



Palladocarbosilane dendrons in supercritical carbon dioxide. Catalytic behaviour in the asymmetric hydrovinylation of styrene

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ABSTRACT

The palladocarbosilane dendrons **1** and **2**, containing the *P*-stereogenic phosphine fragment at the focal point are soluble in supercritical CO₂ medium and capable to catalyze the asymmetric hydrovinylation of styrene with good activity and enantiomeric excesses.

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1. Introduction

Supercritical carbon dioxide (scCO₂) has been widely used as an alternative green reaction medium to environmentally unfriendly organic solvents. Numerous metal-catalyzed homogeneous reactions in scCO₂ have shown excellent results in terms of conversion and enantioselectivity [1–3]. However, the great limitation for the employment of CO₂ as a medium resides in the poor solubility of the generally polar homogeneous catalysts in this solvent. Consequently, an important challenge consisting in finding CO₂-philic groups able to enhance the solubility of the catalysts in the supercritical medium has emerged. In this context, besides the well-known fluorocarbons [4,5] and others [6,7], trimethylsilyl units have been shown to be good scCO₂-philic groups [8,9] with the additional interest that the synthesis of species containing such kind of units is generally inexpensive. Recently, de Jesús and co-workers [10] applied these concepts in the area of dendrimers and they demonstrated that palladium dendrimers containing functionalized phosphines with trialkylsilyl groups are relatively soluble in scCO₂ and capable to catalyze selected Heck coupling reactions. In the last years, our group has been interested in the study of the catalytic behaviour of metal-containing

carbosilane dendrimers [11–13] and recently we extended our studies to those metal-containing dendrimers functionalized with *P*-stereogenic phosphines in the surface [14,15] in order to apply them in asymmetric catalysis. In particular, a group of pallado-dendrimers (**A** and **B** in Fig. 1) were used as catalysts in the asymmetric hydrovinylation of styrene in dichloromethane [16] and scCO₂ solvents (Scheme 1) [17]. The comparison of the catalytic results according to the nature of the solvent indicated that the activity decreased moderately in the supercritical medium, but similar selectivities and enantiomeric excesses were found in both cases. These promising results prompted us to undertake the synthesis of related carbosilane dendrons functionalized at the focal point (**1** and **2** in Fig. 2) with the *P*-stereogenic unit MePPh(2-biphenyl) [18]. The general aim of our research was to check their catalytic behaviour in scCO₂ in order to compare with that exhibited by the parent dendrimers. With respect to this, we expected that the high ratio alkylsilyl groups:palladium atom would enhance the solubility of these species in the supercritical solvent, improving, as a result, the effectiveness of the catalysts. On the other hand, we were also interested in knowing whether the steric effects generated by the restricted access to the palladium centers in the dendrons, which are supposed to be sterically protected (or even partially buried) by the arms of the dendron, would affect their reactivity, selectivity and, mainly, enantioselectivity.

Thus, in this paper we report the catalytic behaviour in scCO₂ of the two allylpalladium carbosilane dendrons **1** and **2** (Fig. 2) in the asymmetric hydrovinylation of styrene.

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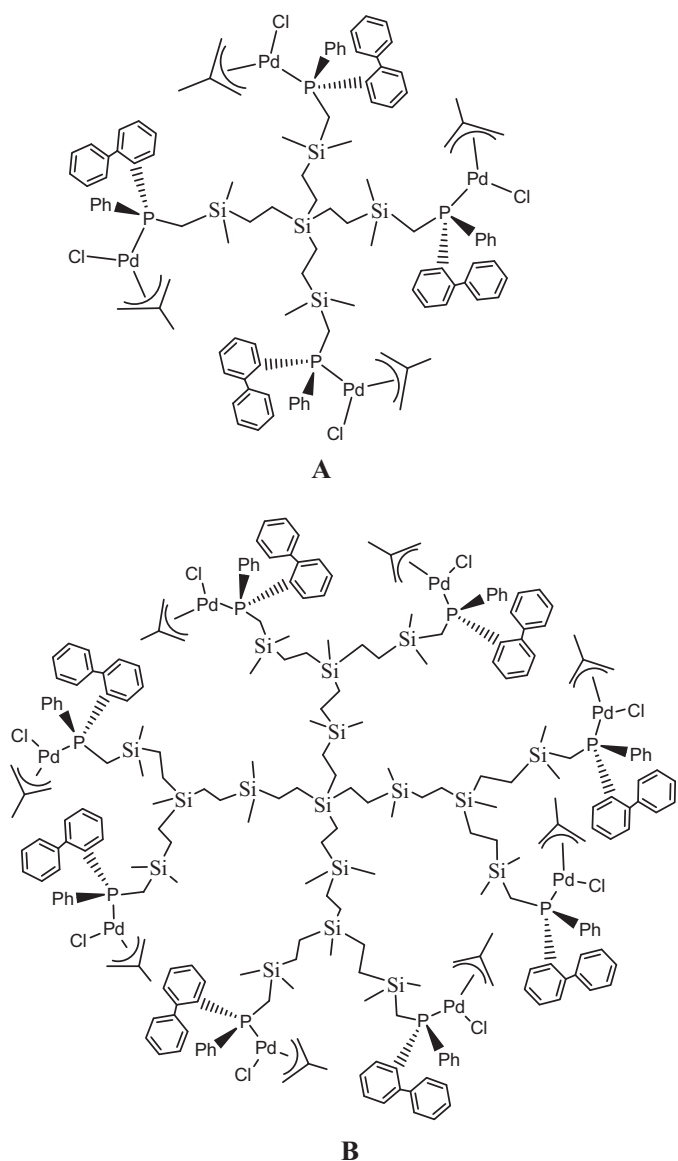
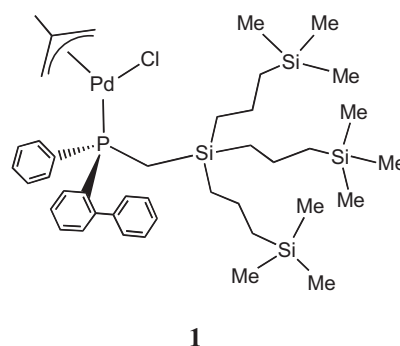


Fig. 1. Palladodendrimers **A** and **B** previously studied in the asymmetric hydrovinylation of styrene [17].

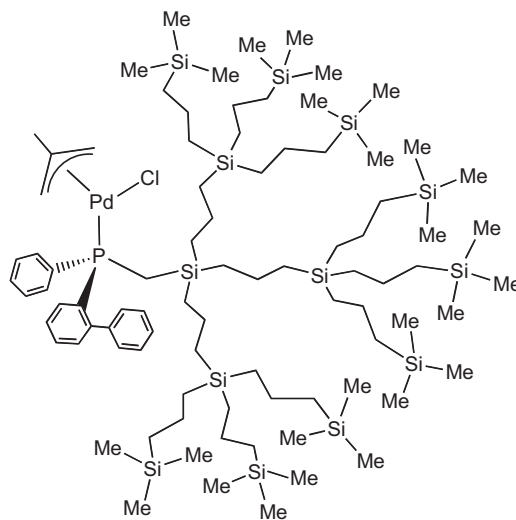
2. Experimental procedures

2.1. General catalytic procedure

A mixture of the suitable palladium complex (2.7×10^{-5} mol Pd) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) (5.3×10^{-5} mol) was loaded into a 25 mL stainless steel reactor vessel and the system was purged. Degassed styrene (8.0×10^{-3} mol) was introduced in vacuum. Then ethylene was charged (0.15×10^7 , 20 °C) and liquid carbon dioxide introduced. The contents were heated (35 or 45 °C), and compressed carbon dioxide was introduced to attain the desired reaction pressure. The mixture was magnetically stirred (750 rpm) for 2 h. After the reaction, the vessel was cooled with ice water to 0 °C and slowly



1



2

Fig. 2. Palladodendrons studied in this work in the asymmetric hydrovinylation of styrene in $scCO_2$ medium.

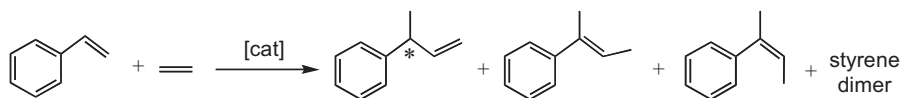
depressurized to atmospheric pressure through a cold trap. The reaction mixture was extracted with CH_2Cl_2 and HCl 10% solution (10 mL) was added. The mixture was stirred for 10 min in order to quench the catalyst. The CH_2Cl_2 layer was decanted off and dried with Na_2SO_4 . The quantitative distribution of products and their ee values were determined by GC analysis.

For the solubility experiments, a 10 mL stainless steel reactor vessel equipped with two windows was used and the same concentration of the corresponding palladium dendron, styrene and Na[BARF] was maintained.

3. Results and discussion

The asymmetric homogeneous palladium catalyzed hydrovinylation of styrene in $scCO_2$ was tested by using the palladium-containing dendrons **1** and **2** showed in Fig. 2. The synthesis of these species has been reported elsewhere [18].

It is well established that for the hydrovinylation takes place, the precatalyst should be previously activated with a chloride-abstracting agent. Generally, it is accepted that the key



Scheme 1. Hydrovinylation of styrene.

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