Construction and Probing of Multisite Chiral Catalysts: Dendrimer Fixation of C_2-Symmetrical Diphosphinerhodium Complexes

Gerald D. Engel and Lutz H. Gade*[a]

Abstract: A series of chiral phosphine-functionalized poly(propyleneimine) (PPI) dendrimers was synthesized by the reaction of carboxyl-linked C_2-chiral pyrphos ligand (pyrphos = 3,4-bis(diphenylphosphino)pyrrolidine) with zeroth – fourth generation PPI using ethyl-*N,N*-dimethylaminopropylcarbodiimide (EDC)/1-hydroxybenzotriazol as a coupling reagent. The dendrimers obtained were characterized by NMR spectroscopy and elemental analysis as well as FAB and MALDI-TOF mass spectrometry, which established their molecular masses of up to 20 700 amu. Metalation of the multi-site phosphines with $[Rh(COD)_2]BF_4$ cleanly yielded the cationic rhodo-dendrimers containing up to 32 metal centers (for the fourth generation species), representing the largest chiral phosphine dendrimer catalyst studied to date. The complete metalation of the chiral phosphine sites was demonstrated by ^{31}P NMR spectroscopy and the observation of the coordination-shifted AB part of the ABX spin system ($\delta_A = 33.9$, $\delta_B = 32.9$; $^1J_{Rh,P} = 150$, 153 Hz; $^2J_{P,P} = 28$ Hz). The relationship between the size/generation of the dendrimer and its catalytic properties was established in the asymmetric hydrogenation of *Z*-methyl-α-acetamidocinammate and dimethyl itaconate. A decrease in both activity and selectivity of the dendrimer catalysts was observed on going to the higher generations.

Keywords: catalysis · dendrimers · hydrogenation · rhodium

Introduction

Since the report of the first example of catalysis with a dendrimer-immobilized transition metal complex (the Kharasch reaction), which was catalyzed by nickel(II) complexes containing NCN-pincer ligands,[1] a number of dendrimer catalysts have been synthesized and studied.[2] In particular, a variety of dendritic chelating phosphine derivatives have attracted much attention.[3] Reetz and co-workers prepared phosphine-functionalized poly(propyleneimine) (PPI) dendrimers and studied the catalytic activity of their Pd, Rh, and Ir complexes. For the Heck-type C–C coupling catalysis with the Pd derivatives they found a greater catalyst stability for the higher generation dendrimers than for the corresponding mononuclear system.[4] The palladium catalysts were also used in allylic substitution reactions performed in a membrane reactor,[5] as well as hydroformylations for the rhodium compounds.[6] The dendrimer systems employed in catalytic reactions include carbosilane dendrimers,[7] the poly(amido-amino) (PAMAM) dendrimers developed by Tomalia and co-workers[8] and the PPI dendrimers mentioned above.[9] In most cases the variation of the catalyst performance as a function of the dendrimer generation was only very small. There are several reports on the use of chiral catalyst systems, most notably amino alcohol-zinc alkyl compounds attached to PPI cores reported by Meijer et al.,[10] the Ti-TADDOL systems studied by Seebach and co-workers as well as the chiral Salen systems reported by Jacobsen et al.[11] The only previous example of asymmetric rhodium-catalyzed hydrogenation of prochiral olefines was reported by Togni et al. who immobilized their chiral ferrocenyl diphospines ("Josiphos") at the end groups of dendrimers, thus obtaining systems of up to 24 chiral metal centers in the periphery.[12] The fact that the catalytic properties of the dendrimer catalysts were almost identical to those of the mononuclear catalysts was interpreted as manifestation of the independence of the individual catalytic sites in the macromolecular systems.

Chiral diphosphines are the most widely and successfully used ligands in the asymmetric catalytic hydrogenation of C=C and C=O double bonds.[13] However, most of the systems which have been routinely employed to this end do not offer a straightforward method of functionalization that allows their attachment to dendrimers. A notable exception is the pyrrolidine derivative "pyrphos" first reported by Nagel and co-workers in the mid 1980s which contains a symmetrically placed nitrogen atom to which linker and spacer units for ligand fixation may be directly attached.[14–16]

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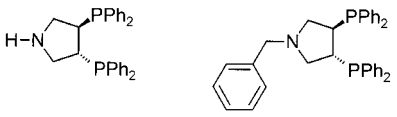


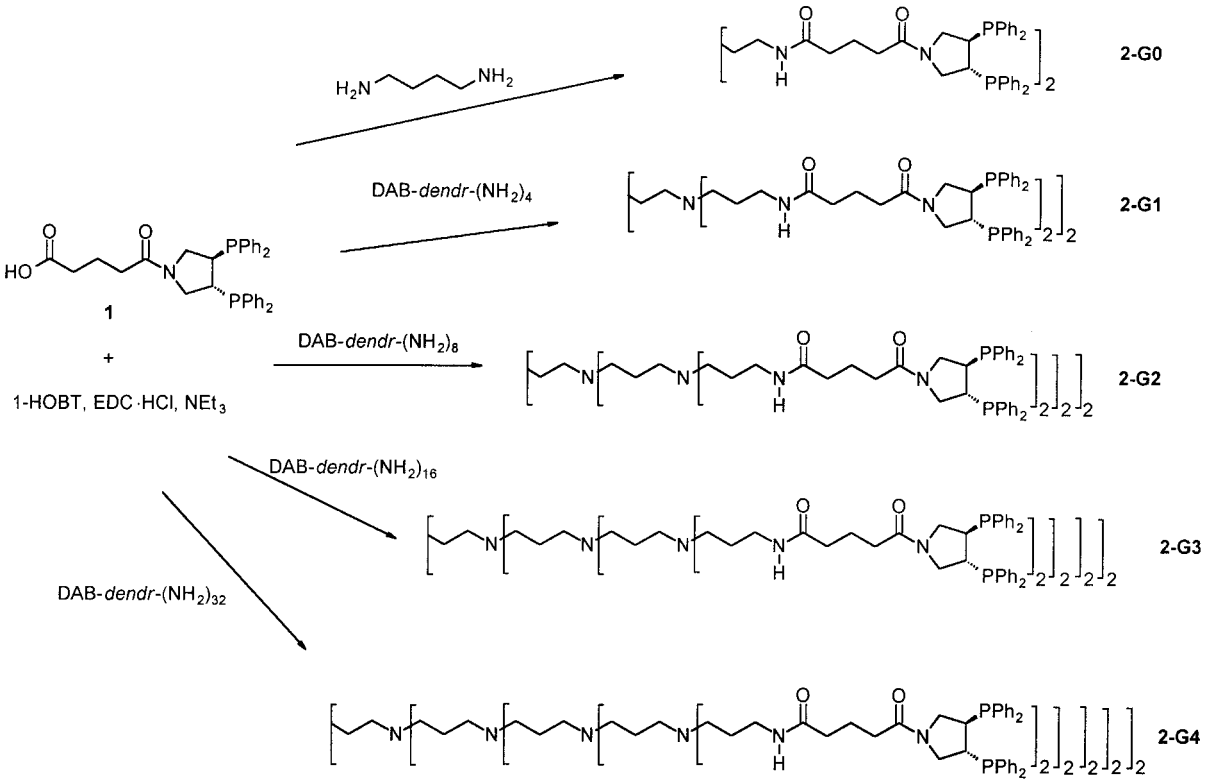
Pyrphos Deguphos

A number of N-functionalized derivatives have been synthesized and studied, including the N-benzyl derivative "deguphos" which is being used in an industrial cationic rhodium hydrogenation catalyst for acetamidocinnamic acid derivatives. Stereoselectivities of greater than 99% *ee* were obtained with these derivatives which have also been immobilized on Merrifield polymers,[17] silica gel,[18] "tentagel",[19] and other support materials.[20] In general, the stereoselectivity of the immobilized systems was similar to those obtained with the mononuclear complexes. A fixation to the core or the periphery of a dendrimer has not been reported to date and it was interesting to compare these results obtained in the surface immobilization of the pyrphosrhodium complexes with the catalyst performance in the more densely packed "surface" of a dendritic molecular system. The aim was to obtain dendrimer catalysts, based on the pyrphos ligand, which possessed molecular uniformity within the accuracy of the analytical and spectroscopic methods available for such systems and to assess the way the catalyst characteristics depend on the dendrimer size and thus the number and density of the reactive centers.

Results and Discussion

Synthesis and characterization of the "pyrphos"-functionalized poly(propyleneimine) dendrimers: The fixation of the pyrphos ligand at the periphery of poly(propyleneimine) dendrimers was achieved by using a strategy based on carbodiimide/1-hydroxybenzotriazol-induced condensation, which was developed in polypeptide synthesis. As a catalyst-linker unit, we chose the coupling product of pyrphos with glutaric anhydride **1** (Scheme 1).[14] The synthesis of the functionalized poly(propyleneimine) (PPI) dendrimers required a quantitative coupling reaction of the compound **1** with the amino end groups of the dendrimer. This was conveniently achieved by a standard method of peptide synthesis,[21] using ethyl-*N*,*N*-dimethylaminopropylcarbodiimide (EDC) which allows extraction into an aqueous solution of the urea formed in the coupling process and thus a facile purification of the dendrimer product. In the same way, an excess of **1**, employed to guarantee the complete functionalization of the PPI dendrimer, could be completely separated by extraction of the crude product with a basic aqueous solution.

As is shown in Scheme 1, the modified pyrphos ligand **1** could thus be coupled with the series of PPI dendrimers from generations 0–4 giving the respective phosphine dendrimers **2-G0**–**2-G4** in excellent purity and yield. All compounds were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis and, most significantly, FAB or MALDI TOF mass spectrometry. The high topological symmetry of the dendrimers **2-G0**–**2-G4** is reflected in their ^{1}H NMR spectra in which the resonance patterns are almost identical due to the coincidence of the core signals upon going to higher generations (Figure 1).



Scheme 1. Coupling of the chiral phosphine carboxylate **1** with the amino end groups of the poly(propyleneimine) dendrimers of generations 0–4 (DAB=1,4-diaminobutane).

0947-6539/02/0818-4320 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 18

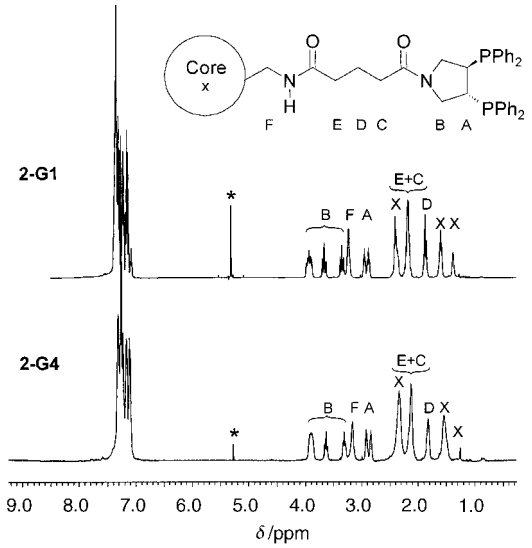


Figure 1. Comparison of the 500 MHz ^{1}H NMR spectra of **2-G0** and **2-G4** demonstrating the similarity in the resonance patterns (* = CH_2Cl_2).

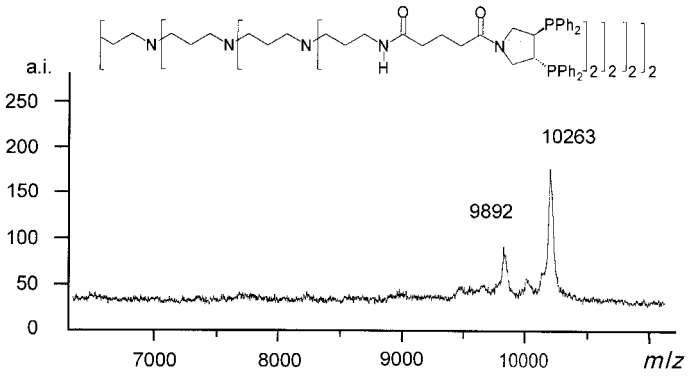


Figure 2. MALDI-TOF mass spectrum of the third-generation phosphine-functionalized dendrimer **2-G3**.

The chemical shift of the signal attributed to the amido-NH protons in the fourth generation dendrimer **2-G4** was determined in a ^{1}H COSY experiment and found to be $\delta =$ 7.42. This resonance signal is thus shifted to lower field by 0.85 ppm with respect to **2-G0** and by 0.36 ppm relative to **2-G1**. This effect may be related to the increasing tendency of these protons to engage in hydrogen bonding between NH and C=O groups upon going to the higher generation dendrimers.

The complete functionalization of the NH_2 end groups in the whole series of dendrimers may be deduced from the ^{13}C NMR spectra (within the accuracy of the chosen method), which display the relatively simple resonance patterns that are characteristic for symmetrically functionalized species. The accidental coincidences of some of the resonance signals in the derivatives of the higher generations have been previously observed in substituted PPI dendrimers.[22] The carbon nuclei adjacent to the amino-N atoms are characteristically broadened due to quadrupolar relaxation of the ^{14}N nuclei. After the phosphine fixation, the resonance signals at around $\delta =$ 40 ppm which are assigned to the CH_2NH_2 end groups in the dendrimer starting materials have completely disappeared, likewise those of the $CH_2CH_2NH_2$ carbon nuclei at $\delta =$ 30 ppm. Instead the corresponding resonances attributable to the $CH_2NHC{=}O$ and $CH_2CH_2NHC{=}O$ nuclei are observed at $\delta = 37.7 - 38.2$ ppm and $\delta = 26.9$ ppm, respectively, in accordance with previous observations for functionalized PPI dendrimers.[4] The ^{13}C NMR studies have also shown that the excess of the phosphine carboxylic acid **1** (with its characteristic carboxyl resonance at $\delta = 177.5$ ppm) employed in the synthesis of the dendrimers **2-G0**–**2-G4** was completely extracted upon washing the crude reaction products with a basic aqueous solution.

The most conclusive method for the characterization of dendrimers remains mass spectrometry. While the molecular ions of **2-G0** and **2-G1** were detected by FAB mass spectrometry, the higher generation dendrimer phosphines were characterized by MALDI TOF spectrometry. This method also allowed assessment of the sample purity along with detection of the molecular ion peaks and characteristic fragment peaks. The MALDI TOF spectrum of the third-generation dendrimer **2-G3** is displayed in Figure 2.

The molecular ion peak at 10263 amu is clearly visible along with the fragment peaks at 10077 amu $[M - PPh_2]^+$ and 9892 amu $[M - 2PPh_2]^+$. There is no indication of incomplete functionalization of the PPI dendrimer which would lead to peaks lying at $n \times 500$ amu (the molecular mass of the phosphine carboxylate **1**) below the molecular ion peak. It also proved possible to detect the molecular ion of the fourth-generation phosphine dendrimer **2-G4** at about 20640 amu, which is close to the the limit accessible by the MALDI-TOF technique. The mass values for the molecular ion peaks of the whole series of dendrimer phosphines are listed in Table 1 along with the theoretical values for the most abundant isotopomers.

Table 1.

Compound (most abundant isotopomer)	Found (m/z)	Theoretical value
2-G0	1159	1158
2-G1	2459	2457
2-G2	5059	5054
2-G3	10263	10249
2-G4	20632	20637

Synthesis of the multisite cationic pyrphos-rhodium metallodendrimers: The pyrphos-functionalized dendrimers **2-G0**–**2-G4** were treated with exactly one equivalent of $[Rh(cod)_2]BF_4$ (cod = 1,5-cyclooctadiene) per diphosphine unit at ambient temperature in CH_2Cl_2. The metalation was complete within seconds, as was evident from the change of color from dark red to orange-yellow, and established by monitoring the conversion by ^{31}P NMR spectroscopy (Scheme 2). The corresponding rhododendrimers **3-G0**–**3-G4** were isolated as orange-yellow powders which are very soluble in CH_2Cl_2, less so in methanol and practically insoluble in diethyl ether and *n*-pentane. As was found for the mononuclear cationic rhodium complexes,[14, 15, 23] the metallodendrimers are stable towards air and moisture.

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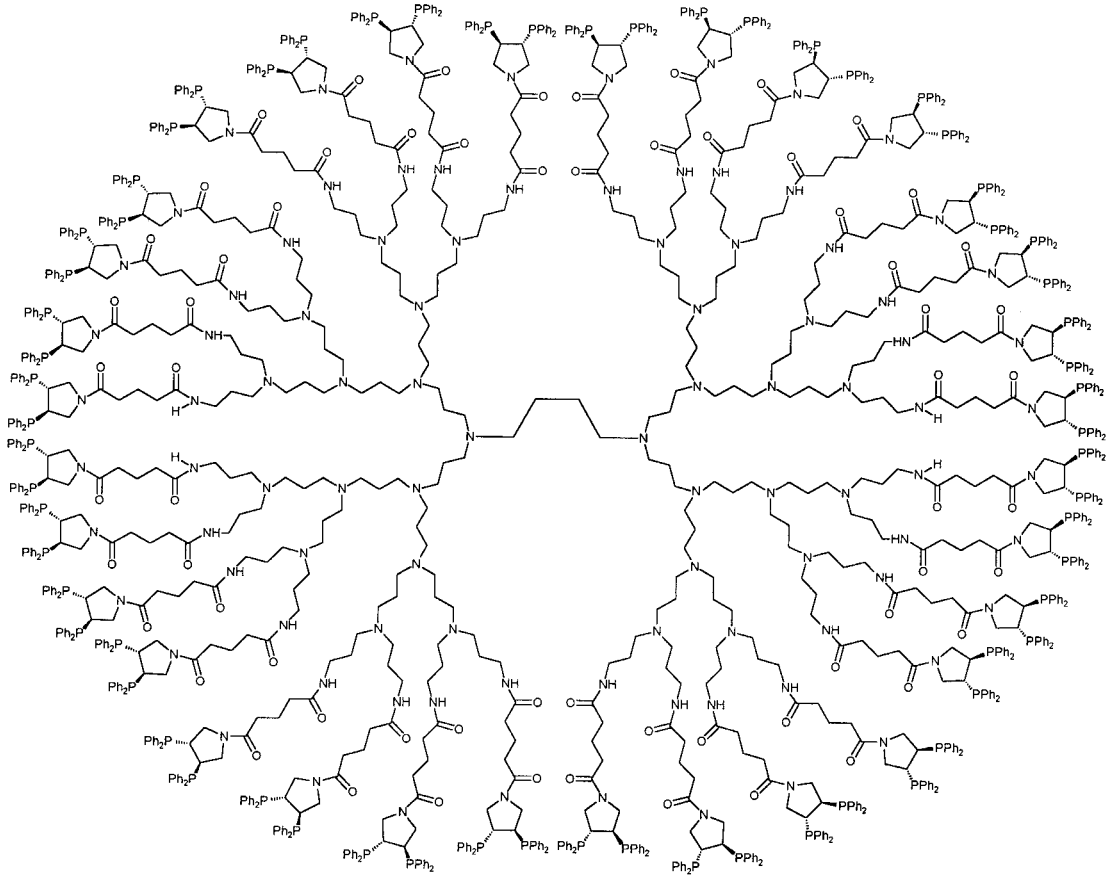
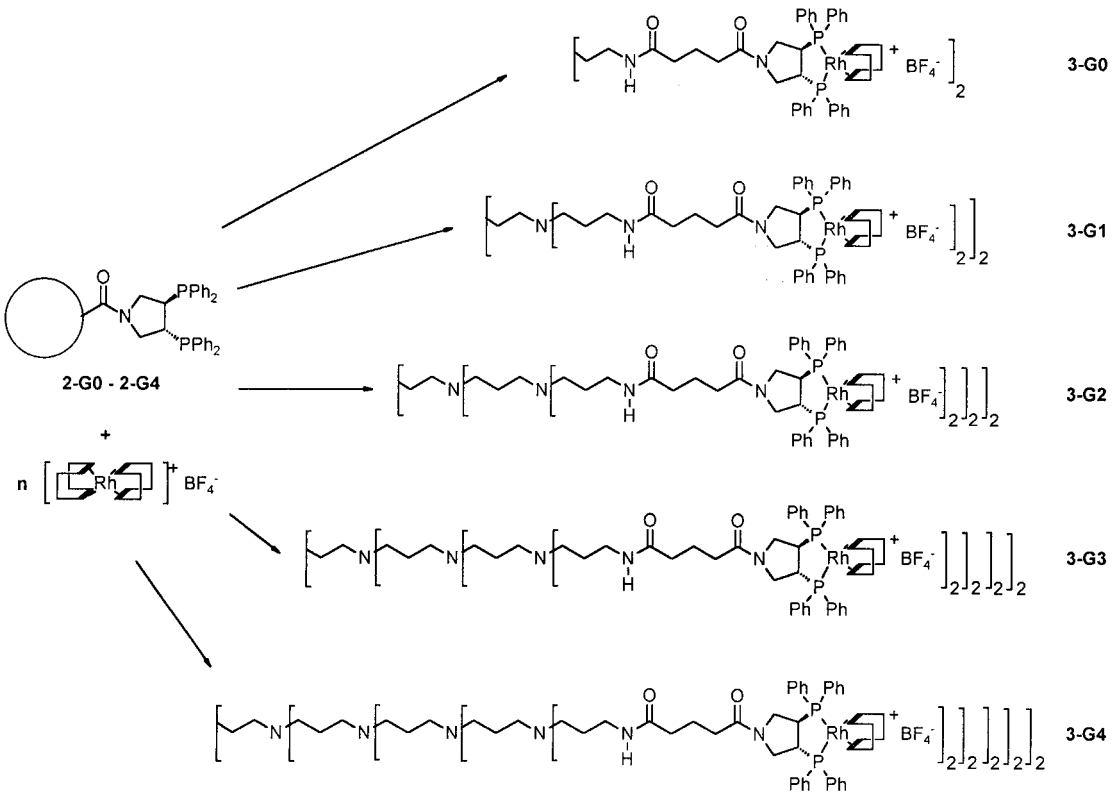


2-G4



Scheme 2. Synthesis of the metallodendrimers **3-G0**–**3-G4** by reaction of **2-G0**–**2-G4** with $[Rh(cod)_2]BF_4$.

0947-6539/02/0818-4322 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 18

Complete metalation was established by elemental analysis as well as by NMR spectroscopy. The ^{31}P NMR spectra, in particular, clearly demonstrate the absence of unreacted phosphine units after the complete conversion, as is shown in Figure 3 for the fourth-generation rhododendrimer **3-G4**. Instead of the resonance of the free phosphine unit at $\delta =$ −12.1 ppm, the well-resolved AB part of the ABX system is observed, which is shifted to lower field ($\delta_A = 33.9$ ppm, $\delta_B = 32.9$ ppm) due to the metal complexation. The $^1J_{Rh,P}$ coupling constants of 150 and 153 Hz are within the expected range for such phosphinerhodium compounds, likewise the $^2J_{P,P}$ coupling of 28 Hz.[12b, 14]

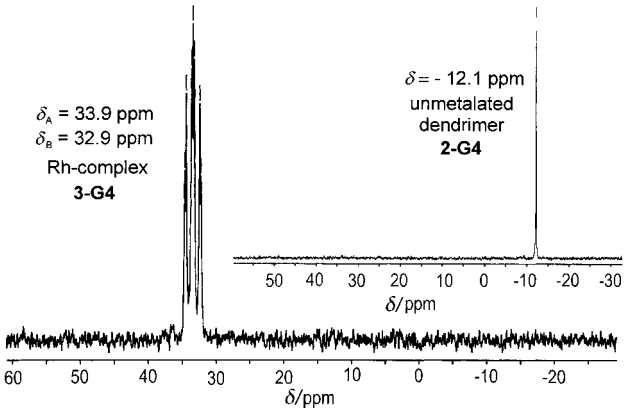
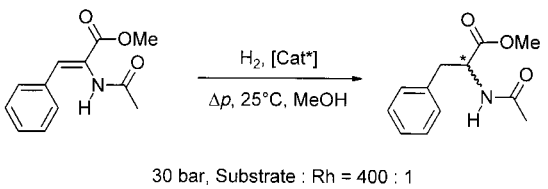


Figure 3. ^{31}P NMR spectrum of the fourth-generation rhododendrimer **3-G4** showing the complete metalation of the phosphine binding sites.

The complete metalation of even the fourth-generation dendrimer indicates that the electrostatic repulsion between the cationic rhodium centers is offset by the binding capability of the phosphine ligands. These remain sufficiently accessible as to allow the generation of the complete series of catalyst precursors **3-G0**–**3-G4** containing 2, 4, 8, 16, and 32 metal centers, respectively.

Asymmetric catalytic hydrogenation of dimethyl itaconate and methyl acetamidocinnamate: To establish the relationship between the size/generation of the dendrimer and its catalytic properties the rhododendrimers **3-G0**–**3-G4** were employed in the asymmetric hydrogenation of *Z*-methyl-α-acetamidocinnamate as a standard reference system for chiral cationic rhodium hydrogenation catalysts (Scheme 3).[24]

These are intermediates in the synthesis of dopamine derivatives and thus of pharmacological interest.[25] Mono-



Scheme 3.

nuclear N-substituted pyrphos-rhodium catalysts have been previously shown to induce enantioselectivities of 90–100% *ee*. As the standard reaction conditions we chose a substrate:catalyst (catalytic site) ratio of 400:1, 30 bar hydrogen pressure, and a reaction temperature of $25 \pm 1\,^{\circ}C$. The conversion was monitored by GCMS (the peak intensity of the components being calibrated relative to those of authentic, pure samples) and it was found that the activity decreases in regular increments upon going from **3-G0** to **3-G4** as is shown in Figure 4a.

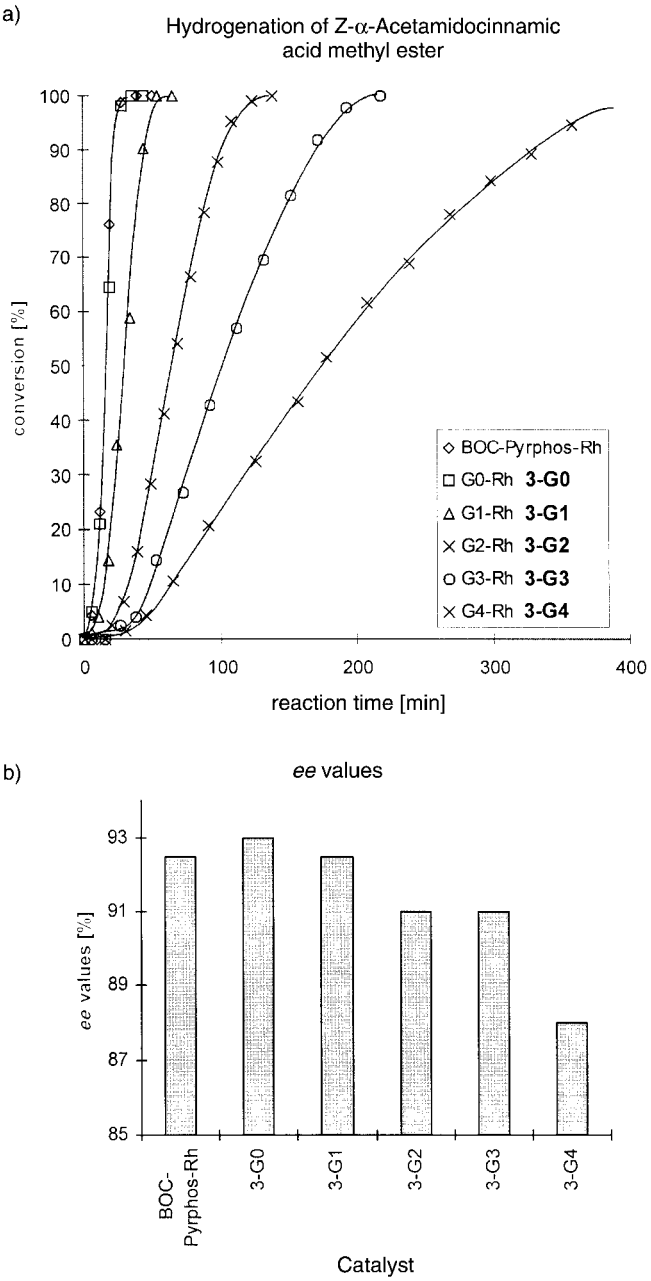
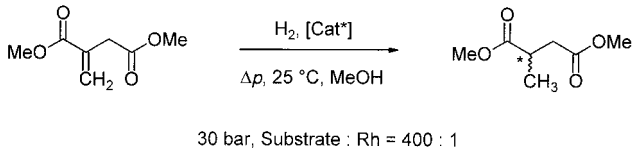


Figure 4. a) Conversion curves of the asymmetric hydrogenation of *Z*-methyl-α-acetamidocinnamate for the different catalyst generations. b) Enantioselectivity of the asymmetric hydrogenation of *Z*-methyl-α-acetamidocinnamate for the different catalyst generations.

In the same way as the activity of the catalysts decreased upon going to the higher dendrimer generations there was a decrease in the selectivity of the systems from the second

generation onwards. The average enantiomeric excesses for the hydrogenation of *Z*-methyl-α-acetamidocinammate with **3-G0** to **3-G4** are displayed in Figure 4b.

The decrease of enantioselectivity from 93% to 88% on going from **3-G2** to **3-G4** is significant, but only really appreciable at the fourth generation. To establish the size-selectivity relationship with a substrate that was expected to be more sensitive to the structural changes, we chose dimethyl itaconate (Scheme 4) which starts out at a lower enantioselectivity for the mononuclear complex and zeroth generation dendrimer (78% and 74% *ee*, respectively).



Scheme 4.

The results of the asymmetric hydrogenation of dimethyl itaconate confirm these considerations and display a very sensitive dependence of the catalyst performance on the dendrimer size. As was observed for *Z*-methyl-α-acetamidocinammate, the reaction rate decreased in relatively regular increments upon going to the higher dendrimer generations as is shown in Figure 5a. Whereas the conversion using the mononuclear catalyst [Rh(BOC-pyrphos)(cod)]BF_4 was found to be complete after 30 mins, the fourth-generation rhododendrimer derived from **3-G4** required about 230 min under otherwise identical reaction conditions.

The reduction in activity observed for both hydrogenations may be due to the reduced accessibility of all metal centers in the higher generation dendrimers. The effect of increasing approach of end groups in dendrimers at higher generations has been demonstrated inter alia by the modified photophysics of immobilized dyes found in Meijer's group[26] and a reduced activity in the Kharasch reaction studied by van Koten et al.[27] The reduction in catalyst selectivity is even more pronounced in the conversion of dimethyl itaconate than for *Z*-methyl-α-acetamidocinammate: from 77.5% *ee* in the mononuclear BOC-pyrphos-rhodium complex to 60% *ee* in the third and fourth-generation dendrimer catalysts (Figure 5b). The given values were found to be independent of the hydrogen pressure, which was varied between 10 and 50 bar.

It is known that in the presence of tertiary amines, which may weakly coordinate to the metal centers, the catalyst

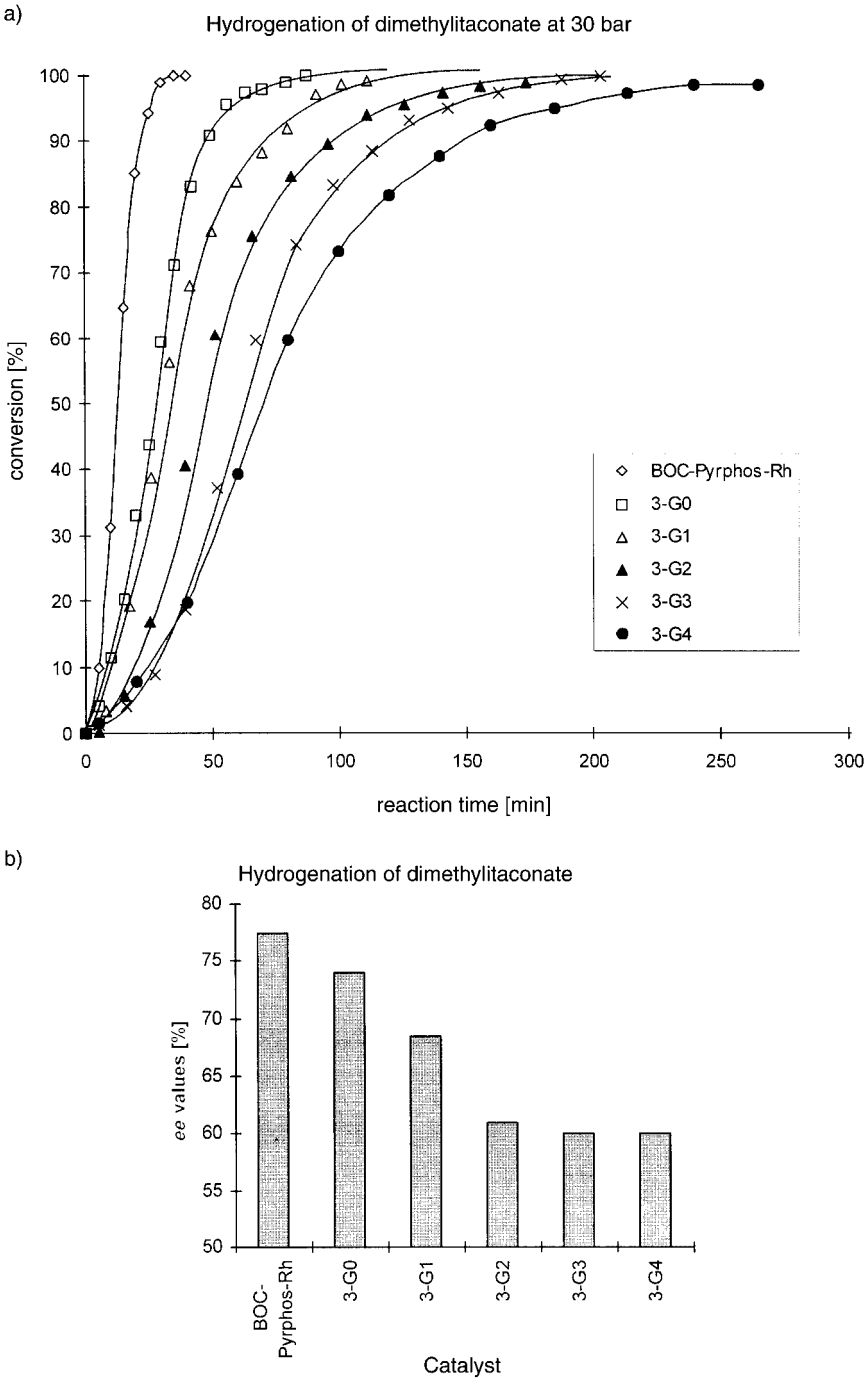


Figure 5. a) Conversion curves of the asymmetric hydrogenation of dimethyl itaconate for the different catalyst generations. b) Enantioselectivity of the asymmetric hydrogenation of dimethyl itaconate for the different catalyst generations.

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performance of cationic rhodium complexes is reduced. However, upon monitoring the enantiomeric excess of the reaction product during the course of the reaction, it became apparent that the loss in selectivity is mainly due to a low stereoselectivity at low conversion while it increases during the course of the reaction to almost the level of the mononuclear catalysts. This may be associated with the hydrogenolytic decoordination of the COD ligands leading, intitially, to non-uniform mixtures of still complexed and already decomplexed, active metal centers. There is no sign of decomposition in the rhododendrimers during the course of the reaction which might be responsible and thus the loss in selectivity is mainly due to this early phase.

Conclusion

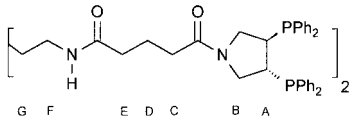
In this first study on the dendrimer fixation of the C_2-chiral pyrphos ligand system we have shown an efficient and convenient route to uniform metallodendrimer products based on previous work on solid support fixation of this type of ligand. This has given access to chemically pure rhododendrimers even for the higher generations and the fixation of up to 32 catalytic centers at the periphery of the PPI dendrimer. It has also demonstrated the loss in activity and selectivity associated with the transition to the dendritic macromolecules containing a high surface density of cationic metal complexes. An important factor governing the properties of the metallodendrimers as catalysts is certainly the flexibility of the dendrimer core, which is high in the given case and allows for the bending back of the attached rhodium complexes to the inside of the otherwise globular molecule. This reduces the accessiblity of the catalytic centers and at the same time renders their immediate environment less uniform than originally envisaged. A more rigid dendrimer core, such as the polyamide core of the family of PANAM dendrimers, may partially suppress this negative effect. This is the objective of current and future research in our laboratory.

Experimental Section

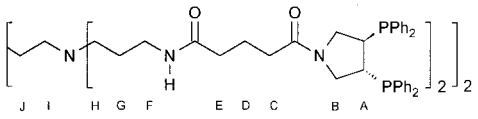
All manipulations were performed under an inert-gas atmosphere of dried nitrogen in standard (Schlenk) glassware. Solvents were dried according to standard procedures and saturated with N_2. Water, hydrochloric acid and KOH solution were degassed by stirring under vacuum for 3×10 min. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze–pump–thaw" cycles and dried over 4 Å molecular sieves. Solids were separated from suspensions by centrifugation thus avoiding filtration procedures. The centrifuge employed was a Rotina 48 (Hettich Zentrifugen, Tuttlingen, Germany) which was equipped with a specially designed Schlenk tube rotor.[28]

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on the following spectrometers: A Bruker AC 200 FT NMR spectrometer (^{1}H: 200.13, ^{13}C: 50.3 MHz), a Bruker AC 300 FT NMR spectrometer (^{1}H: 300.17, ^{13}C: 75.5, ^{31}P: 121.5 MHz), a Bruker AMX 400 or a Avance 400 FT NMR spectrometer (^{1}H: 400.16, ^{13}C: 100.6 MHz) or a Bruker ARX 500 FT NMR spectrometer (^{1}H: 500.13, ^{13}C: 125.8 MHz) with tetramethylsilane or H_3PO_4 as a reference. The IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. Melting points were determined using Electrothermal IA 9100 apparatus and are not corrected. Mass spectrometric measurements (FAB, ESI, MALDI-TOF) were carried out by the Service Commun de la Spectrometrie de Masse at the Université Louis Pasteur, Strasbourg. $[\alpha]_D$ values were determined by using a Perkin-Elmer 241 Polarimeter. Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at Strasbourg. *N*-(4-Carboxylbutanoyl)-pyrphos,[14] $[(1,5\text{-cod})_2\text{Rh}]\text{BF}_4$,[29] and *Z*-methyl-$\alpha$-acetamido-cinnamate[30] were synthesized according to the literature. The other starting materials were obtained commercially and used without further purification.

General procedure for the syntheses of the phosphane dendrimers: A mixture of *N*-(4-carboxylbutanoyl)-pyrphos (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 the suspension was added the respective amino-terminated poly(propylene)imine dendrimer, dissolved in DMF. The solution was allowed to come to room temperature and stirred for 48–90 h. All volatiles were completely removed in vacuo. The residue was taken up in CH_2Cl_2 (20 mL) and thoroughly extracted with 0.2 N KOH (3×15 mL), H_2O (2×15 mL), 0.2 N hydrochloric acid (3×15 mL), and 0.2 N KOH (15 mL, 4–6 times). The solvent was removed in vacuo. The residue was dissolved in toluene, which was afterwards removed under vaccuum. This drying procedure was repeated several times. Finally, the resulting white solid was washed with *n*-pentane and dried in vacuo yielding the phosphane dendrimers as off-white powders.

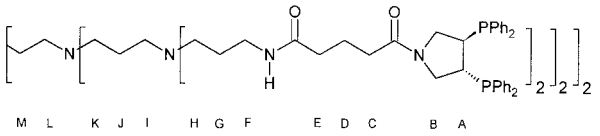


G0-DAB-*dendr*-(glutaroyl-pyrphos)$_2$: Yield: 517 mg (446 μmol, 98%); m.p.: 91–104 °C, ^{1}H NMR (300.16 MHz, $CDCl_3$, 295 K): $\delta = 7.10$–7.40 (m, 40H; $H_{aromat.}$), 6.57 (t, $^3J_{H,H} = 6.0$ Hz, 2H; NH), 3.85–4.02 (m, 4H; H^B_{trans}), 3.69 (pseudo-t, $|^2J_{H_{cis}H_{trans}}| = 12.8$ Hz, $^3J_{H,P} = 12.8$ Hz, 2H; H^B_{cis}), 3.35 (pseudo-t, $|^2J_{H_{cis}H_{trans}}| = 11.7$ Hz, $^3J_{H,P} = 11.7$ Hz, 2H; H'^B_{cis}), 3.15–3.24 (m, 4H; H^F), 2.82–2.99 (m, 4H; H^A), 2.16–2.25 (m, 8H; H^{C+E}), 1.83–1.94 (m, 4H; H^D), 1.44–1.48 ppm (m, 4H; H^G); $\{^1H\}^{13}$C NMR (50.3 MHz, $CDCl_3$, 297 K): $\delta = 172.9$ (C_q; HNC=O), 171.1 ($C_{q'}$ O=*C*N (ring)), 135.4–136.3 (m; C_q, $C_{i,aromat.}$), 133.5 (d, $|^2J_{C,P}| = 21$ Hz, CH; $C_{o,aromat.}$), 128.3–129.6 (m, CH; $C_{m+p,aromat.}$), 48.8 (m, CH_2; C^B), 48.0 (m, CH_2; $C^{B'}$), 39.2 (m, CH; C^A), 39.0 (CH_2; C^F), 37.2 (m, CH; $C^{A'}$), 35.6 (CH_2; $C^{C/E}$), 33.5 (CH_2; $C^{E/C}$), 27.0 (CH_2; C^G), 21.0 ppm (CH_2; C^D); $\{^1H\}^{31}$P NMR (121.5 MHz, $CDCl_3$, 295 K): $\delta = -12.1$ ppm (s, br); IR (KBr): $\tilde{\nu} = 3426$ w, 3307 m (ν(N–H)), 3050 w, 2928 w, 2868 w, 1642 vs (br, ν(C=O)), 1542 w, 1480 w, 1433 vs (ν(P–Ph)), 1329 w, 1250 w, 1198 w, 1093 m, 1026 m, 999 m, 912 w, 740 s (δ(C–$H_{aromat.}$)), 696 (δ(C–$H_{aromat.}$)), 506 m, 481 w cm^{-1}; $[\alpha]_D^{20} = +121.2°$ ($c = 0.474$, $CHCl_3$); MS (FAB): *m*/*z* (%): 1159 (55) $[M+H]^+$, 973 (12) $[M - PPh_2 + H]^+$, 185 (100) $[PPh_2]^+$; elemental analysis calcd (%) for $C_{70}H_{74}N_4O_4P_4$ (1158.28): C 72.53, H 6.43, N 4.83; found: C 72.12, H 6.41, N 4.78.

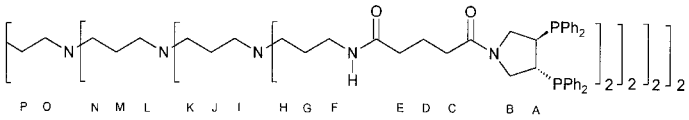


G1-DAB-*dendr*-(glutaroyl-pyrphos)$_4$: Yield 835 mg (240 μmol, 90%); m.p.:84–98 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$, 300 K) $\delta = 7.10$–7.38 (m, 80H; $H_{aromat.}$), 7.06 (t, $^3J_{H,H} = 5.3$ Hz, 4H; NH), 3.85–3.97 (m, 8H; H^B_{trans}), 3.64 (pseudo-t, $|^2J_{H,H}| = 12.9$ Hz, $^3J_{H,P} = 12.9$ Hz, 4H; H^B_{cis}), 3.33 (pseudo-t, $|^2J_{H,H}| = 11.8$ Hz, $^3J_{H,P} = 11.8$ Hz, 4H; H^B_{cis}), 3.21 (m, 8H; H^F), 2.91–2.94 (m, 4H; H^A), 2.85–2.88 (m, 4H; H^A), 2.35–2.40 (m, 12H; H^{H+I}), 2.13–2.22 (m, 16H; H^{C+E}), 1.80–1.86 (m, 8H; H^D), 1.55–1.60 (m, 8H–H^G), 1.34–1.38 ppm (m, 4H; H^J); $\{^1H\}^{13}$C NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 172.5$ (C_q, HNC=O), 171.0 (C_q, NC=O), 135.4–136.4 (m; C_q, $C_{i,aromat.}$), 133.2–133.6 (m; CH, $C_{m,aromat.}$), 128.5–129.4 (m, CH; $C_{o+p,aromat.}$), 53.9 (CH_2; C^I), 52.1 (CH_2; C^H), 48.7 (pseudo-t, $|^2J_{C,P}| = 11$ Hz, $^3J_{C,P'} = 11$ Hz, CH_2; C^B), 48.0 (pseudo-t, $|^2J_{C,P}| = {}^3J_{C,P} = 10$ Hz, CH_2; $C^{B'}$), 39.0 (pseudo-t, $^1J_{C,P} = |^2J_{C,P'}| = 17$ Hz, CH; C^A), 38.2 (CH_2; C^F), 37.4 (pseudo-t, $^1J_{C,P} = |^2J_{C,P'}| = 17$ Hz, CH; $C^{A'}$), 26.9 (CH_2; C^G), 24.8 (CH_2; C^J), 20.9 ppm (CH_2; C^D); $\{^1H\}^{31}$P NMR (121.5 MHz, $CDCl_3$, 298 K): $\delta = -12.1$ ppm (br s); IR (KBr): $\tilde{\nu} = 3410$ w, 3306 m (ν(N–H)), 3050 w, 2929 m, 1644 vs (br, ν(C=O)), 1538 m, 1433 vs

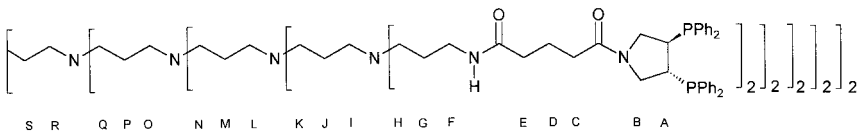
(ν(C–P)), 1250 w, 1092 w, 1026 w, 910 w, 740 s (δ(C–$H_{aromat.}$)), 696 vs (δ(C–$H_{aromat.}$)), 506 m; $[\alpha]_D^{20} = +138.3^\circ$ ($c = 0.48$, $CHCl_3$); MS (FAB): *m*/*z* (%): 2459 (71) $[M]^+$, 2273 (15) $[M - PPh_2]^+$, 2089 (24) $[M - 2PPh_2]^+$, 1230 (25) $[M]^{2+}$, 185 (100) $[PPh_2]^+$; elemental analysis calcd (%) for $C_{148}H_{164}N_{10}O_8P_8$ (2458.78): C 72.30, H 6.72, N 5.70; found: C 72.02, H 6.55, N 5.48.



G2-DAB-*dendr*-(glutaroyl-pyrphos)$_8$: Yield: 488 mg (96.4 μmol, 88%); m.p.: 95–108 °C; ^{1}H NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 7.04-7.48$ (m, 168H; $H_{aromat.}$, N*H*), 3.85–4.00 (m, 16H; H^{B}_{trans}), 3.66 (pseudo-t, $|^2J_{H,H}| = 12.9$ Hz, $^3J_{H,P} = 12.9$ Hz, 8H; H^{B}_{cis}), 3.34 (pseudo-t, $|^2J_{H,H}| = 11.8$ Hz, $^3J_{H,P} = 11.8$ Hz, 8H; $H^{B'}_{cis}$), 3.19–3.25 (m, 16H; H^F), 2.80–3.01 (m, 16H; H^A), 2.30–2.42 (m, 36H; $H^{H+I+K+L}$), 2.10–2.23 (m, 32H; H^{E+C}), 1.80–1.91 (m, 16H; H^D), 1.45–1.68 (m, 24H; H^{G+J}), 1.32–1.40 ppm (m, 4H; H^M); {^{1}H}^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 172.7$ (C_q, HN*C*=O), 171.1 (C_q, O=*C*N(ring)), 135.4–136.4 (m; C_q, $C_{i,aromat.}$), 133.3–133.7 (m, CH; $C_{m,aromat.}$), 128.1–130.0 (m, CH; $C_{o+p,aromat.}$), 54.2 (CH_2, br; C^L), 52.2+51.9 (CH_2, br; C^{H+I+K}), 48.8 (m, CH_2; C^B), 48.0 (m, CH_2; $C^{B'}$), 38.9 (pseudo-t, $^1J_{C,P} = |^2J_{C,P'}| = 17$ Hz, CH; C^A), 38.1 (CH_2; C^F), 37.2 (pseudo-t, $^1J_{C,P} = |^2J_{C,P'}| = 17$ Hz, CH; $C^{A'}$), 35.6 (CH_2; $C^{C/E}$), 33.6 (CH_2; $C^{E/C}$), 26.9 (CH_2; C^G), 25.1 (CH_2; $C^{J/M}$), 24.5 (CH_2; $C^{J/M}$), 21.0 ppm (CH_2; C^D); {^{1}H}^{31}P NMR (121.5 MHz, $CDCl_3$, 297 K): $\delta = -12.2$ (s, br); IR (KBr): $\tilde{\nu} = 3426$ w, 3305 m (ν(N–H)), 3005 m, 2930 m, 2863 m, 2803 m, 1646 vs (br, ν(C=O)), 1543 s, 1480 s, 1433 vs (ν(C–P)), 1337 m, 1277 w, 1250 w, 1210 w, 1157 m, 1093 m, 1026 w, 999 w, 910 w, 741 vs (δ(C–$H_{aromat.}$)), 696 vs (δ(C–$H_{aromat.}$)), 506 s, 480 m; $[\alpha]_D^{20} = +138.0^\circ$ ($c = 0.478$, $CHCl_3$); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene): *m*/*z* (%): 5059 $[M+H]^+$, 5075 $[M+H+O]^+$ (oxidation in the matrix); elemental analysis calcd (%) for $C_{304}H_{344}N_{22}O_{16}P_{16}$ (5057.80): C 72.19, H 6.86, N 6.09; found: C 71.82, H 6.62, N 5.78.

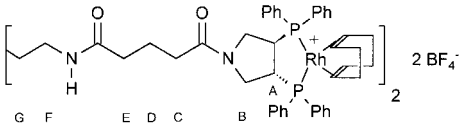


G3-DAB-*dendr*-(glutaroyl-pyrphos)$_{16}$: Yield 659 mg (64.3 μmol, 87%); m.p.: 96–110 °C; ^{1}H NMR (300.17 MHz, $CDCl_3$, 298 K,): $\delta = 7.13-7.42$ (m, 336H; $H_{aromat.}$, NH), 3.82–3.96 (m, 32H; H^{B}_{trans}), 3.63 (pseudo-t, $|^2J_{H,H}| = 12.9$ Hz, $^3J_{H,P} = 12.9$ Hz, 16H; H^{B}_{cis}), 3.32 (pseudo-t, $|^2J_{H,H}| = 11.6$ Hz, $^3J_{H,P} = 11.6$ Hz, 16H; $H^{B'}_{cis}$), 3.15–3.23 (m, 32H; H^F), 2.81–2.96 (m, 32H; H^A), 2.30–2.42 (m, 84H; $H^{H+I+K+L+N+O}$), 2.10–2.18 (m, 64H; H^{E+C}), 1.77–1.88 (m, 32H; H^D), 1.45–1.59 (m, 56H; H^{G+J+M}), 1.28–1.36 ppm (m, 4H; H^P); {^{1}H}^{13}C NMR (125.7 MHz, $CDCl_3$, 283 K): $\delta = 172.6$ (C_q, HN*C*=O), 171.0 (C_q, O=*C*N(ring)), 135.3–136.2 (m; C_q, $C_{i,aromat.}$), 133.3–133.5 (m, CH; $C_{m,aromat.}$), 128.5–129.7 (m, CH; $C_{o+p,aromat.}$), 51.0–53.8 (CH_2, br; $C^{H+I+K+L+N+O}$), 48.6 (pseudo-t, $|^2J_{C,P}| = {}^3J_{C,P'} = 10$ Hz, CH_2; C^B), 47.9 (pseudo-t, $|^2J_{C,P}| = {}^3J_{C,P'} = 10$ Hz, CH_2; $C^{B'}$), 38.8 (pseudo-t, $^1J_{C,P} = |^2J_{C,P'}| = 17$ Hz, CH; C^A), 37.7 (br, CH_2; C^F), 37.0 (pseudo-t, $^1J_{C,P} = |^2J_{C,P'}| = 17$ Hz, CH; $C^{A'}$), 35.4 (CH_2; $C^{C/E}$), 33.6 (CH_2; $C^{E/C}$), 26.8 (CH_2; C^G), 24.1–24.8 (br, CH_2; C^{J+M+P}), 20.9 ppm (CH_2; C^D); {^{1}H}^{31}P NMR (121.5 MHz, $CDCl_3$, 297 K): $\delta = -12.1$ ppm (s, br); IR (KBr): $\tilde{\nu} = 3426$ w, 3305 m (ν(N–H)), 3051 m, 2929 m, 2868 m, 2806 m, 1643 vs (br, ν(C=O)), 1543 s, 1433 vs (ν(C–P)), 1341 m, 1277 w, 1250 w, 1212 w, 1157 m, 1093 m, 1026 w, 999 w, 911 w, 741 vs (δ(C–$H_{aromat.}$)), 696 vs (δ(C–$H_{aromat.}$)), 644 w, 506 s, 480 m; $[\alpha]_D^{20} = +137.3^\circ$ ($c = 0.482$, $CHCl_3$); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene): *m*/*z* (%): 10263 $[M]^+$, 9892 $[M - 2PPh_2]^+$; elemental analysis calcd (%) for $C_{616}H_{704}N_{46}O_{32}P_{32}$ (10255.83): C 72.14, H 6.92, N 6.28; found: C 71.90, H 6.72, N 5.52.



G4-DAB-*dendr*-(glutaroyl-pyrphos)$_{32}$: Yield 445 mg (21.7 μmol, 85%); m.p.: 92–111 °C; ^{1}H NMR (500.14 MHz, $CDCl_3$, 283 K): $\delta = 7.38-7.44$ (m, 32H; NH) 7.11–7.38 (m, 640H; $H_{aromat.}$), 3.83–3.96 (m, 64H; H^{B}_{trans}), 3.63 (pseudo-t, $|^2J_{H,H}| = 12.7$ Hz, $^3J_{H,P} = 12.7$ Hz, 32H; H^{B}_{cis}), 3.31 (pseudo-t, $|^2J_{H,H}| = 11.6$ Hz, $^3J_{H,P} = 11.6$ Hz, 32H; $H^{B'}_{cis}$), 3.12–3.21 (m, 64H; H^F), 2.88–2.96 (m, 32H; H^A), 2.80–2.87 (m, 32H; H^A), 2.23–2.42 (m, 180H; $H^{H+I+K+L+N+O+Q+R}$), 2.05–2.18 (m, 128H; H^{E+C}), 1.77–1.88 (m, 64H; H^D), 1.43–1.61 (m, 120H; $H^{G+J+M+P}$), 1.29–1.34 (m, 4H; H^S); {^{1}H}^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 172.7$ (C_q, HN*C*), 171.1 (C_q, O=*C*N(ring)), 135.4–136.3 (m, C_q, $C_{i,aromat.}$), 133.3–133.5 (m, CH; $C_{m,aromat.}$), 128.4–129.6 (m, CH; $C_{o+p,aromat.}$), 51.0–52.8 (br, CH_2; $C^{H+I+K+L+N+O+Q+R}$), 48.8 (m, CH_2; C^B), 48.0 (m, CH_2; $C^{B'}$), 38.8 (m, CH; C^A), 37.7 (br, CH_2; C^F), 37.1 (m, CH; $C^{A'}$), 35.4 (CH_2; $C^{C/E}$), 33.7 (CH_2; $C^{E/C}$), 26.9 (CH_2; C^G), 24.1–24.8 (br, CH_2; $C^{J+M+P+S}$), 20.9 ppm (CH_2; C^D); {^{1}H}^{31}P NMR (121.51 MHz, $CDCl_3$, 297 K): $\delta = -12.1$ (s, br); IR (KBr): 3438 w, 3306 m (ν(N–H)), 3050 m, 2930 m, 2863 m, 2803 m, 1644 vs (br, ν(C=O)), 1548 m, 1433 vs (ν(P–Ph)), 1343 w, 1250 w, 1181 w, 1157 w, 1093 m, 1067 w, 996 w, 910 w, 741 vs (δ(C–$H_{aromat.}$)), 696 vs (δ(C–$H_{aromat.}$)), 506 m, 481 cm^{-1} w; $[\alpha]_D^{20} = +136.1^\circ$ ($c = 0.476$, $CHCl_3$); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene): m/z (%): 20632 $[M - 6H]^+$, 20684 $[M+3O]^+$ (oxidation in the matrix), 20287 $[M - 2PPh_2]^+$; elemental analysis calcd (%) for $C_{1240}H_{1424}N_{94}O_{64}P_{64}$ (20651.89): C 72.12, H 6.95, N 6.38; found: C 72.30, H 6.87, N 5.97.

General procedure for the metalation reactions: To a solution of the dendritic phosphane (80–120 mg) in CH_2Cl_2 (4 mL) was added [(1,5-cod)$_2$Rh]BF_4 (1.0 equiv per bisphosphane unit) in CH_2Cl_2 (3 mL). The resulting yellow-orange solution was stirred for 18 h at room temperature, then passed through Celite (3 cm) and concentrated to 0.5 mL in vacuo. Upon addition of diethyl ether (20 mL) a yellow-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.

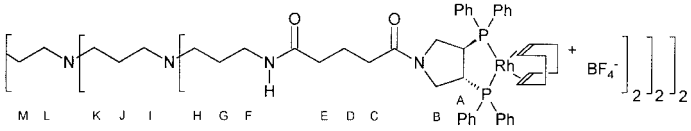


G0-DAB-*dendr*-(glutaroyl-pyrphos-Rh(cod)BF$_4$)$_2$: Yield: 212 mg (121 μmol, 94%); m.p. 223 °C; ^{1}H NMR (300.17 MHz, CD_2Cl_2, 298 K): $\delta = 7.39-7.99$ (m, 40H; $H_{aromat.}$), 6.40–6.46 (m, 2H; NH), 5.15–5.23 (m, 4H; HC= (cod)), 4.50–4.62 (m, 4H; HC= (cod)), 3.72–3.82 (m, 2H; H^B), 3.63–3.71 (m, 2H; H^B), 3.11–3.27 (m, 2H; $H^{A/B}$), 2.88–3.10 (m, 8H; 4 × $H^{A/B}$, H^F), 2.70–2.83 (m, 2H; $H^{A/B}$), 2.37–2.62 (m, 8H; CH_2 (cod)), 2.10–2.28 (m, 8H; CH_2 (cod)), 1.92–2.10 (m, 8H; H^{C+E}), 1.60–1.76 (m, 4H; H^D), 1.30–1.41 ppm (m, 4H; H^G); {^{1}H}^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K): $\delta = 173.5$ (br; C_q, HN*C*=O), 172.1 (C_q, O=*C*N(ring)), 137.0 (CH; $C_{aromat.}$), 133.8 (CH; $C_{aromat.}$, rotamer A), 132.2 (CH; $C_{aromat.}$, rotamer B), 130.1–131.2 (m, CH; $C_{aromat.}$), 128.8 (dd, $^1J_{C,P} = 43$ Hz, $|^2J_{CRh}| = 18$ Hz; C_q, $C_{i,aromat.}$, rotamer A), 126.4 (dd, $^1J_{C,P} = 42$ Hz, $|^2J_{CRh}| = 6$ Hz; C_q, $C_{i,aromat.}$, rotamer B), 104.6 (CH; =CH (cod)), 98.6 (CH; =*C*H (cod)), 44.6 (m, CH_2; C^B), 43.6 (m, CH; C^A), 43.2 (m, CH_2; $C^{B'}$), 41.9 (m, CH; $C^{A'}$), 39.1 (CH_2; C^F), 35.6 (CH_2; $C^{C/E}$), 33.3 (CH_2; $C^{E/C}$), 32.3 (CH_2; cod), 28.8 (CH_2; cod), 26.7 (CH_2; C^G), 21.0 ppm (CH_2; C^D); {^{1}H}^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K): $\delta = 33.9$ (dd, $^1J_{P,Rh} = 147$ Hz, $|^2J_{PP'}| = 28.0$ Hz; P), 33.0 (dd, $^1J_{P',Rh} = 150$ Hz; P′); IR (KBr): $\tilde{\nu} = 3394$ m (ν(N–H)), 3042 w, 2926 m, 2875 w, 1637 vs (ν(C=O)), 1542 w, 1435 s (ν(P–Ph)), 1335 w, 1181 w, 1099 m, 1084 vs, 1057 vs, 996 m, 747 s (δ(C–$H_{aromat.}$)), 696 s (δ(C–$H_{aromat.}$)), 529 m, 519 cm^{-1} m; MS (ESI): *m*/*z* (%): 790 $[M]^{2+}$, 1667 $[M^{2+}+BF_4^-]^+$; elemental analysis calcd (%) for $C_{86}H_{98}B_2F_8N_4O_4P_4Rh_2$ (1755.06): C 58.86, H 5.63, N 3.19; found: C 58.99, H 5.30, N 3.01.

G1-DAB-*dendr*-(glutaroyl-pyrphos-Rh(cod)BF$_4$)$_4$: Yield: 425 mg (116 μmol, 94%); m.p. > 237 °C (decomp); ^{1}H NMR (500.14 MHz, CD_2Cl_2, 300 K): $\delta = 7.41-7.96$ (m, 80H; $H_{aromat.}$), 6.88–6.92 (m, 4H; NH), 5.17–5.26

  0947-6539/02/0818-4326 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 18

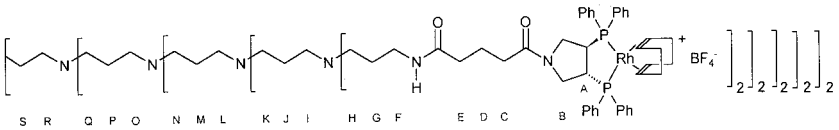
(m, 8H; HC= (cod)), 4.52–4.60 (m, 8H; HC= (cod)), 3.71–3.79 (m, 4H; H^B), 3.64–3.71 (m, 4H; H^B), 3.15–3.25 (m, 4H; $H^{A/B}$), 3.00–3.10 (m, 12H; $4 \times H^{A/B}$, H^F), 2.90–3.00 (m, 4H; $H^{A/B}$), 2.73–2.79 (m, 4H; $H^{A/B}$), 2.50–2.59 (m, 8H; CH_2 (cod)), 2.40–2.49 (m, 8H; CH_2 (cod)), 1.95–2.55 (m, vbr, 12H; H^{H+I}), 2.10–2.23 (m, 16H; CH_2 (cod)), 1.91–2.08 (m, 16H; H^{C+E}), 1.49–1.69 (m, 8H; H^D), superimposed by 1.35–1.60 (m, 8H; H^G), 1.28–1.36 ppm (m, 4H; H^J); $\{^1H\}^{13}C$ NMR (75.5 MHz, $CDCl_3/CD_2Cl_2$, 298 K): $\delta = 173.0$ (br; C_q, HNC=O), 171.4 (C_q, O=CN(ring)), 137.2 (CH; $C_{aromat.}$), 133.4 (CH; $C_{aromat.}$, rotamer A), 131.7 (CH; $C_{aromat.}$, rotamer B), 129.8–131.2 (m, CH; $C_{aromat.}$), 127.1 (dd, $^1J_{C,P} = 44$ Hz, $|^2J_{CRh}| = 27$ Hz; C_q, $C_{i,aromat.}$, rotamer A), 125.6 (d, $^1J_{C,P} = 42$ Hz; C_q, $C_{i,aromat.}$, rotamer B), 103.7 (m, CH; =CH (cod)), 97.9 (m, CH; =CH (cod)), 51.1 (br, CH_2; H^{H+I}), 43.9 (m, CH_2; C^B), 42.9 (m, CH_2; $C^{B'}$), 42.8 (m, CH; C^A), 41.4 (m, CH; $C^{A'}$), 36.7 (br, CH_2; C^F), 34.9 (CH_2; $C^{C/E}$), 32.9 (CH_2; $C^{E/C}$), 31.8 (CH_2; cod), 28.1 (CH_2; cod), 27.1 (CH_2; C^G), 25.4 (CH_2; C^J), 20.5 ppm (CH_2; C^D); $\{^1H\}^{31}P$ NMR (121.5 MHz, CD_2Cl_2, 298 K): $\delta = 33.9$ (dd, $^1J_{P,Rh} = 150$ Hz, $|^2J_{P,P'}| = 28.0$ Hz; P), 33.0 ppm (dd, $^1J_{P',Rh} = 150$ Hz; P′); IR (KBr): $\tilde{\nu} = 3396$ m (ν(N–H)), 3049 w, 2942 m, 2879 w, 1642 vs (br, ν(C=O)), 1542 w, 1435 s (ν(P–Ph)), 1333 w, 1182 w, 1096 m, 1084 vs, 1058 vs br, 998 m, 748 s (δ(C–$H_{aromat.}$)), 696 s (δ(C–$H_{aromat.}$)), 535 s, 519 s, 475 m; elemental analysis calcd (%) for $C_{180}H_{212}B_4F_{16}N_{10}O_8P_8Rh_4$ (3650.36): C 59.22, H 5.85, N 3.84; found: C 59.04, H 5.94, N 3.79.



G2-DAB-*dendr*-(Glutaroyl-Pyrphos-Rh(COD)BF_4)$_8$: Yield: 189 mg (25.4 μmol, 99%); m.p.: >245 °C (decomp); ^1H NMR (300.17 MHz, CD_2Cl_2, 298 K): $\delta = 7.40–7.99$ (m, 160H; $H_{aromat.}$), 6.75–6.92 (m, 8H; NH), 5.16–5.23 (m, 16H; *H*C= (cod)), 4.50–4.62 (m, 16H; HC= (cod)), 3.64–3.77 (m, 16H; H^B), 3.14–3.27 (m, 8H; $H^{A/B}$), 2.89–3.13 (m, 32H; $16 \times H^{A/B}$, H^F), 2.67–2.82 (m, 8H; $H^{A/B}$), 2.35–2.65 (m, 32H; CH_2 (cod)), superimposed by 2.30–2.64 (m, vbr, 36H; $H^{H+I+K+L}$), 2.11–2.26 (m, 32H; CH_2 (cod)), 1.87–2.08 (m, 32H; H^{C+E}), 1.45–1.79 (m, 40H; H^D,H^{G+J}), 1.28–1.34 ppm (m, 4H; H^M); $\{^1H\}^{13}C$ NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 172.6$ (br; C_q, HNC=O), 171.1 (C_q; O=CN (ring)), 137.1 (CH; $C_{aromat.}$), 133.2 (CH; $C_{aromat.}$, rotamer A), 131.5 (CH; $C_{aromat.}$, rotamer B), 128.5–131.7 (m, CH; $C_{aromat.}$), 126.9 (dd, $^1J_{C,P} = 44$ Hz, $|^2J_{CRh}| = 22$ Hz; C_q, $C_{i,aromat.}$, rotamer A), 125.6 (d, $^1J_{C,P} = 42$ Hz; C_q, $C_{i,aromat.}$, rotamer B), 103.7 (m, CH; =CH, COD), 97.7 (m, CH; =CH, cod), 50.0–51.9 (br, CH_2; $H^{H+I+K+L}$), 43.7 (m, CH_2; C^B), 42.5 (m, CH; C^A), 41.3 (m, CH; $C^{A'}$), 40.7 (m, CH_2; $C^{B'}$), 36.7 (br, CH_2; C^F), 34.6 (CH_2; $C^{C/E}$), 32.7 (CH_2; $C^{E/C}$), 31.6 (*C*H_2; COD), 27.8 (*C*H_2; COD), 26.0 (CH_2; C^{G+J}), 25.6 (CH_2; C^M), 20.7 ppm (CH_2; C^D); $\{^1H\}^{31}P$ NMR (121.5 MHz, CD_2Cl_2, 297 K): $\delta = 33.9$ (dd, $^1J_{P,Rh} = 150$ Hz, $|^2J_{P,P'}| = 28.0$ Hz; P), 32.8 ppm (dd, $^1J_{P',Rh} = 147$ Hz; P′); IR (KBr): $\tilde{\nu} = 3403$ m (ν(N–H)), 3061 w, 2946 m, 2869 w, 1644 vs (br, ν(C=O)), 1538 w, 1435 s (ν(P–Ph)), 1335 w, 1185 w, 1096 m, 1084 vs, 1058 vs br, 998 m, 748 m (δ(C–$H_{aromat.}$)), 696 s (δ(C–$H_{aromat.}$)), 539 s, 520 s, 478 w; elemental analysis calcd (%) for $C_{368}H_{440}B_8F_{32}N_{22}O_{16}P_{16}Rh_8$ (7440.95): C 59.40, H 5.96, N 4.14; found: C 59.52, H 5.92, N 3.80.

G3-DAB-*dendr*-(glutaroyl-pyrphos-Rh(cod)BF_4)$_{16}$: Yield: 187 mg (12.4 μmol, 94%); m.p.: >274 °C (decomp); ^1H NMR (300.17 MHz, CD_2Cl_2, 298 K): $\delta = 7.40–8.02$ (m, 320H; $H_{aromat.}$), 6.90–7.06 (m, 16H; NH), 5.14–5.24 (m, 32H; HC= (cod)), 4.50–4.61 (m, 32H; HC= (cod)), 3.58–3.80 (m, 32H; H^B), 3.11–3.28 (m, 16H; $H^{A/B}$), 2.85–3.11 (m, 64H; $32 \times H^{A/B}$, H^F), 2.62–2.83 (m, 16H; $H^{A/B}$), 2.30–2.62 (m, 64H; CH_2 (cod)), superimposed by 2.30–2.64 (m, vbr, 84H; $H^{H+I+K+L+N+O}$), 2.10–2.27 (m, 64H; CH_2 (cod)), 1.86–2.07 (m, 64H; H^{C+E}), 1.32–1.77 (m, 88H; H^D,H^{G+J+M}), 1.26–1.30 ppm (m, 4H; H^P); $\{^1H\}^{13}C$ NMR (75.5 MHz, CD_2Cl_2, 298 K): $\delta = 172.9$ (br; C_q, HNC=O), 171.6 (C_q, O=*C*N (ring)), 137.1 (CH; $C_{aromat.}$), 133.8 (CH; $C_{aromat.}$, rotamer A), 132.2 (CH; $C_{aromat.}$, rotamer B), 128.8–132.0 (m, CH; $C_{aromat.}$), 128.0 (dd, $^1J_{C,P} = 44$ Hz, $|^2J_{CRh}| = 18$ Hz; C_q, $C_{i,aromat.}$, rotamer A), 125.6 (d, $^1J_{C,P} = 39$ Hz; C_q, $C_{i,aromat.}$, rotamer B), 104.7 (m, CH; =*C*H (cod)), 98.4 (m, CH; =CH (cod)), 51.1–53.0 (br, CH_2; $H^{H+I+K+L+N+O}$), 44.6 (m, CH_2; C^B), 43.6 (m, CH_2; $C^{B'}$), 43.4 (m, CH; C^A), 41.8 (m, CH; $C^{A'}$), 37.9 (br, CH_2; C^F), 35.5 (CH_2; $C^{C/E}$), 33.4 (CH_2; $C^{E/C}$), 32.4 (CH_2; cod), 28.8 (CH_2; cod), 26.8–28.0 (br, CH_2; $C^{G+J+M+P}$), 21.1 ppm (CH_2; C^D); $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2, 297 K): $\delta = 33.9$ (dd, $^1J_{P,Rh} = 148$ Hz, $|^2J_{P,P'}| = 28.0$ Hz; P), 33.0 (dd, $^1J_{P',Rh} = 150$ Hz; P′); IR (KBr): $\tilde{\nu} = 3419$ m (ν(N–H)), 3054 w, 2935 m, 2881 w, 1640 vs (br, ν(C=O)), 1552 w, 1437 s (ν(P–Ph)), 1337 w, 1181 w, 1163 w, 1121 m, 1096 m, 1086 vs, 1059 vs br, 750 w, 727 m, 696 s (δ(C–$H_{aromat.}$)), 541 m, 521 s; elemental analysis calcd (%) for $C_{744}H_{896}B_{16}F_{64}N_{46}O_{32}P_{32}Rh_{16}$ (15022.21): C 59.49, H 6.01, N 4.29; found: C 59.78; H 5.88, N 3.97.

G4-DAB-*dendr*-(glutaroyl-pyrphos-Rh(cod)BF_4)$_{32}$: Yield: 172 mg (5.70 μmol, 89%); m.p.: >248 °C (decomp); ^1H NMR (300.17 MHz, CD_2Cl_2, 298 K): $\delta = 7.12–8.05$ (m, 672H; $H_{aromat.}$, NH), 5.15–5.27 (m, 64H; HC= (cod)), 4.48–4.63 (m, 64H; HC= (cod)), 3.58–3.77 (m, 64H; H^B), 3.15–3.30 (m, 32H; $H^{A/B}$), 2.85–3.14 (m, 128H; $64 \times H^{A/B}$, H^F), 2.06–2.83 (3 multiplets, vbr, 468H; $32 \times H^{A/B}$, 2x 64H, CH_2 (cod), 180H; $H^{H+I+K+L+N+O+Q+R}$), 1.83–2.06 (m, 128H; H^{C+E}), 1.30–1.64 (m, 184H; H^D,$H^{G+J+M+P}$), 1.25–1.29 ppm (m, 4H; H^S); $\{^1H\}^{13}C$ NMR (75.5 MHz, CD_2Cl_2, 298 K): $\delta = 173.1$ (br; C_q, HNC=O), 171.6 (C_q, O=*C*N(ring)), 137.1 (CH; $C_{aromat.}$), 133.8 (CH; $C_{aromat.}$, rotamer A), 132.2 (CH; $C_{aromat.}$, rotamer B), 128.9–132.1 (m, CH; $C_{aromat.}$), 128.0 (m; C_q, $C_{i,aromat.}$, rotamer A), 125.6 (d, $^1J_{C,P} = 42$ Hz; C_q, $C_{i,aromat.}$, rotamer B), 104.7 (m, CH; =CH, cod), 98.6 (m, CH; =*C*H, cod), 50.9–52.9 (br, CH_2; $H^{H+I+K+L+N+O+Q+R}$), 44.5 (m, CH_2; C^B), 43.6 (m, CH_2; $C^{B'}$), 43.3 (m, CH; C^A), 42.0 (m, CH; $C^{A'}$), 37.9 (br, CH_2; C^F), 35.5 (CH_2; $C^{C/E}$), 33.5 (CH_2; $C^{E/C}$), 32.4 (*C*H_2; cod), 28.7 (*C*H_2; cod), 26.9–28.0 (br, CH_2; $C^{G+J+M+P+S}$), 21.0 ppm (CH_2; C^D); $\{^1H\}^{31}P$ NMR (121.5 MHz, CD_2Cl_2, 297 K): $\delta = 33.9$ (dd, $^1J_{P,Rh} = 150$ Hz, $|^2J_{P,P'}| = 28.0$ Hz; P), 32.9 ppm (dd, $^1J_{P',Rh} = 153$ Hz; P′); IR (KBr): $\tilde{\nu} = 3397$ m (ν(N–H)), 3054 w, 2925 m, 2875 w, 2827w, 1647 vs (br, ν(C=O)), 1541 w, 1480 w, 1435 vs (ν(P–Ph)), 1334 w, 1181 w, 1097 s, 1056 vs br, 996 m, 747 m (δ(C–$H_{aromat.}$)), 696 s (δ(C–$H_{aromat.}$)), 536 m, 519 s, 475 cm^{-1} w; elemental analysis calcd (%) for $C_{1496}H_{1808}B_{32}F_{128}N_{94}O_{64}P_{64}Rh_{32}$ (30184.47): C 59.53, H 6.04, N 4.36; found: C 59.77, H 6.05, N 4.26.



Catalytic investigations: *General*: The course of the catalytic hydrogenations was monitored by GC/MS spectrometry performed with a Shimadzu GC-17A/GCMS-QP5050A. Column: SGE BPX5, 5% phenyl, polysilyphenylene-siloxane, nonpolar, 30 m, 0.22 mm, carrier gas He. The products were analysed by comparison of the recorded mass spectra and retention times with those of authentic samples. The measured relative ratio of the products was calibrated by comparative measurements with known substance ratios using pure substances.

GC/MS-methods: Hydrogenation of dimethyl itaconate: T(injector) = 250 °C, *T*(interface) = 280 °C, 30 m × 0.22 mm, 0.6 mL min^{-1} He (column flow), 61.0 kPa (column pressure), split 1:59. Temperature program: 80 °C, 2 min, 5 °C min^{-1} to 115 °C, 25 °C min^{-1} to 250 °C, 2.5 min. t_R (dimethyl-

methylsuccinate): 7.80 min, t_R (dimethyl itaconate): 8.67 min; hydrogenation of *Z*-α-acetamido cinnamic acid methyl ester: T(injector) = 250 °C, T(interface) = 280 °C, 30 m × 0.22 mm, 0.5 mL min^{-1} He (column flow), 61.0 kPa (column pressure), split 1:70. Temperature program: 130 °C, 0.5 min, 10 °C min^{-1}, 250 °C, 3 min. t_R (methyl *N*-acetylphenylalanate): 9.47 min, t_R (methyl Z-α-acetamidocinnamate): 11.23 min.

The determination of the enantiomeric excesses of 2-methyl-dimethylsuccinate was effected by gas chromatography with a chiral column (chiraldex G-Ta, γ-cyclodextrin, trifluoroacetyl, 20 m × 0.25 mm) in a Shimadzu GC-14A-gas chromatograph with FID detector. Method: T(injector) = 200 °C, T(detector) = 200 °C, split 1:100, 140 kPa, He; T(start) = 60 °C, 0.8 °C min^{-1} to 78 °C, 5 °C min^{-1} to 120 °C, 5 min. t_R (*S* enantiomer) = 17.4 min, t_R (*R* enantiomer) = 18.4 min.

In the case of methyl *N*-acetyl phenylalanate, the *ee* values were determined by measuring the optical rotation and comparison with the literature value $[\alpha]_D^{20} = +101.5°$ (c = 1.0, $CHCl_3$).[31]

General procedure for the hydrogenation experiments: The ratio Rh/substrate was 1:400 in all cases. About 12 mg of the catalyst precursor was put under an inert-atmosphere. The calculated amount of substrate was added and the mixture was dissolved in absolute methanol (70 mL). The clear solution was transferred to a laboratory autoclave (Büchi mini-clave drive) under N_2. The inert gas was displaced with hydrogen. The pressure was set to the chosen value and the reaction started by stirring. The temperature was kept constant at 25 ± 1 °C with a water bath. For sample taking, the stirrer was stopped at distinct times, a small quantity (ca. 100 μL) of the solution was taken with a dipping tube. The stirrer was then restarted and the pressure reset. The sample was dissolved in methanol (2 mL) and analyzed by GC/MS-spectrometry.

Workup of the hydrogenated solution; 2-methyl-dimethylsuccinate: The solvent was removed under light vacuum. The catalyst was precipitated by the addition of diethyl ether. The mixture was filtered over a layer of silica and dried over Na_2SO_4. The solution was brought to a concentration of about 1 mg substance/1 mL solvent and analyzed by gas chromatography.

Methyl *N-acetyl phenylalanate*: The solution was reduced to dryness. The residue was purified by chromatography (silica gel, diethyl ether). After removal of the solvent the product was dried under vaccuum.

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