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New phosphorus dendrimers with chiral ferrocenyl phosphine-thioether ligands on the periphery for asymmetric catalysis

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Abstract

Chiral ferrocenyl phosphine-thioether ligands have been covalently bound on the periphery of 4 phosphorus dendrimers (generations 1–4) having a cyclotriphosphazene core and on one model compound. These new dendrimers proved to be efficient ligands for the palladium-catalyzed asymmetric allylic substitution reaction (ee up to 93%).

Keywords: Ferrocenes; Phosphorus dendrimers; P,S ligands; Asymmetric catalysis

1. Introduction

Dendrimers represent a new and fascinating class of regular highly branched and well-defined macromolecules [1] which found numerous promising applications in materials chemistry, biology, etc. but also as homogenous catalysts with the catalytic sites in the core or at the periphery of the dendrimers [2]. However, although a very large number of catalytic systems using dendrimers have already been described, much less reports on asymmetric catalysis with chiral dendrimers have been disclosed [3]. We have been interested since a long time in the synthesis of phosphorus-containing dendrimers [4] and more recently in the synthesis of such dendrimers bearing ferrocene moieties [5]. In addition, we recently took interest in chiral P,S ligands. This type of ligands is still uncommonly used in asymmetric catalysis [6] but had been, however, successfully used in various asymmetric catalytic systems [7]. Therefore, we developed new chiral ferrocenyl P,S [8] ligands ((**S**)-**4R**, Scheme 1) which proved to efficiently promote the palladium catalyzed asymmetric allylic substitution [8a]. The aim of our project was to graft such ferrocenyl P,S ligands on the surface of phosphorus dendrimers and to test them in the asymmetric allylic substitution reaction.

2. Results and discussion

2.1. Synthesis of the dendrimers

One step of the synthesis of phosphorus-based dendrimers is the quantitative reaction of phenols on PCl bonds on the periphery of the growing dendrimer [4]. So, we needed a compound (**S**)-**4R** bearing a phenol in order to covalently bind it to the surface of phosphorus-containing dendrimers (Schemes 1 and 2). We then decided to used (**S**)-**1** for this purpose.

Compounds (**S**)-**4R** were synthesized by reaction of alcohol (**S**)-**2** and thiol RSH in presence of fluoroboric acid [8a]. The same procedure was carried out to obtain the corresponding thioether (**S**)-**3** using 4-hydroxythiophenol as thiol. In this case, only the desired product (**S**)-**3** was obtained in high yields (Scheme 1): no product of O-alkylation or from Friedel–Crafts reaction were detected. Finally, compound (**S**)-**1** was obtained by desulfuration

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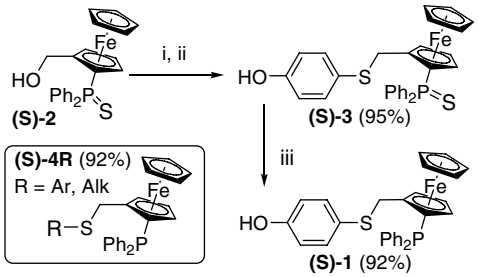
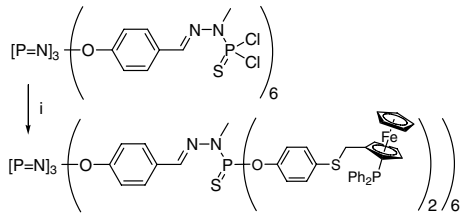


Scheme 1. Synthesis of P,S ligand (**S**)-**1**. Conditions: (i) HBF_4, (ii) *p*-HSC_6H_4OH, (iii) $P(NMe_2)_3$.



Scheme 2. Synthesis of dendrimer $\mathbf{G}_1$. Conditions: (i) (**S**)-**1** (12 eq.), Cs_2CO_3 or HNa (12 eq.), THF, RT overnight.

of (**S**)-**3** using tris(dimethylamino)phosphine (Scheme 1) [8a].

The structure of **3** has been confirmed by X-ray diffraction analysis of the racemic mixture [9] on monocrystals (Fig. 1) [10]. As observed in related ferrocene derivatives [11], the S attached to the phosphine group is endo with respect to the Cp ring (−0.83(2) Å) whereas the S attached to the phenol group is exo by 1.72(2) Å. The two Cp rings are nearly eclipsed and bond lengths and angles within the ferrocene moiety are as usual. The most interesting feature is the occurrence of hydrogen bond between the hydroxyl group of the phenol and the phosphine sulfur atom of a neighboring molecule [O–H: 0.82 Å; H···S: 2.356 Å; O···S: 3.170 Å; O–H···S 172.4°] resulting in the formation of an infinite zig-zag like chain (see Fig. 2).

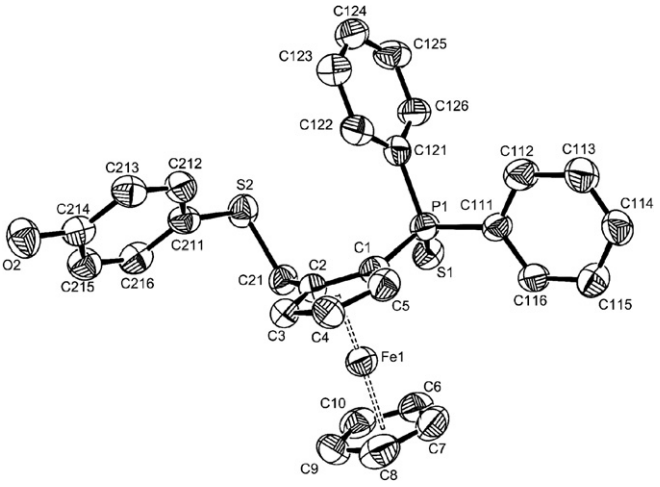


Fig. 1. X-ray structure of compound (±)-**3**.

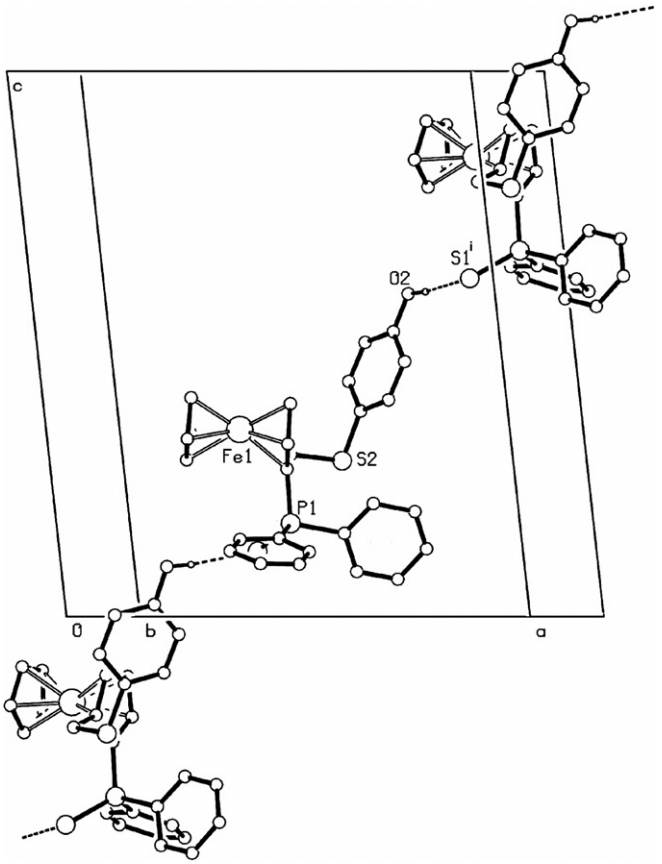


Fig. 2. Partial packing view showing the O–H···S hydrogen bonding and the formation of infinite chains developping parallel to the (1 0 −1) plane. [Symmetry code: (i) $1/2 + x$, $1/2 - y$, $1/2 + z$.]

The sodium salt of the phenol ferrocene (**S**)-**1** is readily obtained by reaction with sodium hydride in THF. The subsequent reaction of 12 equivalents of the sodium salt of (**S**)-**1** with the first generation dendrimer terminated with $-P(S)Cl_2$ functions proceeds smoothly at room temperature in THF overnight. The chiral dendrimer $\mathbf{G}_1$ is obtained in nearly quantitative yield after work up (Scheme 2) as a reddish powder which is sensitive to oxidation.

The reaction is monitored by ^{31}P NMR, which shows first a deshielding of the signal corresponding to the phosphorus atoms that undergo the reaction, from $\delta =$ 66.5 ppm for $\mathbf{G}_1$ to $\delta =$ ca. 72 ppm for the intermediate mono-arylated –P(S)Cl(O-Ar) terminations. The second chlorine substitution is accompanied by a shielding of the P(IV) surface atoms to ca. 66.2 ppm for $\mathbf{G}_1$.

The same procedure is applied to the second, third and fourth generation of $P(S)Cl_2$ terminated dendrimers, leading to dendrimers $\mathbf{G}_n$ ($n = 2, 3, 4$) possessing theoretically 24, 48 and 96 ferrocenyl (P,S) ligands, respectively (see Fig. 3). The completion of all the reactions reported here has been evidenced by TLC monitoring and multinucleus NMR.

The compound **0**, standing as a model of a monomeric single dendrimeric ending was obtained in a similar fash-

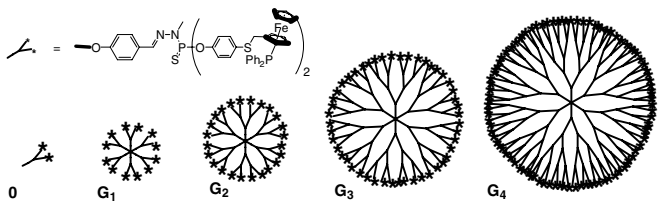


Fig. 3. Gallery of dendrimers and branch termini model.

ion, starting from crystalline PhCH=N–N(Me)P(S)Cl_2. The nucleophilic substitution of the chlorine atoms was performed in THF using either cesium carbonate or sodium hydride as a base. Lack of differences in solubility between (**S**)-**4** and **0** imposed a silica gel chromatography to obtain pure samples of the accurate branched termini model.

2.2. Catalysis

The different dendrimers were used in the allylic substitution reaction [12] under classical conditions (Table 1). The reaction times for completion were almost the same for the dendrimers of different sizes and the corresponding monomeric ligand (**S**)-**4** (Table 1).

In every case, isolated yields were very high and enantioselectivities very close to the one observed for the monomeric (**S**)-**4**. The dendrimeric structures do not affect very much the course of the catalytic reaction: no positive or negative dendritic effects [3,13] were observed in this reaction. Furthermore, we tested the influence of an excess of ligand $\mathbf{G_4}$ related to palladium: as for the monomeric ligand, the catalytic properties observed with a twofold excess of P,S ligand on the surface of the dendrimer were very similar to the ones observed with a 1.05 ligand/metal ratio (Table 1, entries 6 and 7).

The first attempts to reuse the dendritic catalysts have been carried out with $\mathbf{G_4}$ simply by precipitation with pentane at the end of the catalytic reaction (Table 1, entry 8). The catalytic activity and the enantioselectivity decreased significantly. So, further studies towards an efficient recycling of these dendrimeric catalysts, for instance, by screening of solvants for the precipitation or by more sophisticated methods, like continuous homogeneous catalysis with nanofiltration [14], will be necessary.

2.3. Conclusion

In conclusion, chiral ferrocenyl P,S ligands have been successfully grafted on the surface of phosphorus-containing dendrimers of various sizes (from model compound **0** with 2 ferrocenyl P,S ligands to generation 4 with 96 ferrocenyl P,S ligands). These new dendrimeric ligands were successfully used in the asymmetric allylic substitution: the catalytic properties of the original monomeric ligand were left almost unaffected after grafting on the different dendrimeric scaffolds, as shown by comparison of activities between the monomer itself, the dendrimers $\mathbf{G_{1-4}}$ and the branch termini model **0**. Indeed, these organometallic dendrimers are efficient soluble polymer-supported catalysts [15].

3. Experimental

3.1. General

All reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. Commercial samples were used as received. All solvents were dried before use. Thin layer chromatography was carried out on Merck Kieselgel 60F254 precoated silica

Table 1
Palladium-catalyzed asymmetric allylic substitution

Entry	Ligand[a]	Reaction time	Conversion (%)	Yield[b] (%)	ee[c] (%)
1	(**S**)-**4Ph**	2 h:30 min	100	96	93
2	**0**	2 h:30 min	100	95	91
3	$\mathbf{G_1}$	3 h	100	89	93
4	$\mathbf{G_2}$	3 h	100	93	92
5	$\mathbf{G_3}$	3 h	100	94	90
6	$\mathbf{G_4}$	2 h:30 min	100	92	91
7	$\mathbf{G_4}$[d]	2 h:30 min	100	87	92
8	$\mathbf{G_4}$[e]	6 h	100	88	81

[a] Reaction run with 0.5 mmol of *rac*-1,3-diphenylprop-2-enyl acetate, 1 mmol of dimethylmalonate, 1 mmol of BSA, a catalytic amount of LiOAc, the ligand and 0.01 mol of dimeric palladium precursor (2 mol% in palladium as $[PdCl(allyl)]_2$) in 2 mL of dichloromethane at RT; with a 1.05 P,S ligand/Pd ratio.

[b] Isolated yield.

[c] (*R*) configuration,determined by ^{1}H NMR using Eu-(+)-$(hfc)_3$ as chiral chemical shift reagent.

[d] P,S ligand/Pd ratio was 2.

[e] Reused catalyst: at the end of a catalytic run, the dendrimer was precipitated and washed with dry pentane under argon. After evaporation under vacuum, the remaining oil was reused by adding 2 mL of dry dichloromethane, 0.5 mmol of *rac*-1,3-diphenylprop-2-enyl acetate, 1 mmol of dimethylmalonate, 1 mmol of BSA and a catalytic amount of LiOAc.

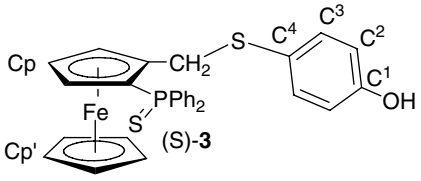
gel plates. Preparative flash chromatography was performed on Merck Kieselgel. Instrumentation: Bruker AC200, AM250, ARX250, AMX400 and DPX300 (^{1}H, ^{13}C and ^{31}P NMR), Hewlett–Packard HP MSD 7590 (GC/MS). Elemental analyses were performed by the Service d'Analyse du Laboratoire de Chimie de Coordination, Toulouse (France).

3.2. Published procedures

Dendrimers terminated with $P(S)Cl_2$ groups [16] were synthesized according to published procedures.

(*S*)-2-Thiodiphenylphosphino-(4-hydroxyphenylthiomethyl)ferrocene was synthesized from (*S*)-2-thio-diphenylphosphino-(hydroxymethyl)ferrocene and 4-hydroxythiophenol by a published procedure (yield = 95%) [8a].

3.2.1. Synthesis of (*S*)-2-thiodiphenylphosphino-(4-hydroxyphenylthiomethyl)ferrocene (***S***)–(***3***)



^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$) δ = 44.5 ppm.

^{1}H NMR (500.3 MHz, $CDCl_3$) δ = 3.79 (1H, br s, Cp-H); 4.12 (1H, d (AB), J_{HH} = 13.5 Hz, CH_2); 4.27 (1H, m, Cp-H); 4.31 (5H, s, Cp′-H); 4.39 (1H, m, Cp-H); 4.43 (1H, d (AB), J_{HH} = 13.5 Hz, CH_2); 6.73 (2H, br d (AB), J_{HH} = 8.6 Hz, C^2-H); 7.15 (2H, br d (AB), J_{HH} = 8.6 Hz, C^3-H); 7.56–7.39 (6H, m, PPh_2); 7.72–7.66 (2H, m, PPh_2); 7.8–7.80 (2H, m, PPh_2) ppm.

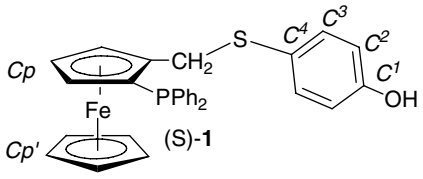
^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ = 35.5 (s, CH_2); 69.5 (d, J_{CP} = 10.4 Hz, Cp); 71.3 (s, Cp′); 74.0 (d, J_{CP} = 95.2 Hz, Cp_{ipso}); 74.2 (d, J_{CP} = 9.2 Hz, Cp); 75.0 (d, J_{CP} = 12.5 Hz, Cp); 89.6 (d, J_{CP} = 12.0 Hz, Cp_{ipso}); 116.3 (s, C^2); 127.3 (s, C^4); 128.5 (d, J_{CP} = 14.3 Hz, PPh_2); 128.6 (d, J_{CP} = 14.5 Hz, PPh_2); 131.7 (d, J_{CP} = 2.7 Hz, $2CPPh_2$); 132.5 (d, J_{CP} = 10.8 Hz, PPh_2); 132.6 (d, J_{CP} = 10.7 Hz, PPh_2); 133.8 (d, J_{CP} = 90.5 Hz, quat PPh_2); 134.3 (s, C^3); 134.8 (d, J_{CP} = 89.5 Hz, quat PPh_2); 155.5 (s, C^1) ppm.

$[\alpha]_D$ = +47.6 ($CHCl_3$, c = 0.6) MS (DCI, NH_3) *m/e*: 541 (M+1, 100%), 415 (M-Ar, 59%).

Elem. Anal. Calc. for $C_{29}H_{25}FeOPS_2$ (540.47 g mol^{-1}): C, 64.55; H, 4.66. Found: C, 64.36; H, 4.53%.

3.2.2. Synthesis of (*S*)-2-diphenylphosphino-(4-hydroxyphenylthiomethyl)ferrocene (***S***)–(***1***)

The desulfuration of (*S*)-2-thiodiphenylphosphino-(4-hydroxyphenylthiomethyl)-ferrocene into (*S*)-2-diphenylphosphino-(4-hydroxyphenylthiomethyl)ferrocene was carried out using tris(dimethylamino)phosphine [8a] (yield = 91%).



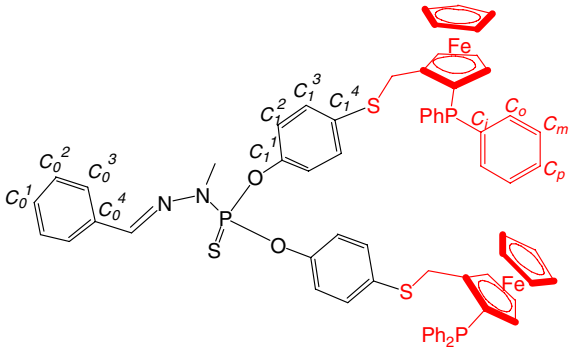
^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$) δ = −21.5 ppm.

^{1}H NMR (500.3 MHz, $CDCl_3$) δ = 3.84 (1H, m, Cp-H); 4.03 (5H, s, Cp′-H); 4.06 (2H, br s, CH_2); 4.29 (1H, br t, *J* = 2.5 Hz, Cp-H); 4.37 (1H, m, Cp-H); 6.74 (2H, m, C^2-H); 7.21 (2H, m, C^3-H); 7.3–7.2 (5H, m, PPh_2); 7.45–7.40 (3H, m, PPh_2); 7.65–7.60 (2H, m, PPh_2) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ = 36.4 (s, CH_2); 70.0 (s, Cp); 70.3 (s, Cp′); 71.9 (d, J_{CP} = 3.7 Hz, Cp); 72.2 (d, J_{CP} = 3.6 Hz, Cp); 75.9 (d, J_{CP} = 6.8 Hz, Cp_{ipso}); 90.7 (d, J_{CP} = 25.8 Hz, Cp_{ipso}); 116.4 (s, C^2); 127.4 (s, C^4); 128.3 (s, PPh_2); 128.4 (d, J_{CP} = 6.0 Hz, PPh_2); 128.6 (d, J_{CP} = 8.0 Hz, PPh_2); 129.7 (s, PPh_2); 132.9 (d, J_{CP} = 17.6 Hz, PPh_2); 134.4 (s, C^3); 135.6 (d, J_{CP} = 21.1 Hz, PPh_2); 137.9 (d, J_{CP} = 7.2 Hz, quat PPh_2); 140.1 (d, J_{CP} = 7.9 Hz, quat PPh_2); 155.5 (s, C^1) ppm.

3.2.3. Synthesis of model compound ***0***

To a suspension of cesium carbonate (609 mg, 1.86 mmol) in 10 mL of THF was added ferrocene (**S**)-**1** (440 mg, 0.86 mmol). The mixture was stirred for 3 h at room temperature and then was added dropwise a solution of PhCH=NN(Me)$P(S)Cl_2$ (112 mg, 0.42 mmol) in 5 mL of THF at room temperature. The resulting mixture was stirred overnight at room temperature and then centrifuged. The clear solution was then concentrated under reduced pressure and precipitated with pentane. The resulting yellow powder was subjected to column chromatography (CH_2Cl_2) to afford the expected compound **0** as a yellow powder in 80% yield (774 mg).



^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ = −20.7 (s,Cp-PPh_2); 66.1 (s, PS) ppm.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.36 (d, $^3J_{HP}$ = 10.5 Hz, 3H, P-N-Me); 3.83 (br s, 2H, Cp-H);

4.03 (br s, 10H, Cp′-H); 4.07 (s, 4H, CH_2); 4.26 (s, 2H, Cp-H); 4.37 (s, 2H, Cp-H); 7.19–7.79 (m, 34H, H_{arom} and CH=N) ppm.

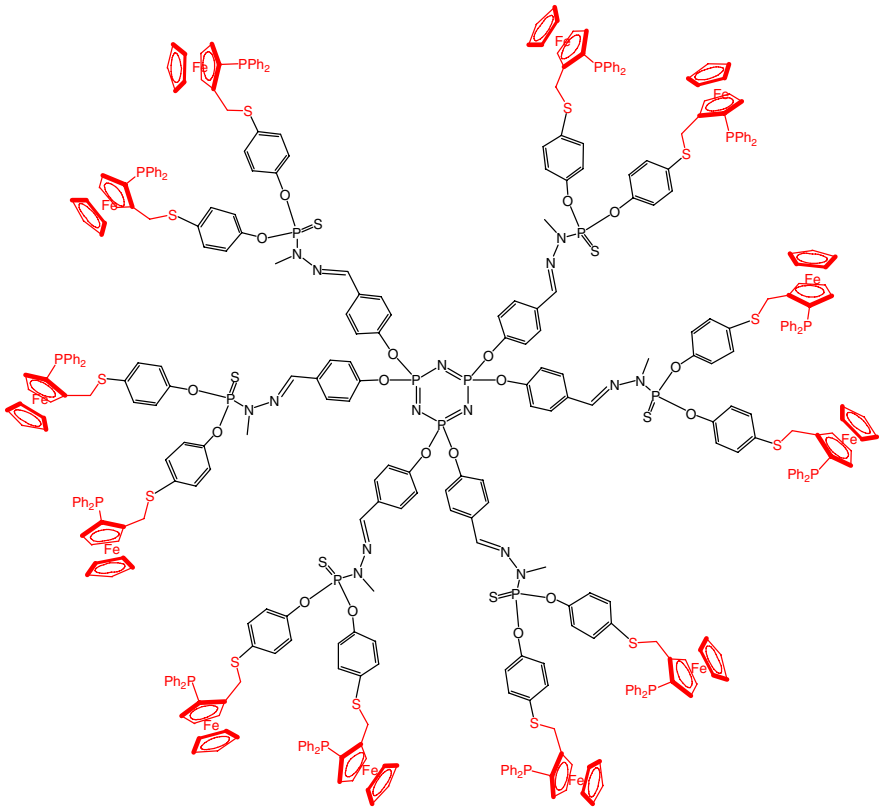
$^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$) $\delta = 33.37$ (d, $^2J_{CP} = 12.1$ Hz, P-N-Me); 34.91 (d, $^3J_{CP} = 12.0$ Hz, CH_2); 70.1 (s, Cp); 70.3 (s, Cp′), 71.91 (d, $^2J_{CP} = 3.0$ Hz, Cp); 72.13 (br s, Cp); 75.8 (d, $J_{CP} = 7.8$ Hz, Cp_{ipso}); 89.5 (d, $J_{CP} = 26.2$ Hz, Cp_{ipso}); 122.26 (d, $^3J_{CP} = 6.2$ Hz, C_1^2); 127.5 (s, C_0^2); 128.42 (br d, $^3J_{CP} = 5.9$ Hz, C_m); 128.46 (s, C_p); 128.61 (d, $^3J_{CP} = 8.1$ Hz, C_m); 129.21 (s, C_1^3); 129.68 (s, C_0^3); 129.92 (s, C_0^1); 131.88 (s, C_1^4); 132.86 (d, $^2J_{CP} = 17.7$ Hz, C_o); 134.08 (s, C_0^4); 135.43 (d, $^2J_{CP} = 20.8$ Hz, C_o); 138.12 (d, $^1J_{CP} = 8.2$ Hz, C_i); 140.12 (d, $^3J_{CP} = 13.8$ Hz, CH=N); 140.72 (d, $^1J_{CP} = 8.1$ Hz, C_i); 150.03 (d, $^2J_{CP} = 6.2$ Hz, C_1^1) ppm.

Elem. Anal. Calc. for $C_{66}H_{57}Fe_2N_2O_2P_3S_3$ (1211 g mol^{-1}): C, 65.46; H, 4.74; N, 2.31. Found: C, 65.56; H, 4.85; N, 2.25%.

3.3. Synthesis of dendrimers

3.3.1. Synthesis of dendrimer G_1

To a suspension of 8 mg (0.33 mmol) of sodium hydride in 20 mL of THF was added 167 mg (0.33 mmol) of ferrocene (**S**)-**1**. The mixture was stirred for 3 h at room temperature and then added dropwise to a solution of first generation phosphorus dendrimer capped with 6 $P(S)Cl_2$ end groups (50 mg, 0.027 mmol) in 20 mL of THF at room temperature. The resulting mixture was stirred overnight at room temperature and then centrifuged. The clear solution was then concentrated under reduced pressure and precipitated with ether. The resulting powder was dried and washed twice with 40 mL of a mixture ether–pentane (1/1) to afford the expected dendrimer $\mathbf{G}_1$ as a yellow powder in 91% yield (184 mg).



$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) $\delta = -20.8$ (s, Cp-PPh_2); 11.8 (s, N_3P_3); 66.2 (s, P_1) ppm.

^1H NMR (300 MHz, $CDCl_3$) $\delta = 3.21$ (d, $^3J_{HP} = 10.2$ Hz, 18H, P-N-Me); 3.74 (br s, 12H, Cp-H); 3.97 (br s, 60H, Cp′-H); 4.04 (s, 24H, CH_2); 4.22 (s, 12H, Cp-H); 4.33 (s, 12H, Cp-H); 7.09–7.69 (m, 198H, H_{arom} and CH=N) ppm.

$^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$) $\delta = 33.12$ (d, $^2J_{CP} = 12.2$ Hz, P-N-Me); 34.92 (d, $^3J_{CP} = 12.5$ Hz, CH_2); 69.67 (s, Cp); 69.86 (s, Cp′), 71.48 (d, $^2J_{CP} = 3.1$ Hz, Cp); 71.66 (br s, Cp); 75.86 (d, $J_{CP} = 7.9$ Hz, Cp_{ipso}); 89.52 (d, $J_{CP} = 26.2$ Hz, Cp_{ipso}); 121.39 (br s, C_0^2); 121.77 (br s, C_1^2); 127.89 (d, $^3J_{CP} = 7.7$ Hz, C_m); 128.06 (s, C_p); 128.17 (d, $^3J_{CP} = 8.2$ Hz, C_m); 129.21 (s, C_0^3); 131.27 (s, C_1^3); 132.22 (s, C_0^4); 132.35 (d, $^2J_{CP} = 17.7$ Hz, C_o); 134.05 (s, C_1^4); 135.12 (d, $^2J_{CP} = 18.7$ Hz, C_o); 137.06 (d,

$^{1}J_{CP} = 8.4$ Hz, C_i); 139.64 (d, $^{3}J_{CP} = 13.9$ Hz, CH=N); 139.71 (d, $^{1}J_{CP} = 8.0$ Hz, C_i); 148.98 (d, $^{2}J_{CP} = 6.6$ Hz, C_1^1); 148.98 (br s, C_0^1) ppm.

Elem. Anal. Calc. for $C_{396}H_{336}Fe_{12}N_{15}O_{18}P_{21}S_{18}$ (7491 g mol^{-1}): C, 63.49; H, 4.52; N, 2.80. Found: C, 63.57; H, 4.60; N, 2.72%.

3.3.2. Synthesis of dendrimer G_2

To a suspension of 5 mg (0.21 mmol) of sodium hydride in 20 mL of THF was added 102 mg (0.20 mmol) of ferrocene (**S**)-**1**. The mixture was stirred for 3 h at room temperature and then added dropwise to a solution of second generation phosphorus dendrimer capped with 12 $P(S)Cl_2$ end groups (40 mg, 8.3×10^{-3} mmol) in 20 mL of THF at room temperature. The resulting mixture was stirred overnight at room temperature and then centrifuged. The clear solution was then concentrated under reduced pressure and precipitated with ether. The resulting powder was dried and washed twice with 40 mL of a mixture ether–pentane (1/1) to afford the expected dendrimer $\mathbf{G_2}$ as a yellow powder in 89% yield (119 mg).

$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$) $\delta = -20.8$ (s,Cp-PPh_2); 11.8 (s, N_3P_3); 66.0 (s, P_1); 66.2 (s,P_2) ppm.

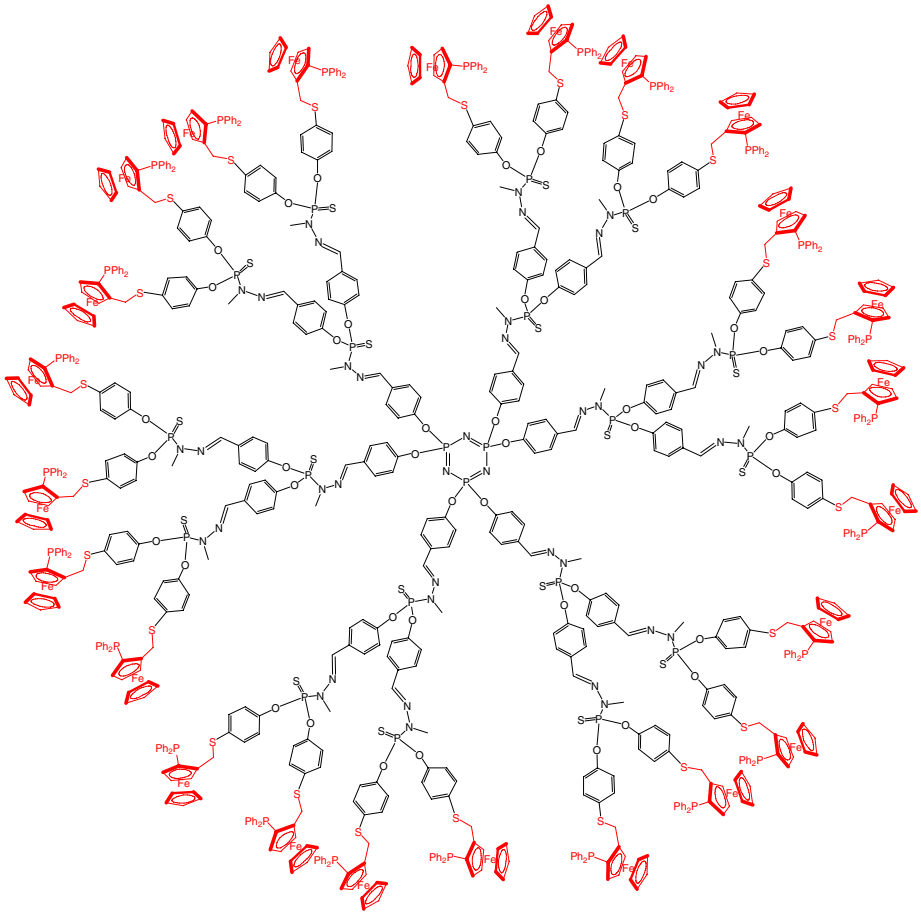
^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 3.21$ (br d, $^{3}J_{HP} = 10.5$ Hz, 54H, P-N-Me); 3.77 (br s, 24H, Cp-H); 3.95 (br s, 120H, Cp′-H); 4.03 (s, 48H, CH_2); 4.21 (s, 24H, Cp-H); 4.32 (s, 24H, Cp-H); 7.02–7.72 (m, 426H, H_{arom} and CH=N) ppm.

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$) $\delta = 33.46$ (d, $^{2}J_{CP} = 13.3$ Hz, P-N-Me); 34.87 (d, $^{3}J_{CP} = 12.5$ Hz, CH_2); 70.05 (s, Cp); 70.27 (s, Cp′); 71.90 (d, $^{2}J_{CP} = 3.0$ Hz, Cp); 72.01 (br s, Cp); 75.29 (d, $J_{CP} = 8.0$ Hz, Cp_{ipso}); 89.98 (d, $J_{CP} = 31.6$ Hz, Cp_{ipso}); 121.03 (br s, C_0^2); 122.25 (br d, $^{3}J_{CP} = 3.9$ Hz, $C_{1,2}^2$); 128.29 (d, $^{3}J_{CP} = 9.1$ Hz, C_m); 128.43 (s, C_p); 128.56 (d, $^{3}J_{CP} = 8.0$ Hz, C_m); 129.60 (s, $C_{0,1}^3$); 131.77 (s, C_2^3); 132.21 (s, $C_{0,1}^4$); 132.74 (d, $^{2}J_{CP} = 17.6$ Hz, C_o); 134.33 (s, C_2^4); 135.47 (d, $^{2}J_{CP} = 21.2$ Hz, C_o); 137.06 (d, $^{1}J_{CP} = 8.4$ Hz, C_i); 139.64 (br d, $^{3}J_{CP} = 13.7$ Hz, CH=N); 139.71 (d, $^{1}J_{CP} = 8.0$ Hz, C_i); 149.52 (br d, $^{2}J_{CP} = 6.4$ Hz, C_2^1); 151.72 (br s, $C_{0,1}^1$) ppm.

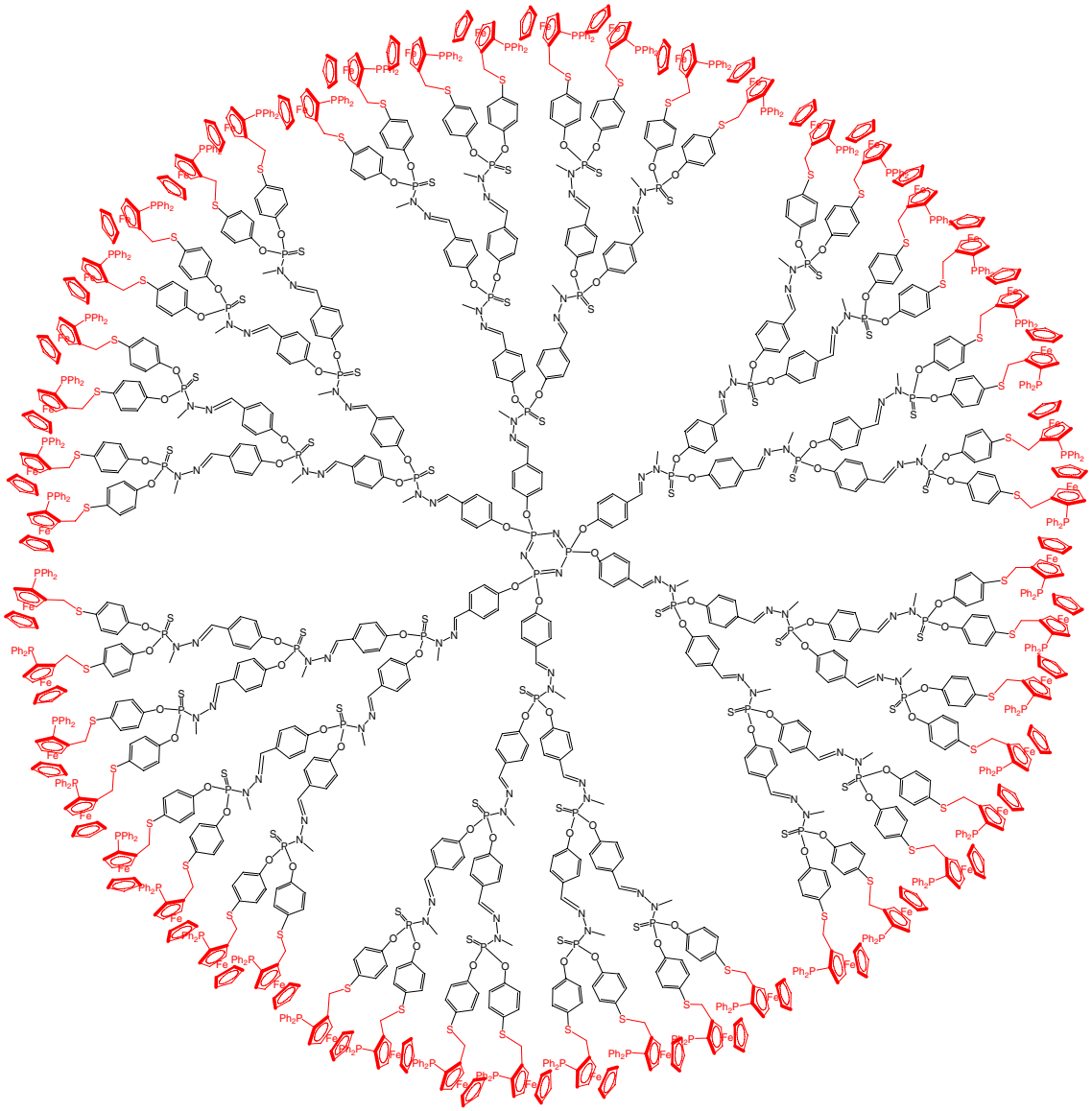
Elem. Anal. Calc. for $C_{840}H_{720}Fe_{24}N_{39}O_{42}P_{45}S_{42}$ (16 114 g mol^{-1}): C, 62.61; H, 4.50; N, 3.39. Found: C, 62.62; H, 4.59; N, 3.32%.

3.3.3. Synthesis of dendrimer G_3

To a suspension of 13 mg (0.52 mmol) of sodium hydride in 20 mL of THF was added 250 mg (0.49 mmol) of ferrocene (**S**)-**1**. The mixture was stirred for 3 h at room temperature and then added dropwise to a solution of third generation phosphorus dendrimer capped with 24 $P(S)Cl_2$ end groups (100 mg, 9.3×10^{-3} mmol) in 20 mL of THF at room temperature. The resulting mixture was stirred



overnight at room temperature and then centrifuged. The clear solution was then concentrated under reduced pressure and precipitated with ether. The resulting powder was dried and washed twice with 40 mL of ether to afford the expected dendrimer $\mathbf{G_3}$ as a yellow powder in 93% yield (360 mg).



$^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) $\delta = -20.8$ (s, Cp-PPh_2); 11.7 (s, N_3P_3); 66.2 (br s, $P_{1,2,3}$) ppm.

^1H NMR (200 MHz, $CDCl_3$) $\delta = 3.22$ (br s, 126H, P-N-Me); 3.74 (br s, 48H, Cp-H); 3.92 (br s, 240H, Cp′-H); 4.03 (s, 96H, CH_2); 4.23 (s, 48H, Cp-H); 4.28 (s, 48H, Cp-H); 7.02–7.72 (m, 882H, H_{arom} and CH=N) ppm.

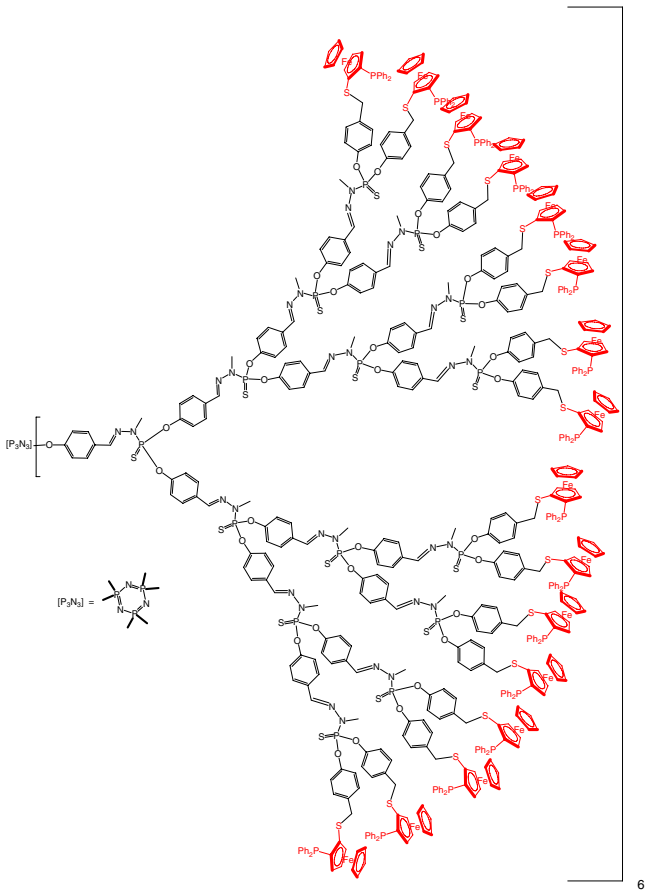
$^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$) $\delta = 33.07$ (d, $^2J_{CP} = 12.6$ Hz, P-N-Me); 34.47 (d, $^3J_{CP} = 12.2$ Hz, CH_2); 69.66 (s, Cp); 69.84 (s, Cp′); 71.90 (d, $^2J_{CP} = 3.0$ Hz, Cp); 72.01 (br s, Cp); 75.29 (d, $J_{CP} = 8.0$ Hz, Cp_{ipso}); 89.98 (d, $J_{CP} = 31.6$ Hz, Cp_{ipso}); 121.03 (br s, C_0^2); 122.25 (br d, $^3J_{CP} = 3.9$ Hz, $C_{1,2,3}^2$); 128.29 (d, $^3J_{CP} = 9.1$ Hz, C_m); 128.43 (s, C_p); 128.56 (d, $^3J_{CP} = 8.0$ Hz, C_m); 129.60 (s, $C_{0,1,2}^3$); 131.77 (s, C_3^3); 132.21 (s, $C_{0,1,2}^4$); 132.74 (d, $^2J_{CP} = 17.6$ Hz, C_o); 134.33 (s, C_3^4); 135.47 (d, $^2J_{CP} = 21.2$ Hz, C_o); 137.06 (d, $^1J_{CP} = 8.4$ Hz, C_i); 139.64 (br d, $^3J_{CP} = 13.7$ Hz, CH=N); 139.71 (d, $^1J_{CP} = 8.0$ Hz, C_i); 149.52 (br d, $^2J_{CP} = 6.4$ Hz, C_3^1); 151.72 (br s, $C_{0,1,2}^1$) ppm.

Elem. Anal. Calc. for $C_{1728}H_{1488}Fe_{48}N_{87}O_{90}P_{93}S_{90}$ (36 360 g mol^{-1}): C, 62.22; H, 4.50; N, 3.65. Found: C, 62.38; H, 4.59; N, 3.56%.

3.3.4. Synthesis of dendrimer G_4

To a suspension of 6 mg (0.25 mmol) of sodium hydride in 20 mL of THF was added 109 mg (0.21 mmol) of ferrocene (**S**)-**1**. The mixture was stirred for 3 h at room temperature and then added dropwise to a solution of fourth

generation phosphorus dendrimer capped with 48 $P(S)Cl_2$ end groups (50 mg, 2.21×10^{-3} mmol) in 20 mL of THF at room temperature. The resulting mixture was stirred overnight at room temperature and then centrifuged. The clear solution was then concentrated under reduced pressure and precipitated with ether. The resulting powder was dried and washed twice with 40 mL of ether to afford the expected dendrimer $\mathbf{G_4}$ as a yellow powder in 93% yield (139 mg).



$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) $\delta = -20.8$ (s, Cp-PPh_2); 11.8 (s, N_3P_3); 66.0 (br s, $P_{1,2,3,4}$) ppm.

^1H NMR (300 MHz, $CDCl_3$) $\delta = 3.24$ (br s, 270H, P-N-Me); 3.77 (br s, 96H, Cp-H); 3.98 (br s, 480H, Cp′-H); 4.05 (s, 192H, CH_2); 4.22 (s, 96H, Cp-H); 4.33 (s, 96H, Cp-H); 7.01–7.82 (m, 1794H, H_{arom} and CH=N) ppm.

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) $\delta = 33.49$ (d, $^2J_{CP} = 12.9$ Hz, P-N-Me); 34.93 (d, $^3J_{CP} = 12.2$ Hz, CH_2); 69.99 (s, Cp); 70.26 (s, Cp′); 71.97 (d, $^2J_{CP} = 3.0$ Hz, Cp); 72.05 (br s, Cp); 75.49 (d, $J_{CP} = 8.1$ Hz, Cp_{ipso}); 90.08 (d, $J_{CP} = 31.4$ Hz, Cp_{ipso}); 121.03 (br s, C_0^2); 122.21 (br d, $^3J_{CP} = 4.3$ Hz, $C^2_{0,1,2,3,4}$); 128.29 (d, $^3J_{CP} = 8.4$ Hz, C_m); 128.43 (s, C_p); 128.56 (d, $^3J_{CP} = 7.9$ Hz, C_m); 129.59 (s, $C^3_{0,1,2,3}$); 131.86 (s, C_4^3); 132.17 (br s, $C^4_{0,1,2,3}$); 132.79 (d, $^2J_{CP} = 17.8$ Hz, C_o); 134.23 (s, C_4^4); 135.47 (d, $^2J_{CP} = 21.3$ Hz, C_o); 137.86 (d, $^1J_{CP} = 8.2$ Hz, C_i); 139.64 (br d, $^3J_{CP} = 13.6$ Hz, CH=N); 139.71 (d, $^1J_{CP} = 8.0$ Hz, C_i); 149.52 (br s, C_4^1); 151.72 (br s, $C^1_{0,1,2,3}$) ppm.

Elem. Anal. Calc. for $C_{3504}H_{3024}Fe_{96}N_{183}O_{186}P_{189}S_{186}$ (67 852 g mol^{-1}): C, 62.02; H, 4.49; N, 3.79. Found: C, 62.15, H, 4.55; N, 3.68%.

3.4. Catalytic studies: palladium-catalysed allylic substitution

In a Schlenk tube, under argon, a mixture of dendrimer (2.1 mol% of P,S chelate), 1,3-diphenylprop-2-enyl acetate (0.126 g, 0.5 mmol) and $[Pd(C_3H_5)Cl]_2$ (1.8 mg, 2 mol% of palladium) was dissolved in dry dichloromethane (2 mL). Dimethyl malonate (0.115 mL, 1 mmol), potassium acetate and N,O-bis(trimethylsilyl)acetamide (BSA) (0.250 mL, 1 mmol) were added to the resulting solution. The reaction was carried out at room temperature and monitored by TLC for disappearance of acetate. After complete reaction, the mixture was quenched with a saturated aqueous solution of ammonium chloride (20 mL). The aqueous phase was extracted with dichloromethane, the combined organics were dried over magnesium sulfate, filtered and the solvents evaporated. The conversion was calculated from the crude reaction mixture by ^1H NMR spectroscopy. Subsequent purification by chromatography on silica eluting

Table 2
Crystal data and structure refinement

Identification code	**S-(3)**
Empirical formula	$C_{29}H_{25}FeOPS_2$
Formula weight	540.43
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	15.8446(18)
b (Å)	8.7666(9)
c (Å)	18.108(3)
α (°)	90
β (°)	96.456(15)
γ (°)	90
Volume (Å^3)	2499.3(5)
Z	4
D_{calc} (Mg/m^3)	1.436
Absorption coefficient (mm^{-1})	0.856
$F(000)$	1120
Crystal size (mm)	$0.33 \times 0.23 \times 0.2$
θ Range for data collection (°)	1.81–20.89
Index ranges	$-15 \leqslant h \leqslant 15$, $-8 \leqslant k \leqslant 8$, $-18 \leqslant l \leqslant 18$
Reflections collected	12 698
Independent reflections (R_{int})	2604 (0.1454)
Completeness to $\theta = 20.89°$ (%)	98.5
Absorption correction	Empirical (DIFABS)
Maximum and minimum transmission	0.6893 and 0.2258
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2604/0/308
Goodness-of-fit on F^2	0.959
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0767$, $wR_2 = 0.1896$
R indices (all data)	$R_1 = 0.1221$, $wR_2 = 0.2193$
Largest difference in peak and hole (e Å^{-3})	0.408 and −0.473

with dichloromethane/pentane (1:1) afforded the product as colorless oil. The enantiomeric excess was determined by ^{1}H NMR spectroscopy using the chiral shift reagent (+) Eu(hfc)$_3$.

3.5. X-ray crystallographic study

Single crystal was mounted under inert perfluoropolyether at the tip of glass fibre and cooled in the cryostream of the Stoe IPDS diffractometer. Data were collected using the monochromatic Mo Kα radiation ($\lambda = 0.71073$). The final unit cell parameters were obtained by the least-squares refinement of a large number of selected reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

The structure was solved by direct methods (SIR-97 [17]) and refined by least-squares procedures on F^2 with the SHELXL-97 program [18] using the integrated system WINGX(1.63) [19]. H atoms were introduced at calculated positions and treated as riding on their parent atoms [d(CH) = 0.96 Å, d(OH) = 0.82 Å] with a displacement parameter equal to 1.2U_{eq} (C_6H_5, CH_2, OH) times that of the parent atom. Owing to the poor diffracting ability of the crystal, refinement was carried out using only the reflections with a Bragg angle less than 21°. The Molecular views were realised with the help of ORTEP-III [20]. Crystal data and refinement parameters are shown in Table 2.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure of compound **3** have been deposited with the Cambridge Crystallographic Data Centre. CCDC 602136 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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