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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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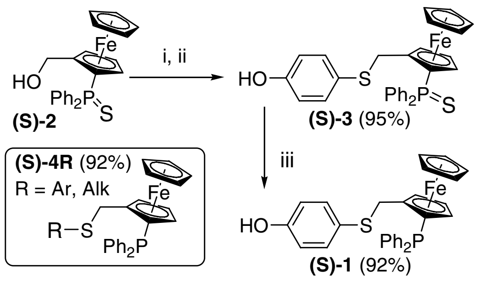
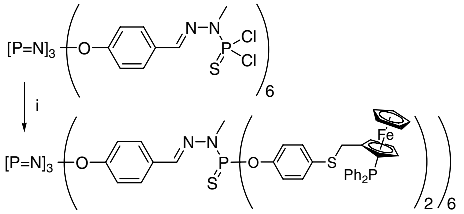


Scheme 1. Synthesis of P,S ligand (**S**)-**1**. Conditions: (i) HBF_4, (ii) *p*-HSC_6H_4OH, (iii) $P(NMe_2)_3$.



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).

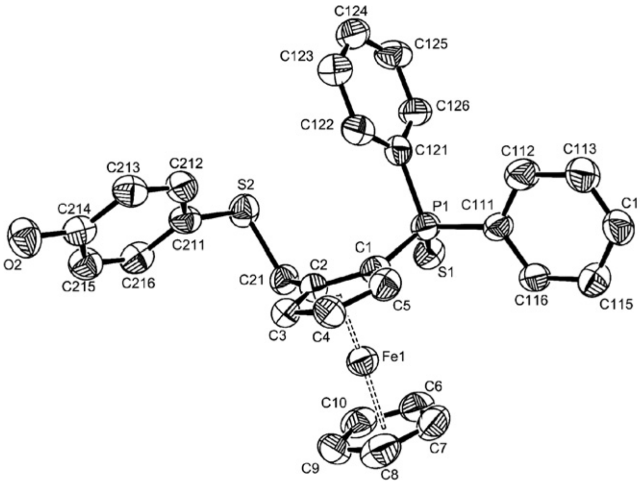


Fig. 1. X-ray structure of compound (±)-**3**.

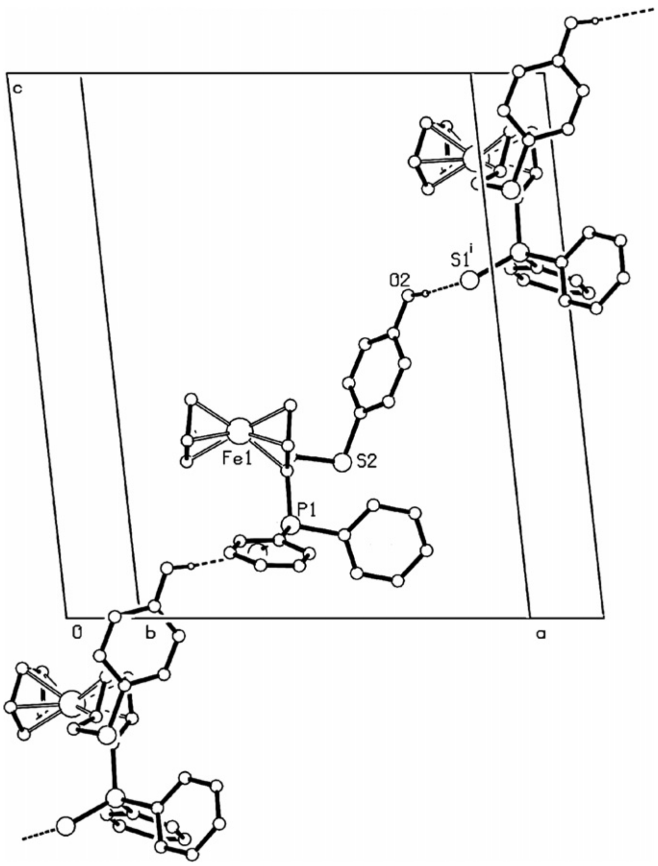


Fig. 2. Partial packing view showing the O–H···S hydrogen bonding and the formation of infinite chains developping parallel to the (1 0 −1) plane. [Symmetry code: (i) 1/2 + *x*, 1/2 − *y*, 1/2 + *z*.]

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-