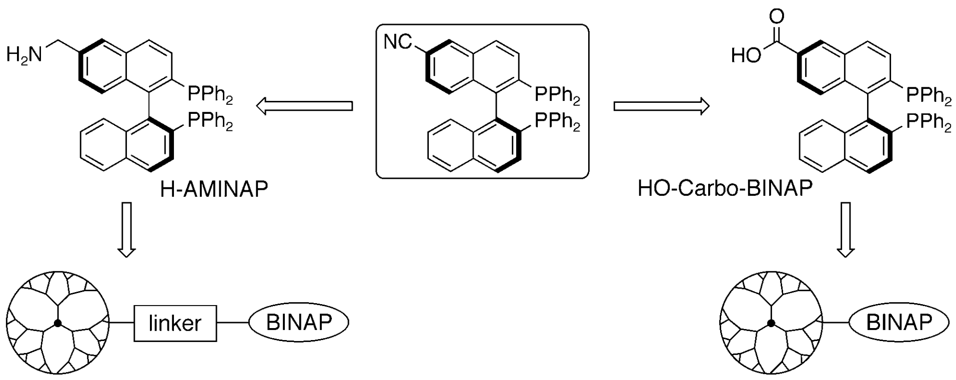
Keywords: asymmetric catalysis; BINAP; catalyst immobilization; dendrimers; hydrosilylation; hyperbranched polymers

Introduction

In 1980 Noyori et al. synthesised the chiral diphosphine BINAP.[1] Up to now this ligand has found various applications in asymmetric catalysis, resulting in the desired chiral products in good to excellent enantioselectivities of up to 99% *ee*. Apart from the most popular BINAP-ruthenium and BINAP-rhodium complexes that catalyse the hydrogenation of olefins and ketones,[2–4] many other transition metal-BINAP complexes were discovered to be active as catalysts in miscellaneous chemical transformations. The Pt(II) complexes, for example, show enantioselectivities of up to 99% *ee* in the asymmetric Diels–Alder reaction of acryloyl-*N*-oxazolidinone and cyclopentadiene,[5] whereas the Pd(II) complexes are good catalysts in the asymmetric allylation of unsymmetrical 1,3-diketones, where enantioselectivities of 89% *ee* have been obtained in the reaction of 2-acetyl-4,4-dimethylcyclohexanone with cinnamyl acetate.[6]

The BINAP-copper(I) complexes have also found use as catalysts. A very recent example is the conjugate reduction of 2-pyridyl vinyl sulfones, affording the chiral sulfones with yields and enantioselectivities of 90% and higher.[7] A more established reaction catalysed by diphosphine-Cu(I) complexes is the hydrosilylation of aryl ketones. Using acetophenone as substrate the BINAP-Cu catalyst was found to give moderate enantioselectivity (75% *ee*) compared with other diphosphine ligands tested by Lipshutz et al.[8] By variation of the reaction conditions the enantioselectivity could be improved to over 90% *ee*.[9]

Fan et al. synthesised a variety of functionalised BINAP-ligands bearing dendritic wedges.[10–15] To attach the polyaryl ether dendrons to the ligand they introduced amino groups in the 5- or 5,5′-positions. Those dendritic ligands have been tested as catalysts



Scheme 1. Attachment of the BINAP ligand on dendrimers with (*left*) and without (*right*) an additional linking unit.

in various hydrogenation reactions, showing similar enantioselectivities as the BINAP ligand itself but with improved recycling properties.

A methylene amino-functionalised BINAP ligand ("H-AMINAP") has been attached to the periphery of poly(propylene imine) (PPI) and poly(amido amine) (PAMAM) dendrimers using glutaric acid as a linking unit.[16] It has been demonstrated that these dendritic systems can be used as "ligands" in the copper-catalysed hydrosilylation of acetophenone without any loss of enantioselectivity resulting from their immobilisation onto the dendrimer compared to the mononuclear ligand Benzoyl-AMINAP.[16]

In addition to dendrimers that are characterised by their monodispersity and high regularity,[17] hyperbranched polymers have also been used as soluble supports for catalysts.[18] In contrast to dendrimers, these supports are polydisperse and randomly branched. Their production is much cheaper since they are generated in one-step processes. Nevertheless it has been shown that catalysts immobilised on hyperbranched polymers may possess similar properties as regular dendritic systems.[19] It is because of this relationship that dendrimer catalysts may serve as model systems for catalysts attached to hyperbranched polymers.

Results and Discussion

The function of the linking unit in immobilised catalysts is an important factor. Depending on the size of the catalyst, the linking unit can determine the density of the catalytically active centres in the immobilised system.[20] Additionally, the linker acts as a spacer between the catalyst and the support and will influence the catalytic properties, owing to an enhanced mobility of the active centres.[21]

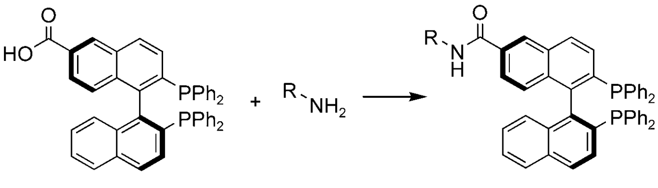
Therefore, we decided to investigate the influence of the linking unit on the immobilised BINAP ligands in more detail. In our previous work, the AMINAP ligand was attached to the periphery of PPI- and PAMAM-dendrimers using glutaric acid as a linking unit.[16] This linker is relatively long and enables a high mobility of the fixed ligands. On the other hand this flexibility may also lead to a backfolding of the catalytic active sites into the interior of the dendritic structure. Because of this, we have now synthesised a series of dendritic BINAP ligands with much shorter ligand-support linking units.

The previously reported AMINAP ligand was prepared from (*R*)-6-Cyano-BINAP[22] as a starting material. By hydrolysis of the cyano function it is also possible to create a carboxyl group directly on the binaphthyl backbone of the ligand[22] that should allow a direct attachment of the ligand to the amino end groups in PPI and – in principle – also PAMAM dendrimers without an additional linking unit (Scheme 1).

Synthesis and Characterisation of the Mononuclear Carbo-BINAP Reference Systems

The direct attachment of the Carbo-BINAP ligand to the periphery of dendrimers is expected to lead to a stronger influence of the supporting material on the ligated catalysts than has been the case with glutaric acid previously employed as linker.[16] Therefore, four mononuclear reference ligands were synthesised, which were thought to represent a range of steric environments relevant to the functionalised dendritic target compounds. To this end, the carboxyl group of HO-Carbo-BINAP was coupled with the primary amines methylamine, *n*-propylamine, *tert*-butylamine, and benzylamine (Scheme 2) using ethyl-*N*,*N*-dimethylcarbodiimide (EDC) and 1-hydroxybenzotriazole as coupling reagents, a strategy well known in polypeptide synthesis.[23]

Crystals of **1**, **2** and **3** suitable for a single crystal X-ray structure analysis were obtained from toluene. The molecular structure of **1** is depicted in Figure 1.



Scheme 2. Synthesis of the mononuclear Carbo-BINAP reference ligands (R = methyl **1**, *n*-propyl **2**, *tert*-butyl **3**, benzyl **4**).

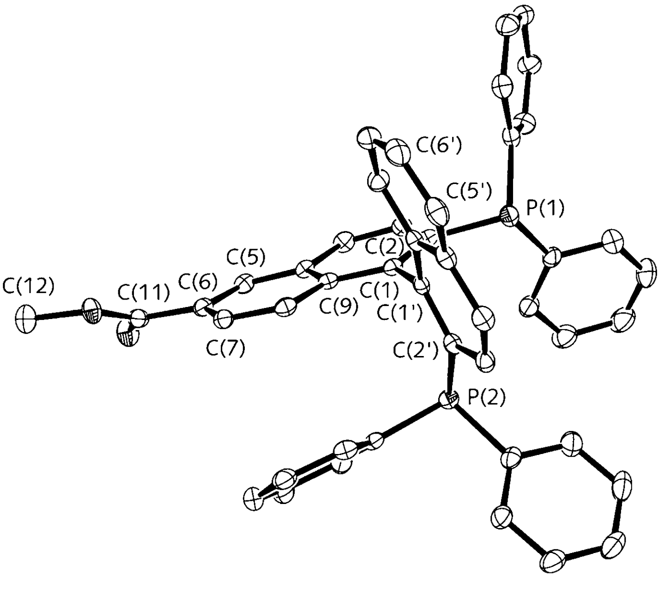


Figure 1. Molecular structure of Carbomethyl-BINAP **1**, hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] of Carbomethyl-BINAP **1**, Carbopropyl-BINAP **2** and Carbo-*tert*-butyl-BINAP **3**.

	1	**2**	**3**
C(1)–C(1′)	1.497(3)	1.504(4)	1.498(2)
C(2)–P(1)	1.841(2)	1.844(3)	1.841(2)
C(2′)–P(2)	1.839(2)	1.845(3)	1.836(2)
C(1)–C(2)	1.385(3)	1.382(4)	1.384(2)
C(1′)–C(2′)	1.386(3)	1.382(4)	1.388(2)
C(1)–C(2)–P(1)	117.9(2)	118.4(2)	118.76(13)
C(1′)–C(2′)–P(2)	118.6(2)	119.2(2)	119.42(12)
N–C(11)–C(6)	116.4(2)	116.7(3)	116.40(16)
C(2′)–C(1′)–C(1)-C(9)	93.3(3)	85.5(3)	86.6(2)

The structures of **2** and **3** are quite similar (allowing for the different substituents R) and are displayed in the Supporting Information. Table 1 provides a comparative listing of the principal bond lengths and angles of compounds **1**–**3**.

The principal structural features are similar to the crystallographically determined molecular structure of the unfunctionalised BINAP.[24] This also holds true for the torsion angles between the two naphthyl fragments . The values are 87.8° in BINAP,[24] 93.3° in **1**, 85.5° in **2** and 86.6° in **3**. The greater angle observed in **1** is tentatively attributed to crystal packaging effects. The corresponding torsion angle in Benzoyl-AMINAP differs with 78.8° more considerably from the angle in the unfunctionalised BINAP ligand.[16] This shows that in this case the functionalisation of the ligand backbone has a larger influence on the torsion angle than in the Carbo-BINAP ligands.

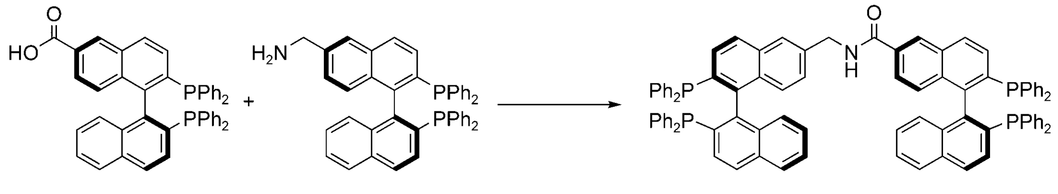
In addition to these mononuclear reference ligands, a bitopic ligand, Bis-BINAP **5**, was synthesised by combination of HO-Carbo-BINAP and H-AMINAP, thus further increasing the steric demand of the "protecting group" (Scheme 3).

The ^{31}P NMR spectrum of **5** clearly indicates the connection of these two differently functionalised BINAP ligands. The signals of the diphosphine halves are observed as AB spin systems at −15.13 and −15.25 ppm for the Carbo-BINAP part ($J_{P,P}$ = 13.5 Hz) and at −15.44 and −15.54 ppm ($J_{P,P}$ = 11.3 Hz) for the AMINAP moiety.

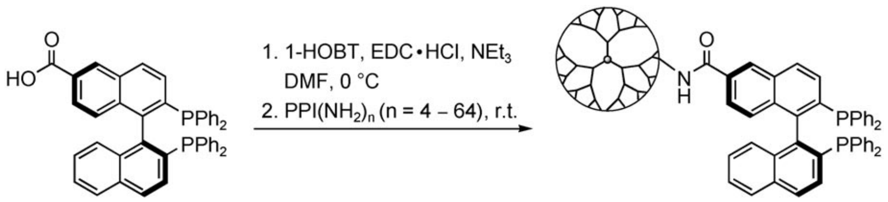
Synthesis and Characterisation of the Carbo-BINAP Functionalised PPI Dendrimers

The essentially complete functionalisation of all amino end groups of PPI dendrimers of generations 1 to 5 was achieved following the same strategy that was developed for the dendritic AMINAP ligands,[16] using ethyl-*N*,*N*-dimethylcarbodiimide (EDC) and 1-hydroxybenzotriazole as coupling reagents and an excess of HO-Carbo-BINAP (Scheme 4).

By this method, Carbo-BINAP functionalised PPI dendrimers have been synthesised, bearing 4 to 64 diphosphines at their periphery without an additional linking unit. All dendritic ligands were characterised by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and elemental analysis. The lower generations up to {G3} have also



Scheme 3. Synthesis of Bis-BINAP **5**.



Scheme 4. Synthesis of the dendritic Carbo-BINAP ligands **6–10**.

been characterised by MALDI-TOF mass spectrometry, indicating a complete functionalisation of all dendritic end groups. In Figure 2 {G2}-DAB-*dendr*-(Carbo-BINAP)$_8$ **7** is depicted as a representative example, illustrating the high topological symmetry of the dendritic ligands.

In contrast, a complete functionalisation of PAMAM dendrimers was not achieved with the Carbo-BINAP ligand as indicated by the ^{31}P NMR spectra. This negative result was obtained even for the lower dendrimer generations and upon employing a greater excess of functionalised ligand. Likewise, longer reaction times or higher reaction temperatures did not lead to complete conversion. This contrasts with the previously reported facile immobilisation of ligand-linker units of AMINAP on PAMAM dendrimers.[16]

Synthesis and Characterisation of the AMINAP and Carbo-BINAP Functionalised Hyperbranched Poly(ethylene imines)

We then investigated whether the immobilisation strategy of both Carbo-BINAP and AMINAP ligands developed for dendrimers as supporting materials was also applicable to the less regularly structured hyperbranched poly(ethylene imines) (PEIs). These were chosen as supports because they exhibit a chemical structure similar to the poly(propylene imine) dendrimers used so far. The hyperbranched polymers are commercially available with different average molecular weights. PEIs with average M$_W$ of 800 (PEI$_{0.8}$), 2000 (PEI$_2$) and 25000 g mol^{-1} (PEI$_{25}$) have been used in this study (for further information about the properties of the hyperbranched PEIs see the Supporting Information and ref.[19]). In Figure 3 a section of a PEI is depicted.

In contrast to the PPI dendrimers that essentially possess only primary amino groups (due to the almost

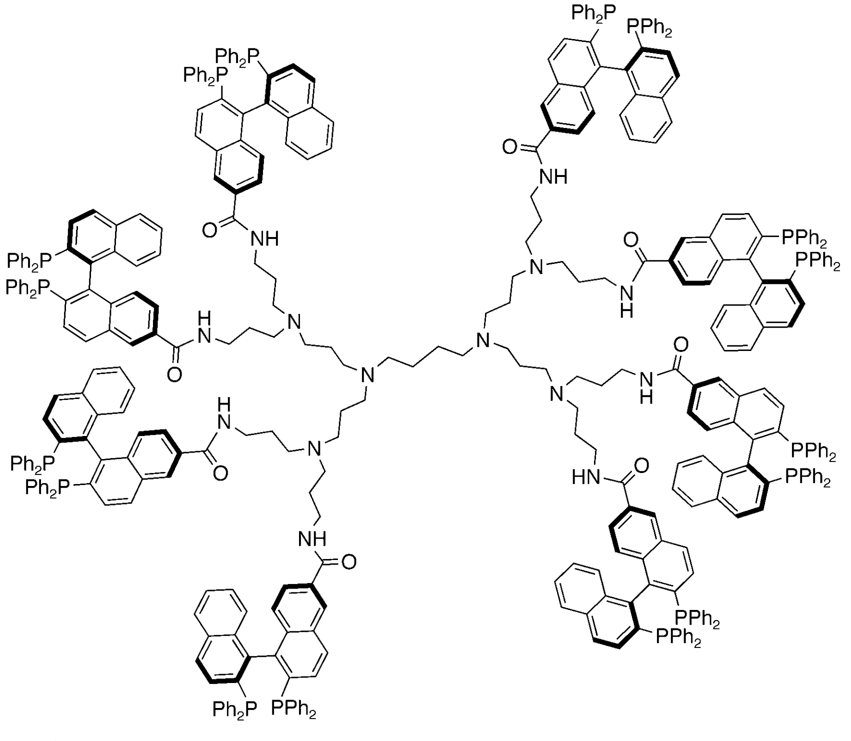


Figure 2. {G2}-DAB-*dendr*-(Carbo-BINAP)$_8$ **7**.

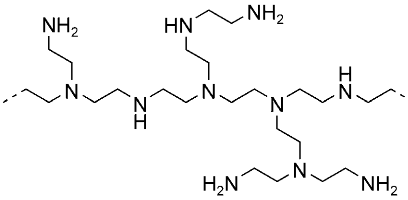
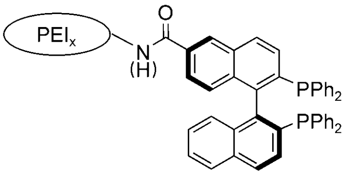


Figure 3. Section of a hyperbranched PEI.

perfect branching of these molecules) there are also secondary amino groups in the hyperbranched PEIs that result from incomplete conversion at some branching points in their one-step synthesis. It was therefore important to functionalise both primary and secondary amino groups in the PEIs because free NH functionalities were thought to act as potential (undesired) ligands in the catalyst assembly. The coupling reagents used for dendrimer functionalisation HOBT and EDC were found to be appropriate for both types of amino functionalities. Using a greater excess of ligand (1.3 equiv. of HO-Carbo-BINAP or HO-Glutaroyl-AMINAP, respectively, per primary and secondary amino group) we were able to synthesise the Carbo-BINAP (**11**–**13**) and Glutaroyl-AMINAP (**14**–**16**) functionalised hyperbranched PEIs depicted in Figure 4.

The degree of functionalisation of these new BINAP-functionalised hyperbranched poly(ethylene imines) was calculated from the elemental analyses obtained for these materials. The results are listed in Table 2, along with the average number of attached BINAP ligands.

According to the elemental analysis, $PEI_{0.8}$ and PEI_2 were functionalised with both BINAP derivatives almost quantitatively. Using the highly polymeric PEI_{25} as support, a degree of functionalisation of 91% has been achieved in both cases yielding catalysts bearing on average 138 BINAPs per molecule!



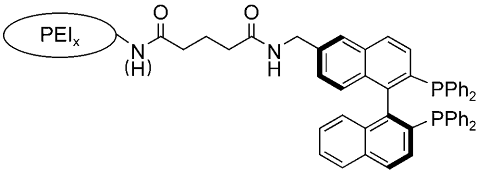


Figure 4. Carbo-BINAP (*top*) and Glutaroyl-AMINAP (*bottom*) functionalised hyperbranched PEIs (x = 0.8, 2, 25).

Table 2. Degree of functionalisation (DF) of the BINAP functionalised PEIs **11**–**16**, along with the number of attached ligands.

	DF [%]	BINAP
$PEI_{0.8}$-(Carbo-BINAP) **11**	100	9
PEI_2-(Carbo-BINAP) **12**	100	26
PEI_{25}-(Carbo-BINAP) **13**	91	138
$PEI_{0.8}$-(Glutaroyl-AMINAP) **14**	100	9
PEI_2-(Glutaroyl-AMINAP) **15**	96	25
PEI_{25}-(Glutaroyl-AMINAP) **16**	91	138

In Figure 5 the ^{1}H NMR spectra of {G2}-DAB-*dendr*-(Carbo-BINAP)$_8$ **7** and $PEI_{0.8}$-(Carbo-BINAP) **11** are depicted for comparison. Both molecules are comparable in size and number of fixed ligands (**7**: 5963 g mol^{-1}, 8 ligands; **11**: 6400 g mol^{-1}, 9 ligands). Nevertheless the resolution of the spectrum corresponding to the hyperbranched system is much lower than that of the regular dendrimer. This is a result of the polydispersity of the hyperbranched support and the irregularity of the structure.

The two spectra depicted in Figure 5 clearly illustrate why it has been proven advantageous in a first step to develop an immobilisation strategy using regularly structured monodisperse dendrimers as supports. These allow a facile characterisation by NMR and mass spectrometry and therefore the determination of "optimal" reaction conditions and work-up procedures for an essentially complete functionalisation and a complete removal of excess ligand as well as coupling regents.

The Enantioselective Cu-Catalysed Hydrosilylation of Acetophenone

In order to investigate the catalytic properties of the new immobilised BINAP ligands and to compare them with those of the dendritic AMINAP ligands published previously,[16] the copper-catalysed hydosilylation of acetophenone was chosen as a test reaction employing the reaction conditions optimised previously (Scheme 5).

In a first run, the mononuclear reference ligands **1**–**4** were tested. After 24 h reaction time all (isolated) yields were excellent (>95%) and the observed enantioselectivities were between 94 and 95% *ee*. This indicates that the different protecting groups do not induce different torsion angles in the copper complexes. Additionally, the nature of the functional group in the 6-position of the ligand backbone does not change the electronic properties of the ligand since these results are similar to those observed using Benzoyl-AMINAP as stereodirecting ligand (95% yield, 94% *ee*). Bis-BINAP **5** was also used as ligand

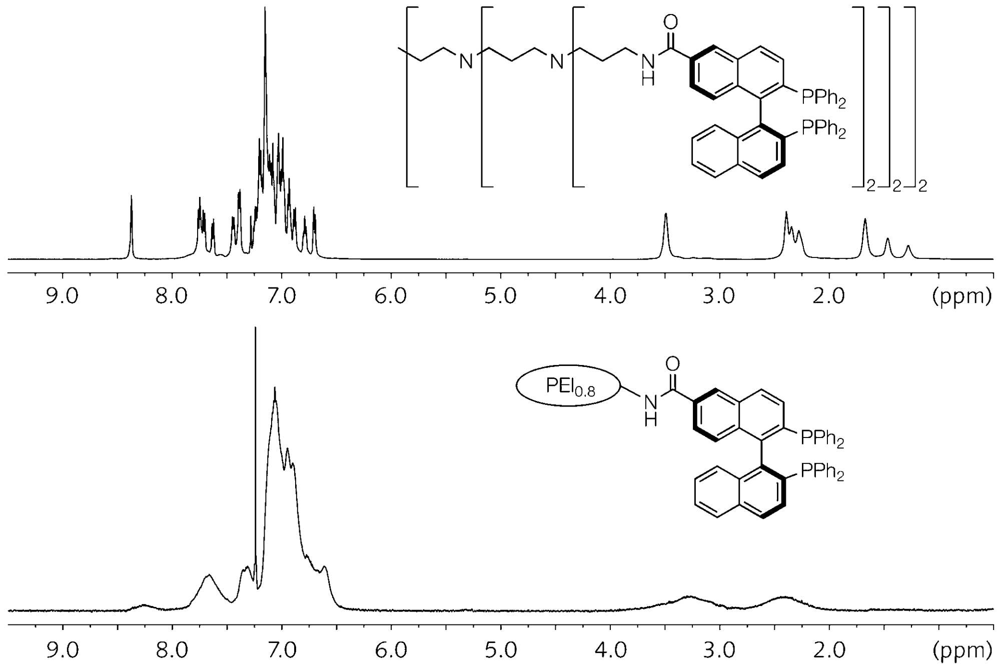
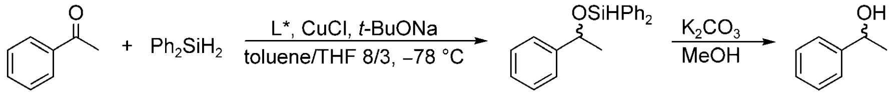


Figure 5. ^{1}H NMR spectra (600 MHz) of {G2}-DAB-*dendr*-(Carbo-BINAP)$_8$ **7** and PEI$_{0.8}$-(Carbo-BINAP) **11**.



Scheme 5. Copper-catalysed hydrosilylation of acetophenone.

in the hydrosilylation of acetophenone giving rise to a yield of 98% at 93% *ee*. This demonstrates that even the attachment of a very large "protecting group" (a second BINAP ligand) does not lead to a change of the biaryl conformation in the ligand backbone and thus the stereoinduction of the system is not influenced.

These initial tests were followed by an investigation of the catalytic properties of the dendritic Carbo-BINAP ligands **6–10**. The results of this study are shown in Figure 6.

In contrast to the results obtained for the dendritic AMINAP copper catalysts (incorporating glutarate linking units!), for which the enantioselectivities and activities remained almost unchanged in the immobilisation and were found to be independent of the dendrimer generation,[16] a considerable variation of stereoinduction was observed for **6–10**. Whereas the first generation system catalysed the reaction with a selectivity of only 34% *ee*, the fifth generation dendrimer reached 90% *ee*. On the other hand, the reaction time required for complete conversion increased from 24 h to 96 h upon going from the mononuclear catalysts to the lower generation dendritic catalysts whilst decreasing again for the higher generation dendrimers.

In order to further investigate this behaviour the catalytic hydrosilylations were performed using only 0.5 equivalents of CuCl per diphosphine unit. The enantioselectivities obtained under these reaction conditions are summarised in Figure 7.

To account for this increase in selectivity of all dendritic Carbo-BINAP ligands **6–10** when using only half an equivalent of copper to values (that are similar to those achieved when using the mononuclear reference ligands as well as the dendritic AMINAP ligands), we propose a partial dismutation and the formation of copper(I) complexes ligated by two BINAP ligands when one equivalent of copper is used. This dismutation appears to be favoured in the small dendritic Carbo-BINAP derivatives. The [Cu(BINAP*)$_2$]$^+$ species (BINAP* = immobilised BINAP) formed in the process are probably catalytically inactive. This explains the reduced activity of the dendrimers compared with the catalytic reference systems with the monotopic BINAP ligands. Upon formation of the [Cu(BINAP*)$_2$]$^+$ complexes, Cu(I) is released and acts as competing achiral catalyst for this reaction, leading to an overall reduction of the stereoselectivity observed for the smaller dendrimer generations. The formation of the homoleptic copper complexes seems to be suppressed with increasing size of the dendrimer

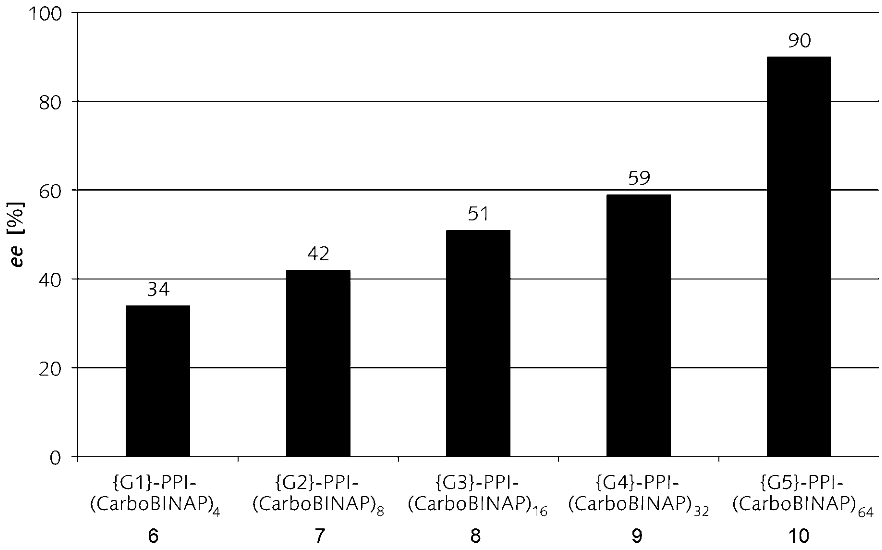


Figure 6. Enantioselectivity of the asymmetric hydrosilylation of acetophenone for the different dendrimer generations (**6**–**10**).

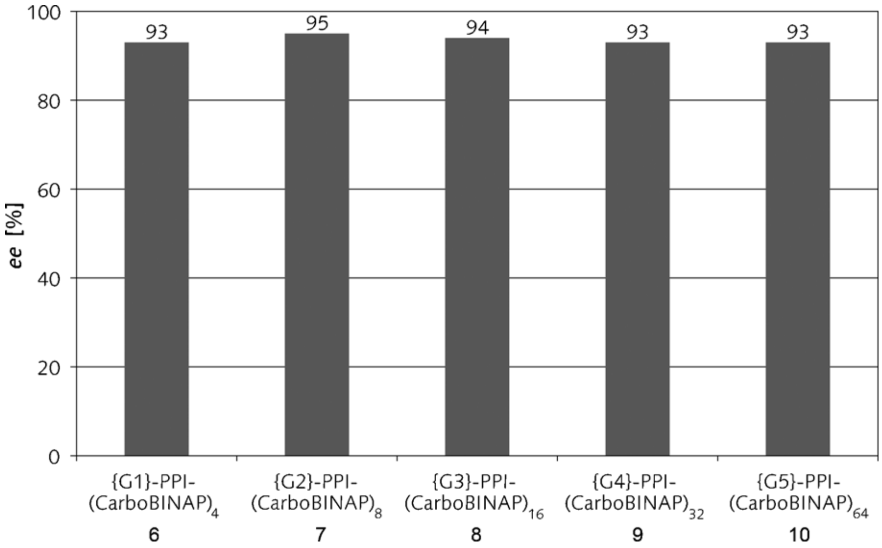


Figure 7. Enantioselectivity of the asymmetric hydrosilylation of acetophenone for the different dendrimer generations (**6**–**10**) using only 0.5 equiv. CuCl per diphosphine unit.

due to the increasing density of ligands in the dendrimer periphery. The conformation of the ligating units required for the complex dismutation does not seem to be favourable under these conditions. This would explain the high level of stereoinduction and activity of the fifth generation Carbo-BINAP ligand **10** even if one equivalent of CuCl is used. All BINAP-copper(I) complexes (mononuclear or dendritic) proved to be substitutionally highly labile which has precluded the direct observation of the proposed redistribution equilibria. The ^{31}P NMR spectra of all metallated phosphines only displayed broad dynamic spectral features at temperatures between 0 and −80 °C. Catalyst **10** was shown to be recyclable by simple precipitation of the catalyst and then reused in three successive catalytic runs without loss of activity (TOFs at 50% conversion of $4.7 \pm 0.3\ \mathrm{h}^{-1}$) or enantioselectivity.

In a next step, the catalysts immobilised on the hyperbrached PEIs were investigated. Table 3 summarises the enantioselectivities induced by the hyperbranched Carbo-BINAP **11**–**13** and AMINAP ligands **14**–**16** for the Cu-catalysed hydrosilylation of acetophenone as reference reaction.

For the Carbo-BINAP ligands attached to the hyperbranched poly(ethylene imines) **11**–**13** uniform high enantioselectivities of 93–94% *ee* and good activities were observed in contrast to the dendritic Carbo-BINAP systems **6**–**10** discussed above. This illustrates

Table 3. Enantioselectivity of the asymmetric hydrosilylation of acetophenone for the different hyperbranched Carbo-BINAP **11–13** and AMINAP ligands **14–16**. For **13** and **16** the results of several runs involving the recycling of the catalysts are given.

Ligand	Run	Yield [%]	*ee* [%]
$PEI_{0.8}$-(Carbo-BINAP) **11**	–	96	94
PEI_2-(Carbo-BINAP) **12**	–	97	93
PEI_{25}-(Carbo-BINAP) **13**	1	100	93
PEI_{25}-(Carbo-BINAP) **13**	2	100	93
PEI_{25}-(Carbo-BINAP) **13**	3	99	93
$PEI_{0.8}$-(Glutaroyl-AMINAP) **14**	–	98	92
PEI_2-(Glutaroyl-AMINAP) **15**	–	98	93
PEI_{25}-(Glutaroyl-AMINAP) **16**	1	95	93
PEI_{25}-(Glutaroyl-AMINAP) **16**	2	95	92
PEI_{25}-(Glutaroyl-AMINAP) **16**	3	94	92

the limits of the use of dendrimer catalysts as model systems for the less regularly structured hyperbranched PEI derivatives. In fact the less densely structured hyperbranched systems **11–13** display the "ideal" behaviour of the mononuclear reference ligands **1–4** not attainable with the dendrimers under standard reaction conditions (1 equivalent of Cu). We note that both PEI_{25}-(Carbo-BINAP) (**13**) and PEI_{25}(Glutaroyl-AMINAP) (**16**) could be precipitated and recycled without loss of activity and selectivity (Table 3).

The use of the hyperbranched AMINAP ligands **14–16** also led to high enantioselectivities of 92–93% *ee*, that are in this case comparable to the results obtained when using the AMINAP-PPI dendrimers as catalysts. This means that employing glutarate as a linking unit neutralises the effects discussed above, and renders the functionalised dendrimers and hyperbranched polymers very similar in their behaviour in enantioselective catalysis.

Conclusions

In summary, a series of immobilised Carbo-BINAP ligands has been synthesised using PPI dendrimers as soluble supports. They contain up to 64 BINAP ligands at their periphery without an additional linking unit. Despite the high steric requirements of the ligand, all dendrimers could be completely functionalised (within the accuracy of the analytical methods) giving the immobilised systems in good yields.

Furthermore, the immobilisation strategy worked out for the fixation of AMINAP ligands with additional linking units as well as of Carbo-BINAP ligands without an additional linking unit on dendrimers has been extended to less regularly built hyperbranched poly(ethylene imines) as soluble supports. In this way, it has been possible to attach (on average) 9, 26, and 138 Glutaroyl-AMINAP or Carbo-BINAP ligands onto PEIs of different molecular weights.

The catalytic properties of these systems in the copper-catalysed hydrosilylation of acetophenone were investigated. The dendritic PPI-bound Carbo-BINAP ligands showed a strong dependence of enantioselectivity and activity on the generation of the dendrimer. The Carbo-BINAP and Glutaroyl-AMINAP ligands immobilised on the hyperbranched polymers, however, displayed activities and enantioselectivities comparable to those of the mononuclear catalysts. The highest generation dendrimers containing the immobilised BINAP ligands could be recycled and re-used several times without any observable loss of activity or selectivity.

Extending the use of these new dendrimer catalysts and those based on hyperbranched polymers to other catalytic reactions is the objective of current and future research in our laboratory.

Experimental Section

The 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 Protected Carbo-BINAP ligands (1–4) and Bis-BINAP (5)

A mixture of (*R*)-6-hydroxycarbonyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (HO-Carbo-BINAP, 1.0 equiv.), EDC·HCl (1.1 equiv.), 1-HOBT (1.5 equiv.) and triethylamine (1.7 equiv.) was stirred in DMF at 0 °C for 40 min. To this suspension was added the respective primary amine dissolved in DMF. The resulting solution was warmed to room temperature and stirred for 48 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 protected Carbo-BINAP ligands as pale yellow powders. Crystals suitable for X-ray analysis of **1**, **2** and **3** were obtained by recrystallisation from toluene.

General Procedure for the Synthesis of the Dendritic Carbo-BINAP ligands (6–10)

A mixture of (*R*)-6-hydroxycarbonyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (HO-Carbo-BINAP, 1.10 equiv.), EDC·HCl (1.21 equiv.), 1-HOBT (1.65 equiv.) and triethylamine (1.85 equiv.) was stirred in DMF at 0 °C for 40 min. To this suspension was added the respective amino-terminated poly(propylene imine) (PPI) dendrimer dissolved in DMF. The resulting solution was warmed to room temperature and stirred for 48 to 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 Carbo-BINAP-functionalised dendrimers as off-white powders.

General Procedure for the Sythesis of the Hyperbranched Carbo-BINAP (11–13) and AMINAP Ligands (14–16)

A mixture of (*R*)-6-hydroxycarbonyl-2,2′-bis(diphenyl-phosphino)-1,1′-binaphthyl (HO-Carbo-BINAP, 1.30 equiv.) or Glutaroyl-AMINAP (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 48 to 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 in vacuo yielding the Carbo-BINAP- and Glutaroyl-AMINAP-functionalised hyperbranched poly(ethylene imines) as off-white powders.

General Procedure for the Hydrosilylation Experiments

The appropriate amount of the dendritic ligand corresponding to 0.03 mmol of diphosphine, 3.0 mg (0.03 mmol) of CuCl and 2.9 mg (0.03 mmol) of *t*-BuONa were dissolved in 2 mL of toluene/THF 8/3 and the resulting mixture was stirred for 30 min at room temperature. Diphenylsilane (210 μL, 1.1 mmol) was then added and the solution cooled to −78 °C. After addition of 117 μL (1.0 mmol) of acetophenone dissolved in 1 mL toluene/THF 8/3, the reaction mixture was stirred for 24 h at this temperature. A solution of K_2CO_3 (3 mL, 1% in methanol) was added to hydrolyse the reaction mixture, then the solvent was removed under vacuum and the residue purified by column chromatography on silica (pentane/diethylether 85/15). Enantioselectivities were determined by GC (Chiraldex β-PM (50 m×0.25 mm); 40 °C, 5 °C min^{-1} to 120 °C, 14 min; t_R [(*R*)-*sec*-phenylethyl alcohol] = 25.59 min, t_R [(*S*)-*sec*-phenylethyl alcohol] = 26.34 min.). For the recycling experiments the catalyst was precipitated at the end of the reaction by addition of diethyl ether and separated by centrifugation. The centrifugate was subsequently hydrolysed as described above and purified. The recycled catalyst was dried under vacuum. Then new solvent and silane were added, the mixture was cooled to −78 °C and the reaction was started again by addition of acetophenone.

X-Ray Crystal Structure Analyses

Crystallographic data for **1**: $C_{46}H_{35}NOP_2{\cdot}C_7H_8$, $M=771.82$, $a=13.6287(13)$, $b=9.8366(9)$, $c=15.7939(14)$ Å, $\beta=99.697(2)°$, $V=2087.1(3)$ Å^3, $Z=2$, space group $P2_1$, $D_{calcd}=1.228$ Mg·m^{-3}, m = 0.145 mm^{-1}. Reflections measd.: 34484, indep.: 7364 [$R_{int}=0.0552$], obsvd. [$I>2\,s(I)$]: 6253. $R(F)$ [$F_o>4\,s(F_o)$] = 0.0332, $wR(F^2)$ [all unique data] = 0.0720, Flack $x=0.02(6)$.

Crystallographic data for **2**: $C_{48}H_{39}NOP_2{\cdot}C_7H_8$, $M=799.88$, $a=13.289(2)$, $b=9.7042(15)$, $c=16.908(3)$ Å, $\beta=94.496(3)°$, $V=2173.7(6)$ Å^3, $Z=2$, space group $P2_1$, $D_{calcd}=1.222$ Mg·m^{-3}, m = 0.141 mm^{-1}. Reflections measd.: 55703, indep.: 14586 [$R_{int}=0.0416$], obsvd. [$I>2\,s(I)$]: 12567. $R(F)$ [$F_o>4\,s(F_o)$] = 0.0448, $wR(F^2)$ [all unique data] = 0.1127, Flack $x=-0.07(8)$.

Crystallographic data for **3**: $C_{49}H_{41}NOP_2{\cdot}C_7H_8$, $M=813.90$, $a=13.1004(14)$, $b=10.1545(11)$, $c=16.7341(18)$ Å, $\beta=95.595(2)°$, $V=2215.5(4)$ Å^3, $Z=2$, space group $P2_1$, $D_{calcd}=1.220$ Mg·m^{-3}, m = 0.140 mm$^{-1.}$ Reflections measd.: 44422, indep.: 2430 [$R_{int}=0.0929$], obsvd. [$I>2\,s(I)$]: 1979. $R(F)$ [$F_o>4\,s(F_o)$] = 0.0467, $wR(F^2)$ [all unique data] = 0.1209, Flack $x=0.00(6)$.

Intensity data were collected at 100 K (Bruker AXS Smart 1000 CCD diffractometer, Mo-K_a radiation, graphite monochromator, 1 = 0.71073 Å) and corrected for Lorentz, polarisation and absorption effects (semiempirical, SADABS).[25] Structure solution: direct methods.[26,27] Refinement: full-matrix least squares methods based on F^2;[27,28] all non-hydrogen atoms anisotropic. Adp and/or distance similarity restraints were applied to the solvent of crystallisation (toluene) in some cases. Hydrogen atoms (except those of the methyl groups and some of the toluene solvent) were located and refined.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC 710932 (**1**), 710933 (**2**) and 710934 (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Phone: +44 1223 336408, Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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