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Synthesis of Peripherally Functionalised Dendritic Binaphthyl (BINAP)-Systems and their Application as Ligands in the Copper-Catalysed Hydrosilylation of Acetophenone

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Dedicated to Professor Andreas Pfaltz on the occasion of his 60th birthday.

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: Two series of peripherally functionalised dendrimers were synthesised based on poly(ethyleneimine) and poly(amidoamine) (PAMAM) dendrimers by reaction of (*R*)-6-*N*-[(γ-carboxyl)butanoyl]-aminomethyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ("Glutaroyl-Aminap") with first to fifth generation PPI and zeroth to fourth generation PAMAM dendrimers using ethyl-*N*,*N*-dimethylcarbodiimide (EDC)/1-hydroxybenzotriazole as coupling reagents. All dendritic ligands were characterised by NMR spectroscopy, elemental analysis and, for generations G0–G3, MALDI-TOF mass spectrometry. The relationship between the size/generation of the dendritic ligands and their catalytic properties was established in the asymmetric hydrosilylation of acetophenone. It could be shown that (*R*)-6-aminomethyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ("H-Aminap") can be attached to the dendrimers without any significant loss of catalytic selectivity compared to the monomeric ligand Benzoyl-Aminap. The selectivities observed in these reactions were higher than those obtained using unfunctionalised BINAP as ligand.

Keywords: asymmetric catalysis; BINAP; copper; dendrimers; hydrosilylation; immobilisation

Introduction

In the assessment of multi-site macromolecular catalysts, such as dendrimer catalysts,[1,2] it is essential to establish whether the immobilised catalyst units retain their identity and are not altered by the nature of the dendrimer backbone. The linker and spacer units employed in the fixation of the catalysts may be crucial in this respect as well as the functional groups present in the dendrimer. Regarding the dendrimer core structure itself, the length and conformational rigidity of the branches and spacers are important factors when evaluating a dendritic catalyst.[3] For immobilised asymmetric catalysts, even subtle conformational changes may significantly influence their stereoselectivity. The interplay of all these factors will generally determine detrimental or beneficial dendrimer effects on catalyst performance.[4]

Here we report the immobilisation of the chiral diphosphine BINAP at the periphery of a series of poly(propyleneimine) (PPI) and poly(amidoamine) (PAMAM) dendrimers in order to employ these polyfunctional phosphines in the Cu(I)-catalysed hydrosilylation of acetophenone as reference reaction.[5] Introduced to enantioselective catalysis by Noyori et al. in 1980,[6] the BINAP ligand has found various applications in asymmetric catalysis, resulting the desired chiral products in good to excellent selectivities. Apart from the most popular BINAP-ruthenium and BINAP-rhodium complexes, that catalyse the hydrogenation of olefins and ketones,[7–9] many other transition metal BINAP complexes were discovered to be active as catalysts in miscellaneous chemical transformations.[10,11]

Fan et al. have synthesised a variety of functionalised BINAP ligands bearing dendritic wedges.[12–17] In order to attach the polyaryl ether dendrons to the ligand they introduced amino groups in the 5- or 5,5′-positions. These dendritic ligands have been tested as catalysts in various hydrogenation reactions, showing similar selectivities as the BINAP ligand itself but improved recycling properties.

BINAP-copper(I) complexes have found use as catalysts, *inter alia*, in the conjugate reduction of 2-pyrid-

yl vinyl sulfones, affording the chiral sulfones with yields and enantioselectivities of 90% and higher.[18] A more established reaction is the hydrosilylation of aryl ketones. Using acetophenone as substrate the BINAP ligand was found to give a relatively low enantioselectivity of 75% compared to other diphosphine ligands tested by Lipshutz et al.[19] By variation of the reaction conditions the selectivity could be improved to over 90%.[20] We report the results of dendrimer immobilisation for this reaction in this work.

Results and Discussion

Synthesis and Characterisation of the BINAP Ligand-Linker Unit as well as a BINAP Reference System

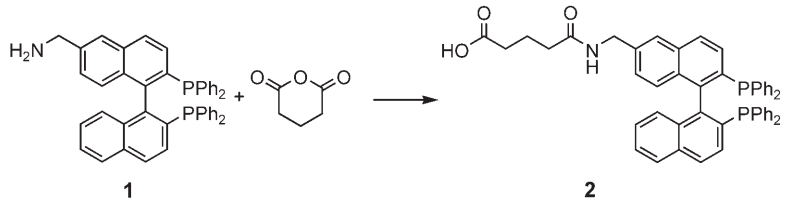
A fixation of the BINAP ligand to the *periphery* of dendrimers has not been reported to date although it is interesting to investigate the catalytic results obtained with the monomeric ligand and compare them with the catalyst performance in the more densely packed "surface" of a dendritic molecular system. The aim was therefore to obtain peripherally functionalised dendritic catalysts based on a functionalised BINAP ligand and to assess the way the catalyst characteristics depend on the dendrimer size and thus the number and density of the reactive centres.

In order to attach BINAP to the peripheral amino end groups of the PPI and PAMAM dendrimers, we decided to introduce a methylenamino function in the 6-position of the binaphthyl backbone of the ligand, a position which was thought to interfere least with the diphosphine binding site of the metal. This was achieved by reduction of the previously reported BINAP derivative (*R*)-6-cyano-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl[21] with $LiAlH_4$, giving (*R*)-6-aminomethyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (H-Aminap) **1** in a yield of 94%. Following the strategy that was developed in our group to synthesise dendritic pyrphos-systems,[22] glutaric acid anhydride was used to attach an appropriate carboxylate linking unit yielding the Glutaroyl-Aminap ligand **2** (Scheme 1).

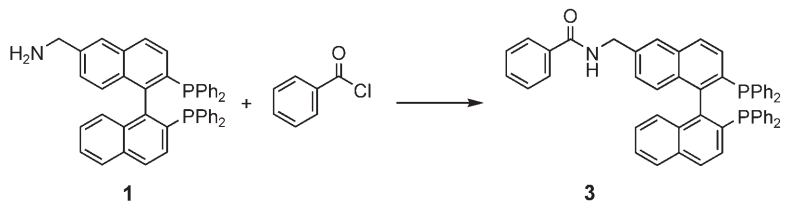
The performance of chiral catalysts containing the BINAP ligand may be dependent on the presence or absence of heterosubstituents in the inaphthyl backbone since they influence the conformational subspace of the ligand skeleton.[23] In order to be able to evaluate the dendrimer catalysts in comparison with an appropriately functionalised mononuclear BINAP-Cu catalyst we synthesised a derivative with similar local steric and electronic properties as **1**, **2** and the functionalised dendrimers. To this end the amino group in H-Aminap **1** was protected by reaction with benzoyl chloride, giving the highly crystalline Benzoyl-Aminap **3** in 75% yield (Scheme 2).

Crystals of **3** suitable for a single crystal X-ray structure analysis were obtained from dichloromethane/methanol. Its molecular structure is depicted in Figure 1 along with the principal bond lengths and angles.

The principal structural features are similar to the crystallographically determined molecular structure of the unfunctionalised BINAP.[24] However, the influence of the substituent in the backbone is manifested in a different torsion angle of the binaphthyl unit. Whereas for BINAP a torsion angle of 87.84° between the two naphthyl fragments is observed, the corresponding angle in **3** is 78.7(4)°. Moreover, a weak (dipole-quadrupole) interaction between the π-system of the protection group and a C–H unit of a phenyl ring bound directly to a P atom is observed [distance(phenyl-centroid)···H = 2.66 Å]. The other



Scheme 1. Synthesis of the Glutaroyl-Aminap **2**.



Scheme 2. Synthesis of the Benzoyl-Aminap **3**.

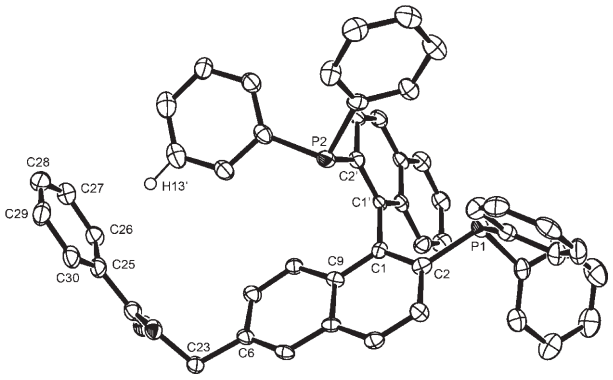


Figure 1. Molecular structure of Benzoyl-Aminap **3**. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(1′) 1.499(5), C(2)–P(1) 1.834(4), C(2′)–P(2) 1.833(4), C(1)–C(2) 1.378(5), C(1′)–C(2′) 1.393(5); C(1)–C(2)–P(1) 118.8(3), C(1′)–C(2′)–P(2) 120.1(3), N–C(23)–C(6) 110.5(3); torsion angle C(2′)–C(1′)–C(1)–C(9) 78.7(4); ring centroid [C(25) C(26) C(27) C(28) C(29) C(30)]···H(13′) 2.66 Å (2.60 Å with CH distance normalised to 1.08 Å).

metric parameters are very similar to those of the parent compound.

Synthesis and Characterisation of the BINAP-Functionalised PPI and PAMAM Dendrimers

The synthesis of the functionalised dendrimers required a quantitative coupling reaction of Glutaroyl-Aminap **2** with the amino end groups of the dendrimer. This was achieved by using ethyl-*N*,*N*-dimethylcarbodiimide (EDC)/1-hydroxybenzotriazole as coupling reagents, a strategy well known in polypeptide synthesis.[25,26] Using this method, Aminap-functionalised PPI and PAMAM dendrimers bearing 4 to 64 diphosphine ligands in their periphery were obtained in good yields (Scheme 3).

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 been also characterised by MALDI-TOF mass spectrometry whilst the higher generations defied an unfragmented transfer into the gas phase.

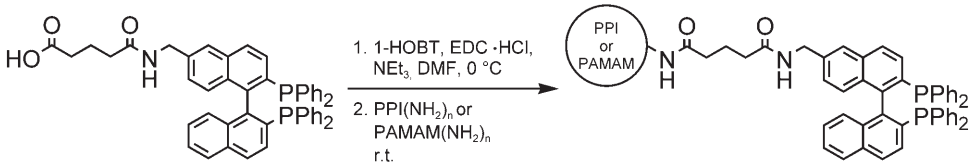
The high topological symmetry of the dendrimers {G1}-PPI-(Glutaroyl-Aminap)$_4$ to {G5}-PPI-(Glutaroyl-Aminap)$_{64}$ and {G0}-PAMAM-(Glutaroyl-Aminap)$_4$ to {G4}-PAMAM-(Glutaroyl-Aminap)$_{64}$, respectively, depicted in Figure 2, is reflected in their NMR spectra, in particular, the ^{13}C NMR spectra of the functionalised PPI dendrimers of the generations 1–5. In all spectra the resonance patterns are virtually superimposible due to the coincidence of the core signals upon going to higher generations. The assignment of the signals in the aromatic region of the spectra as listed in the Experimental Section was achieved with the aid of HMBC and HMQC experiments.

The complete functionalisation of the dendrimers can be assessed with reasonable accuracy by ^{13}C NMR spectroscopy because the signal of the carbon atoms of the (unfunctionalised) CH_2NH_2 groups of the PPI dendrimers at about 40 ppm as well as the signal at around 30 ppm, assigned to the $CH_2CH_2NH_2$ carbon atoms are two characteristic probes. Upon complete functionalisation both disappeared.

Compared to the spectra of the functionalised PPI dendrimers the resolution of the signals in the spectra of the functionalised PAMAM dendrimers is lower as can be easily seen in Figure 3 where the ^{31}P NMR spectra of {G5}-PPI-(Glutaroyl-Aminap)$_{64}$ and {G4}-PAMAM-(Glutaroyl-Aminap)$_{64}$ are shown. Whereas the spectrum of the PAMAM dendrimer shows a broadened resonance at −15.76 ppm, in the ^{31}P NMR spectrum of the PPI dendrimer all signals of the AB system, resulting from the unsymmetrical BINAP-functionalisation, can be detected at −15.63 ppm and −15.73 ppm, with a $^{5}J_{P,P'}$ coupling of 11.2 Hz. This different NMR spectroscopic behaviour is attributed to the differences in internal mobility of the respective molecules and thus relaxation behaviour, the conformationally more flexible PPI giving the sharper signals.

The Enantioselective Cu-Catalysed Hydrosilylation of Acetophenone

In order to assess the relationship between the size/generation as well as the type of the dendritic structure (PPI or PAMAM) and the catalytic properties, the respective functionalised dendrimers, the phosphine functionalised systems were employed as li-



Scheme 3. Coupling of Glutaroyl-Aminap **2** with the amino end groups of the PPI and PAMAM dendrimers.

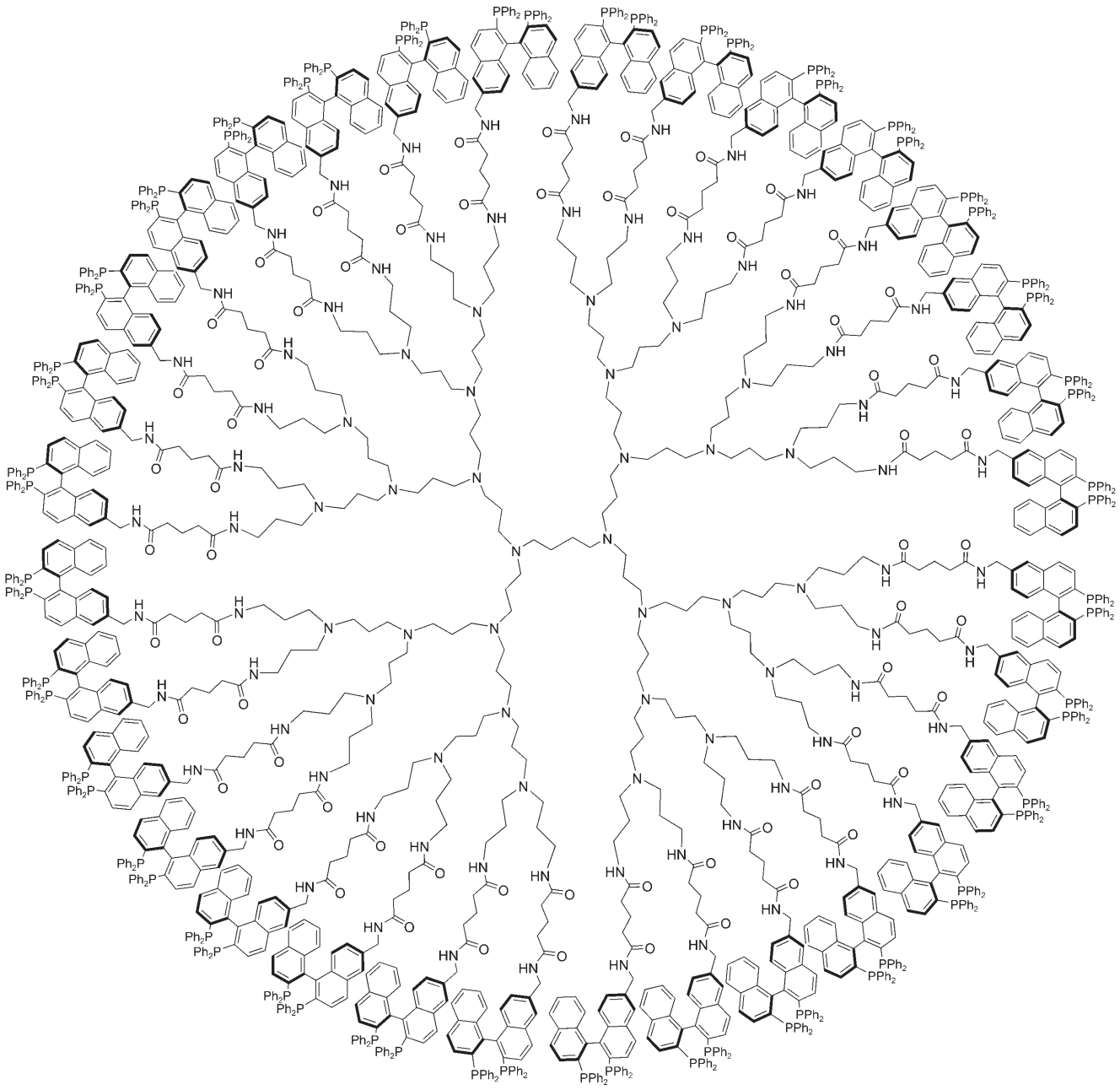
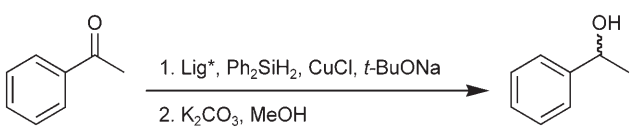


Figure 2. {G4}-PPI-(Glutaroyl-Aminap)$_{32}$ **7**.

gands in the Cu(I)-based asymmetric hydrosilylation of acetophenone (Scheme 4).

The reaction conditions for this reference reaction were optimised using those published by Lipshutz et al.[19] as a starting point. Benzoyl-Aminap **3** was employed as the reference ligand, diphenylsilane was used as a hydrid source and a substrate:catalyst (catalytic site) ratio of 33:1 was chosen in order to allow for short reaction times even at very low temperatures. However, it should be pointed out that the catalyst loading could be reduced below 0.1 mol% leading to turnover numbers of greater than 1000.



Scheme 4. Cu-catalysed hydrosilylation of acetophenone.

A significant increase in selectivity was generally observed on decreasing the reaction temperature, and therefore all subsequent test reactions were carried out at −78 °C. Upon changing the solvent from pure toluene (83% *ee*) to a toluene:THF mixture an im-

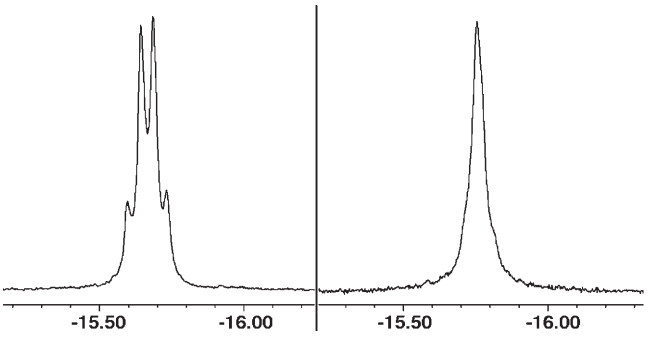


Figure 3. Comparison of the 243 MHz ^{31}P NMR spectra of {G5}-DAB-*dendr*-(Glutaroyl-Aminap)$_{64}$ **8** (*left*) and {G4}-PAMAM-(Glutaroyl-Aminap)$_{64}$ **13** (*right*).

proved selectivity was observed reaching its optimum for a solvent ratio of 8:3 (94% *ee*). However, in contrast to the results obtained under similar reaction conditions by Bellemin–Laponnaz et al.,[20] the selectivity remained unchanged upon variation of the silane from diphenylsilane (*ee* = 94%) to phenylsilane (*ee* = 94%) or phenylmethylsilane (*ee* = 93%). Testing the unfunctionalised BINAP as ligand under these optimised reaction conditions gave a selectivity of 91% *ee* indicating a slight improvement in the enantioselectivity of the hydrosilylation of acetophenone (3% *ee*) due to the functionalisation of the BINAP in the 6-position with an aminomethyl group. In Figure 4 the results of the catalytic tests carried out with the functionalised PPI dendrimers are shown in comparison to the monomeric systems BINAP and Benzoyl-Aminap **3**.

On the whole, it has been found that the selectivity remained almost unchanged by the immobilisation of Aminap, resulting in dendritic ligands that catalyse this reaction with a selectivity of around 93% *ee*, a selectivity which is slightly higher than that of the unfunctionalised BINAP ligand. This absence of a "dendritic" effect indicates that the catalytic conversion is entirely controlled by the first coordination sphere of the copper. This is in part due to the marked coordination preference of Cu(I) for the soft diphosphine compared to the chemically hard functionalities in the dendrimer backbone.

Similar results have been observed using the dendritic PAMAM-ligands as catalysts as it is shown in Figure 5. The lack of influence of the dendrimer structure upon the catalyst performance is another indication that the selectivity of the transformation is due to the shape of the first coordination sphere of the Cu centres.

Conclusions

In summary, two series of immobilised poly(Aminap) ligands have been synthesised, based on PPI and PAMAM dendrimers as backbones. All dendritic ligands were obtained in good yields, resulting in systems containing up to 64 diphosphine ligands at their periphery.

It has been demonstrated that they can be used as ligands in the copper-catalysed hydrosilylation of acetophenone without any loss of selectivity resulting from their immobilisation onto the dendrimer compared to the monomeric ligand Benzoyl-Aminap. Notably, the observed selectivities are even higher than those obtained when using the unfunctionalised BINAP as ligand. This indicates that the Cu(I)-cata-

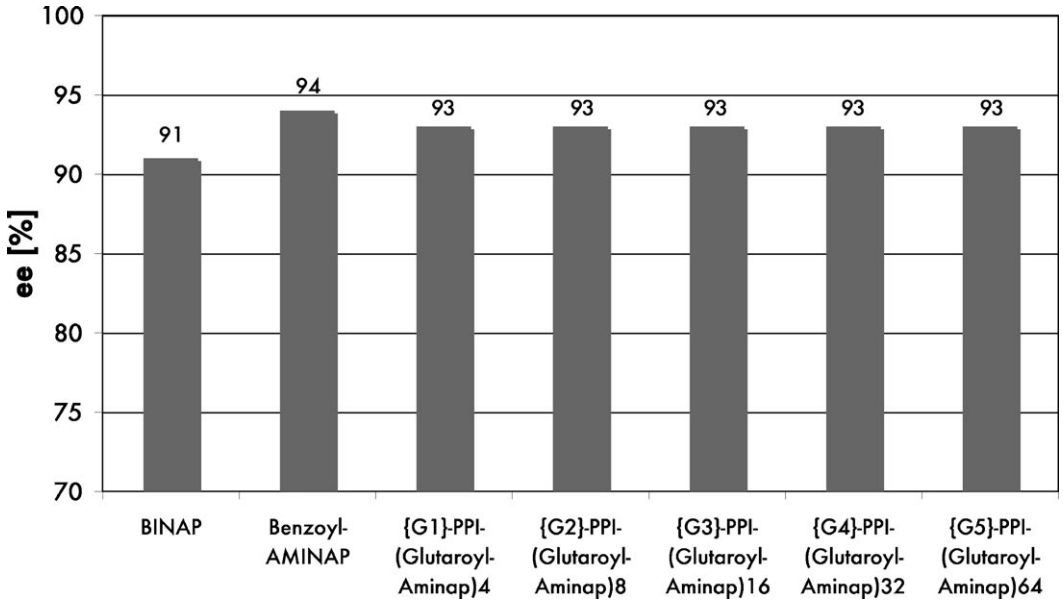


Figure 4. Enantioselectivity of the asymmetric hydrosilylation of acetophenone for the different catalyst generations.

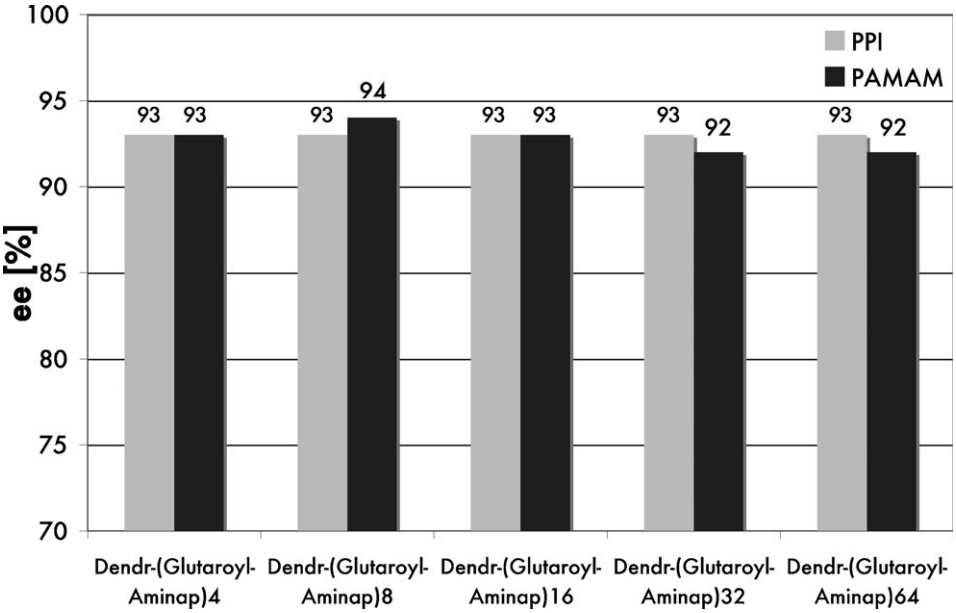


Figure 5. Comparison of the selectivity using functionalised PPI- or PAMAM-dendrimers as ligands.

lysed hydrosilylation of ketones is particularly suited for the development of immobilised catalysts, and we are beginning to turn our attention to cheaper support materials possessing less regular branched structures. Moreover, extending the use of these new dendritic systems as ligands to other catalytic reactions is the objective of current and future research in our laboratory.

As has been emphasised previously, the kinetically controlled stereoselection depends on very small increments of free activation enthalpy. It is therefore an excellent sensitive probe for "dendrimer effects" and will continue to be studied in this fundamental context.[27] As monodispersed macromolecules, chiral dendrimer catalysts provide ideal model systems for less regularly structured but commercially more viable supports such as hyperbranched polymers.[28]

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.

Preparation of (*R*)-6-Aminomethyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (H-Aminap) (1)

(*R*)-6-Cyano-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (2.27 g, 3.50 mmol) was added to a suspension of $LiAlH_4$ (1.01 g, 2.66 mmol) in THF (50 mL) and toluene (100 mL). After stirring for 6 h at 100 °C, the mixture was cooled to 0 °C and hydrolysed by addition of H_2O (3 mL) and KOH solution (1 M, 3 mL). The resulting suspension was filtered and the solvent was removed under vacuum. The residue was disolved in dichloromethane and extracted with brine. The organic phase was dried over $MgSO_4$ and the solvent removed under vacuum to afford **1** as a pale yellow solid. Yield: 2.14 g (94%).

Preparation of (*R*)-6-*N*-[(γ-Carboxyl)butanoyl]-aminomethyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (Glutaroyl-Aminap) (2)

(*R*)-6-Aminomethyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl **1** (1.02 g, 1.57 mmol) and glutaric anhydride (0.20 g, 1.72 mmol) were dissolved in dichloromethane and stirred for 18 h at room temperature. Subsequently, aqueous HCl (1 M, 10 mL) was added. After stirring for 10 min, aqueous KOH (1 M) was added, the aqueous phase removed and the organic layer washed twice more with water (2 × 10 mL). The solvent was removed under vacuum to afford **2** as a pale yellow solid. Yield: 1.12 g (93%).

Preparation of (*R*)-6-*N*-Benzoylaminomethyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (Benzoyl-Aminap) (3)

(*R*)-6-Aminomethyl-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl **1** (1.05 g, 1.61 mmol) was dissolved in pyridine (5 mL) and cooled to 0 °C. Benzoyl chloride (206 μL, 0.25 g, 1.77 mmol) was subsequently added dropwise. After stirring for 2 h at room temperature dichloromethane (5 mL) was added and the solution was extracted with H_2O (1 × 10 mL), aqueous HCl (1 M, 1 × 10 mL), aqueous KOH (1 M, 1 × 10 mL) and then again H_2O (2 × 10 mL). The organic phase was dried over $MgSO_4$ and the solvent removed under vacuum. The residue was recrystallised from dichloromethane/methanol to afford **3** as colourless crystals. Yield: 0.91 g (75%).

General Procedure for the Synthesis of the Functionalised Dendrimers

A mixture of Glutaroyl-Aminap **2** (1.15 equiv.), EDC·HCl (1.27 equiv.), 1-HOBT (1.73 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(-propyleneimine) (PPI) or poly(amidoamine) (PAMAM) 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 white solid was washed several times with *n*-pentane and dried under vacuum yielding the Aminap-functionalised dendrimers as off-white powders. Yields: **4**: 467 mg (79%); **5**: 446 mg (85%); **6**: 442 mg (87%); **7**: 414 mg (81%); **8**: 525 mg (88%); **9**: 437 mg (84%); **10**: 452 mg (82%); **11**: 485 mg (86%); **12**: 501 mg (88%); **13**: 487 mg (84%).

General Procedure for the Hydrosilylation Experiments

The dendritic ligand (0.03 mmol), 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/diethyl ether, 85/15). Enantioselectivities were determined by GC {Chiraldex B-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}.

X-Ray Crystal Structure Analysis of Compound 3

Crystal data: $C_{52}H_{39}NOP_2$, orthorhombic, space group $P2_12_12_1$, a = 9.1301(11), b = 17.959(2), c = 24.074(3) Å, V = 3947.4(8) Å^3, Z = 4, μ = 0.151 mm^{-1}, F_{000} = 1584. Reflections measd.: 65346, indep.: 6966 [R_{int} = 0.129], index ranges $-10 <= h <= 10$, $0 <= k <= 21$, $0 <= l <= 28$, θ range 2.0 to 25°. Intensity data were collected at 100 K with a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å). Data were corrected for Lorentz, polarisation and absorption effects (semiempirical, SADABS, transmission factors: max. 0.7464, min. 0.6510).[29] The structure was solved by direct methods[30] and refined by full-matrix least squares methods based on F^2.[31] All non-hydrogen atoms were given anisotropic displacement parameters. The positions of the hydrogen atoms were taken from difference Fourier syntheses and refined. Final R values [$I > 2\sigma(I)$]: $R(F)$ = 0.0587, $wR(F2)$ = 0.1335, GoF = 0.977, absolute structure parameter 0.02(12). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC 669722. These data can be obtained free of charge http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi? [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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