

Palladocarbosilane dendrimers as catalysts for the asymmetric hydrovinylation of styrene in supercritical carbon dioxide

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Abstract

The palladocarbosilane dendrimers **2** and **3**, containing the *P*-stereogenic phosphine [P(2-biphenyl)PhCH₂] fragment, and the model compound Me₃Si(P(2-biphenyl)PhCH₂)(PdCl(η³-2-MeC₃H₄)), **1**, were tested as precatalysts in the hydrovinylation of styrene, in supercritical CO₂ medium. Na[BARF] was used as a cocatalyst. In all cases, the activity was somewhat less than that observed in CH₂Cl₂, but the selectivity and enantiomeric excess were excellent and comparable with the results obtained using the conventional solvent.

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1. Introduction

Supercritical carbon dioxide is attracting increasing interest as an alternative reaction media to environmentally unfriendly organic solvents. Thus, scCO₂ is a highly effective medium for continuous catalytic reactions, including alkylation, etherification, hydroformylation, oxidation, and hydrogenation, among others [1]. However, due to the low polarity of carbon dioxide, the solubility of conventional, generally polar homogeneous catalysts, is very limited. Therefore, the quest for ligands containing solubilising, scCO₂-philic groups, has become one of the main goals in this area. The most important method so far has been the incorporation of fluorocarbons despite the disadvantages due to their high cost and potential issues concerning degradation [2]. Other scCO₂-philic groups are also known [3]. More recently, trimethylsilyl units have been incorporated to this set [4], because of their generally inexpensive synthesis and the fact that the

trimethylsilyl groups do not affect the electronic properties of the metal centers. In this context, in the area of dendrimers, a relevant report by de Jesús and co-workers [5] showed, for the first time, that a number of palladium dendrimers containing functionalized phosphines with trialkylsilyl groups, were relatively soluble in scCO₂, in clear contrast with the negligible solubility in the same solvent observed for the palladium complex [PdCl₂(PPh₃)₂]. Thus, the enhanced solubility of the dendrimers allowed successfully their employ as precatalysts in a selected Heck coupling reaction in scCO₂ [5]. These interesting findings reveal the high potential of metallodendrimers with carbosilane scaffold as catalysts in supercritical media. One of the advantages of the dendrimers as compared with their monomeric catalysts is that they permit to regulate the number and location of the catalytic entities attached to them and, significantly, they might favour the reuse of the catalysts from the products [6]. Despite this, relatively few examples using metallodendrimers in asymmetric catalysis have been reported so far [7]. The aim of this work was to explore the catalytic properties of a series of palladium dendrimeric chiral phosphines in scCO₂ in order to

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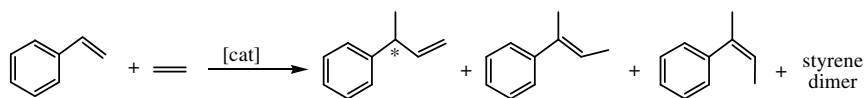
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compare them with the catalytic results, recently obtained by us [8], using dichloromethane as conventional solvent. The process investigated was the hydrovinylation of styrene and the dendrimers used as catalysts, **2** and **3**, contained the *P*-stereogenic phosphine fragments [P(2-biphenyl)PhCH₂] in the periphery. This is the first example of an asymmetric hydrovinylation in scCO₂ using palladium dendrimer catalytic precursors. On the other hand,

only Leitner et al. have studied this reaction in scCO₂ media using, in this case, nickel precursors [9].

2. Results and discussion

The homogeneous palladium catalyzed hydrovinylation of styrene was selected (Scheme 1) in order to investigate the potential for catalysis in scCO₂ of the palladodendrimers



Scheme 1.

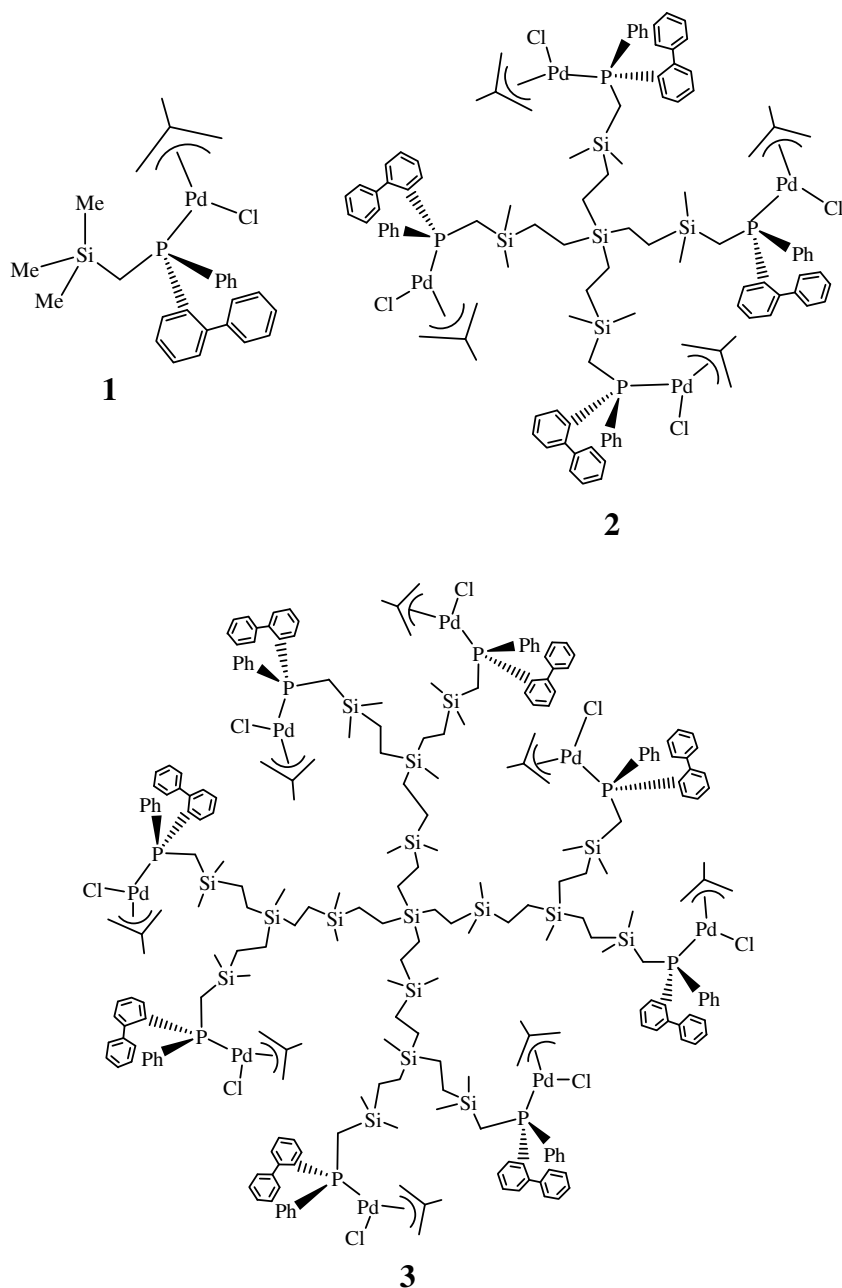


Fig. 1. Carborane compounds used in this paper.

2 and **3**, both of them containing PdCl(η^3 -2-MeC₃H₄) units grafted on their surface. The model compound **1** was also synthesized for comparison purposes (Fig. 1). The synthesis of these species was given elsewhere [8]. As it is well known, the hydrovinylation, consisting of the codimerization of alkenes with ethene to yield 3-substituted-1-butenes, requires the precatalysts to be activated with a chloride-abstracting agent. Previous work in our group [8] on the hydrovinylation of styrene demonstrated that for the palladium-containing dendrimers the best halide abstractor is the sodium salt of the weakly coordinating anion BARF, Na[BARF] (BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate). After a set of experiments designed to optimize the reaction conditions, in terms of temperature, ethylene (and total) pressure, time of reaction and styrene/Pd/Na[BARF] ratio, our experimental results are summarized in Table 1. Previously, we carried out a blank experiment to confirm that no reaction takes place in absence of catalyst.

The first point to emphasize is that the chloride abstraction took place in scCO₂ by using Na[BARF]. The excellent behaviour of this sodium salt as a cocatalyst in scCO₂ using Ni compounds as precatalysts had been described earlier [9b] and shown to be better in

terms of enantioselectivity than the most usually used Et₃Al₂Cl₃.

In general, the activity of the palladium catalysts decreased in scCO₂ medium, in comparison with the results obtained with CH₂Cl₂ [8] (Table 2, note that the Pd/styrene ratio has been changed from 1/500 (CH₂Cl₂) to 1/150 (scCO₂)). This result can be associated with the competition between the ethylene and the CO₂ for the catalytic site. The higher conversion observed (Table 1, entries 4–6) in increasing the partial pressure of ethylene seems to confirm this hypothesis. Inhibitory effect of Lewis basic species has been reported when Ni catalysts were used in this reaction [10]. Furthermore, the low polarity of the scCO₂ media can affect the stability and reactivity of the cationic intermediates and reduce the catalytic activity, as it was observed in other catalytic processes [11]. Remarkably in all cases good selectivities in the formation of 3-Ph-1-Bu were found, even in experiments with high conversions (about 55–63%) and the ratio of dimers was low (2.4% in the worst case) (Table 1, entry 4). The influence of the temperature was assessed and it was found that decrease of temperature implied less activity, as expected, and, consequently, better selectivities (Table 1, entries 7–9).

Table 1
Asymmetric hydrovinylation of styrene in scCO₂ conditions catalyzed by precursors **1**, **2**, and **3**

Entry	Precursor	Temperature (°C)	P ethylene (bar)	Conversion ^a (%)	Selectivity ^b (%)	Dimers (%)	E.e. (%) (<i>S</i>)
1	1	45	15	36.7	96.6	2.3	76
2	2	45	15	38.1	95.1	2.2	71
3	3	45	15	40.2	94.4	2.2	74
4	1	45	30	63.3	94.6	2.4	77
5	2	45	30	56.6	86.6	1.4	72
6	3	45	30	55.3	91.1	2.0	76
7	1	35	15	18.6	98.6	1.3	81
8	2	35	15	19.2	97.2	1.6	71
9	3	35	15	18.7	98.4	1.6	73

Reactions carried out at 4200 Psi of total pressure, 2 h, ratio styrene/Pd/NaBARF 150/1/2.

^a Conversion: total amount of codimers formed.

^b Selectivity: % of 3-phenyl-1-butene with respect to the codimers.

Table 2
Asymmetric hydrovinylation of styrene in CH₂Cl₂ catalyzed by precursors **1**, **2**, and **3** [8]

Entry	Precursor	<i>t</i> (h)	Conversion ^a (%)	Selectivity ^b (%)	Oligomers (%)	E.e. (%) (<i>S</i>)
1	1	2	29.3	99.9	0.9	83
2	2	2	29.5	98.5	1.0	75
3	3	2	27.4	98.6	1.1	79
4	1	6	70.4	97.7	1.8	83
5	2	6	58.4	92.0	1.6	75
6	3	6	63.1	97.1	2.0	81

Reactions carried out at 25 °C, 15 bar of initial pressure of ethylene, 10 mL of CH₂Cl₂, ratio styrene/Pd/NaBARF 500/1/2.

^a Conversion: total amount of codimers formed.

^b Selectivity: % of 3-phenyl-1-butene with respect to the codimers.

It is worth noting that the enantiomeric excesses were excellent (71–81%), the best one corresponding to the model compound **1**. In all the experiments the major enantiomer of the 3-phenyl-1-butene had the absolute configuration *S*. Interestingly, the e.e. values compare well with those found using the same catalytic precursors in CH₂Cl₂ (77–79%) and with the best palladium systems described up to date [12].

3. Conclusions

The activity in the asymmetric hydrovinylation of styrene of the palladium-containing carbosilane dendrimers **2** and **3** and the model compound **1**, in the presence of Na[BARF], decreased in scCO₂ medium, in comparison with the results obtained with the conventional CH₂Cl₂ solvent. However, good selectivities and high enantiomeric excesses (up to 81%) were found, in the line with those reported in CH₂Cl₂, so that the system palladocarbosilane dendrimers/scCO₂ medium seems to have excellent potential in the future.

4. General catalytic procedure

A mixture of the suitable palladium complex (5.3×10^{-5} mol Pd) and NaBARF (1.1×10^{-4} 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 (15 or 30 bar, 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 depressurized to atmospheric pressure through a cold trap. The reaction mixture was extracted with CH₂Cl₂ and HCl 10% solution (10 mL) was added. The mixture was stirred for 10 min in order to quench the catalyst. The CH₂Cl₂ layer was decanted off and dried with Na₂SO₄. The quantitative distribution of products and their e.e. values were determined by GC analysis.

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