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Dendrimers based on cyclophosphazene units and containing chiral ferrocenyl ligands for asymmetric catalysis†

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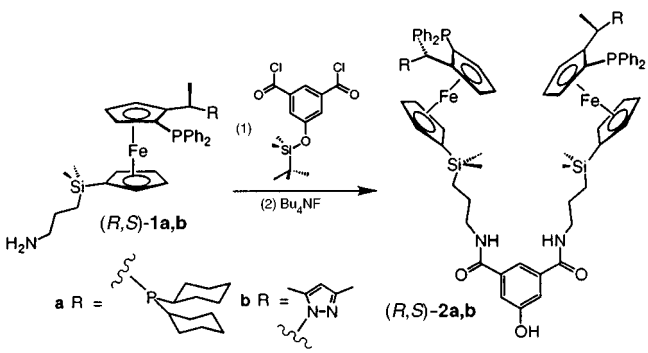
A simple and efficient synthesis and characterization of a series of first generation dendrimers based on cyclophosphazene cores and containing up to 16 peripheral chiral ferrocenyl ligands is described.

Dendrimers,[1] highly branched three-dimensional monodisperse macromolecules, are in principle useful for applications in catalysis, but have still rarely been prepared for this purpose.[2] As an interface between heterogeneous and homogeneous catalysis, such catalysts react in homogeneous solution but may be recycled by means of nanofiltration.[3] We have previously shown that chiral ferrocenyl ligands may be successfully applied to a variety of asymmetric catalytic reactions,[4] and that these ligands could be conveniently functionalised with a view to attaching them to the periphery of dendrimers by a convergent approach.[5] It has been found that such macromolecules, when used in catalytic reactions, do not show relevant differences in terms of stereoselectivity and catalytic activity, as compared to their monomeric congeners and are completely recovered by nanofiltration.[5]

In continuation of our studies, we aimed to improve and simplify the preparation of our dendritic ligands. We report now an efficient three-step synthesis of a new family of dendrimers containing up to 16 chiral ferrocenyl ligand units with PP or PN chelating systems. The synthesis starts from compounds of type **1** and utilises cyclotriphosphazene or tetraphosphazene units as dendrimer cores. Although the N_3P_3 fragment has been used previously in pioneering work by Majoral and co-workers,[1g,h] the next larger oligomeric N_4P_4 phosphazene ring[6] has not been exploited before in dendrimer chemistry. The precursors $N_3P_3Cl_6$ and $N_4P_4Cl_8$ offer more branching points, as compared to more commonly used internal fragments, such as trisubstituted benzenes, or tetrasubstituted adamantanes, implying that, for an equal number of synthetic steps, dendrimers containing a higher number of peripheral units may be obtained. Furthermore, because of the higher internal branching, dendritic particles approaching a spherical shape may be obtained with a lower number of generations.



Scheme 1

Thus, the synthesis of the first-generation dendrimers **$G_1$12PN**, **$G_1$12PP** and **$G_1$16PP**, containing 12, 12 and 16 ferrocenyl groups, respectively, was achieved from intermediates **2** (Scheme 1), obtained by reacting **1** with 5-(*tert*-butyldimethylsiloxy)isophthaloyl dichloride followed by deprotection with Bu_4NF. A slight excess of the sodium salt of **2** was allowed to react in dioxane with $N_3P_3Cl_6$ and $N_4P_4Cl_8$, respectively, affording the desired compounds as orange powders in good yields after purification by column chromatography (Scheme 2).

All new multiple ferrocenyl ligands were characterised by NMR (^{1}H, ^{13}C and ^{31}P) and mass spectroscopy.† As expected, the ^{31}P NMR spectra of the products show one singlet for the cyclophosphazene phosphorus atoms, indicating full substitution of the central core [Fig. 1(*a*)]. The peripheral phosphorus atoms in **$G_1$12PN** display a singlet, whereas **$G_1$12PP** and **$G_1$16PP** each show one pair of doublets with a typical long range $^4J_{PP}$ coupling constant of *ca*. 40 Hz, indicating the equivalence of the ferrocenyl units. The new dendrimers were also characterised by MALDI-TOF mass spectroscopy and in all cases the molecular peak could be detected. Several in-source fragmentations at *m/z* values in good agreement with the calculated ones were observed.† Furthermore, addition of 16 equiv. of $[Rh(COD)_2]BF_4$ to **$G_1$16PP**, for example, led to the corresponding monodisperse species containing 16 equivalent and non-interacting Rh complexes, as indicated by the ABX-spin system in the ^{31}P NMR spectrum of Fig. 1(*b*), displaying $^2J_{PP}$ and $^1J_{PRh}$ coupling constants of 30 and 142 Hz. Preliminary experiments with **$G_1$12PP** and **$G_1$16PP** in the Rh-catalysed hydrogenation of dimethyl itaconate, under the conditions

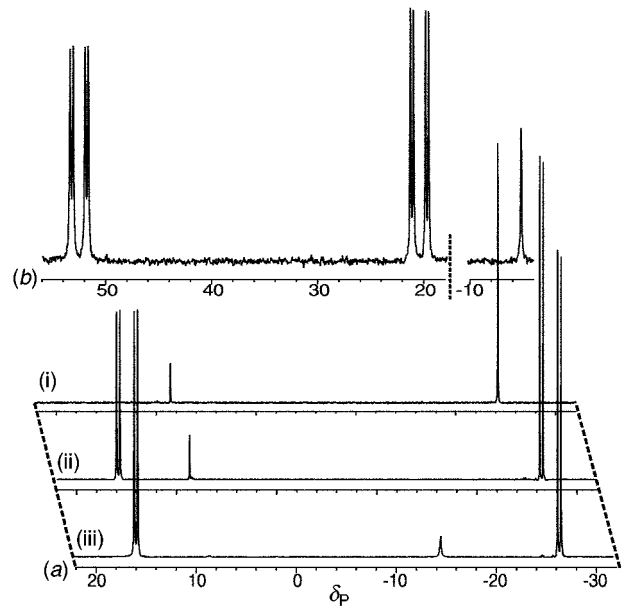
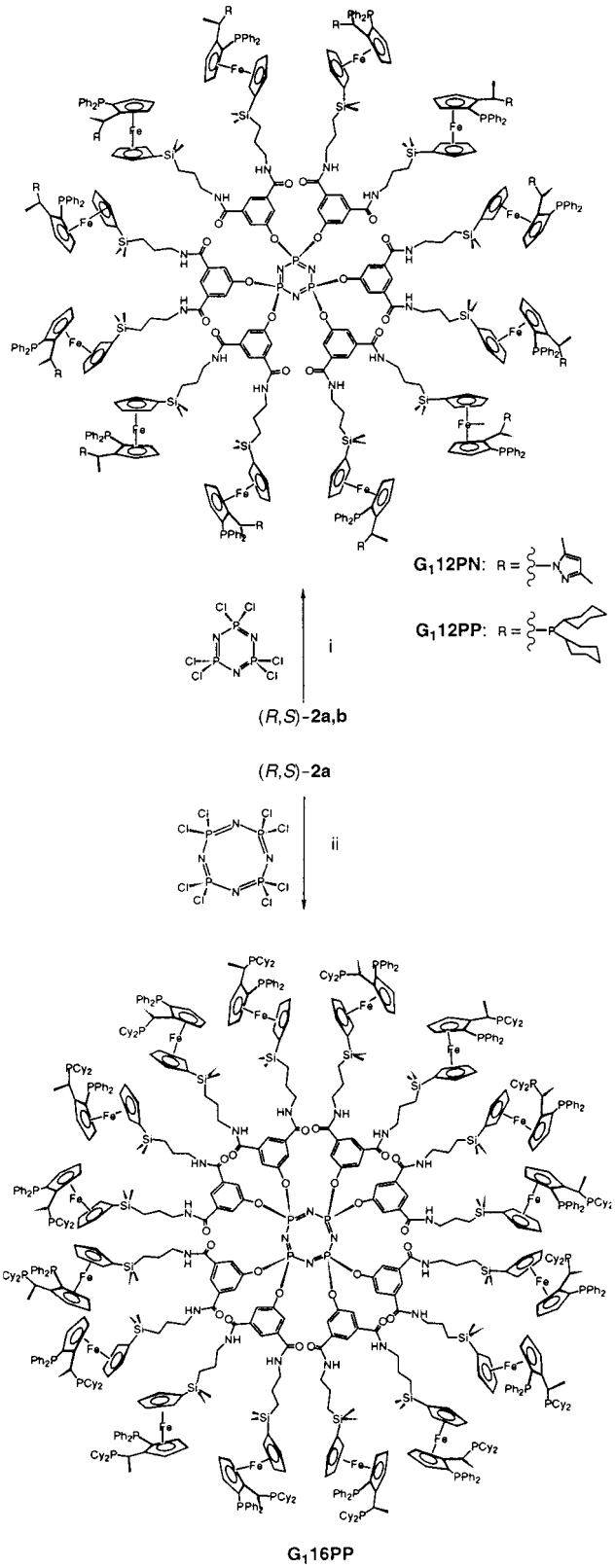


Fig. 1 ^{31}P NMR (101.202 MHz, $CDCl_3$) spectra of G1-dendrimers: (*a*) (i) **$G_1$12PN**, (ii) **$G_1$12PP** and (iii) **$G_1$16PP** and (*b*) **$G_1$16PP** + 16 equiv. of $[Rh(COD)_2]BF_4$.

† Experimental and spectral data for (*R,S*)-**2b**, **$G_1$12PN**, **$G_1$12PP** and **$G_1$16PP** are available from the RSC web site, see http://www.rsc.org/suppdata/cc/1999/2415/



Scheme 2 *Reagents and conditions*: i, Na, MeOH–1,4-dioxane, 60 °C, 1 h, then $N_3P_3Cl_6$, 1,4-dioxane, 16 h (**$G_1$12PN**: 54%, **$G_1$12PP**: 64,5%); ii, Na, MeOH–1,4-dioxane, 60 °C, 1 h, then $N_4P_4Cl_8$, dioxane, 16 h, 83%.

previously reported,[5] afforded the product in *ca*. 98% ee. This indicates that the dendritic structure of the catalyst, as compared to its monomeric version, is not significantly detrimental to enantioselectivity, at least up to the size of **$G_1$16PP**.

We are currently exploiting cyclophosphazenes for the preparation of dendrimers of higher generations, as well as using such dendrimers as catalysts in a continuous asymmetric hydrogenation process. The results of such investigations shall be disclosed in due course.

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Notes and references

† *Selected data* for **$G_1$12PN**: δ_H(250 MHZ, $CDCl_3$)7.93 (s, 36H, C_6H_3), 7.61 (s, 12H, C_6H_3), 7.48 (m, 24 Ph-H), 7.33 (m, 36 Ph-H), 7.02 (m, 36 Ph-H), 6.70 (m, 36H, 24 Ph-H and 12 NH), 5.56 (dq, 12H, 12 C*H*MeN), 5.05 (s, 12 Pz-H), 4.72 (m, 12 Cp-H), 4.36 (m, 12 Cp-H), 4.26 (m, 12 Cp-H), 4.12 (m, 12 Cp-H), 4.04 (m, 12 Cp-H), 3.73 (m, 12 Cp-H), 3.60 (m, 12 Cp-H), 3.21 (m, 24H, 12 CH_2NH), 2.11 (s, 36H, 12 Pz C^5-*Me*), 1.94 (s, 36H, 12 Pz C^3-*Me*), 1.78 (d, 36H, 12 CH*Me*N), 1.43 (m, 24H 12 $CH_2CH_2CH_2$), 0.49 (m, 24H, 12 CH_2Si), 0.12 (s, 36H, 36H of 12 $SiMe_2$), 0.01 (s, 36H, 36H of 12 $SiMe_2$); δ_c(62.86 MHz, $CDCl_3$) 165.7 (C=O), 150.1 (Ar C of C_6H_3), 146.7 (PzC^5), 138.4–127.0 (PPh_2, PzC^3, Ar C of C_6H_3), 123.0 and 121.7 (Ar C of C_6H_3), 101.1 (Pz CH), 94.0 (d, Cp C), 75.2 (d, Cp C), 74.6–70.1 (Cp CH and Cp C), 51.7 (d, *C*HMeN), 43.4 (CH_2N), 24.0 ($CH_2CH_2CH_2$), 20.6 (CH*Me*N), 14.0 (CH_2Si), 13.6 (Pz C^3-*Me*), 11.3 (d, Pz C^5-*Me*), −2.4 ($SiMe_2$), −2.5 ($SiMe_2$); $d3_p$(101.202 MHz, $CDCl_3$) 8.5 (s, Pz), −24.2 (d, PPh_2); *m/z* (MALDI) 8321 ($[M + Na]^+$), 7948 ($[M - \{C_5H_3(PPh_2)(CH(Me)C_5H_7N_2\}]^+$), 6991 ($[M - \{$**2b**$\}]^+$), 6616 ($[6991 - \{C_5H_3(PPh_2)(CH(Me)C_5H_7N_2\}]^+$), 5662 ($[M - \{2 \times$**2b**$\}]^+$), 5291 ($5662 - \{C_5H_3(PPh_2)(CH(Me)C_5H_7N_2\}]^+$).

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