



Suzuki–Miyaura reaction catalyzed by a dendritic phosphine–palladium complex



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ABSTRACT

We prepared several of a new type of a dendritic ligand with a phosphine core by using tris(4-hydroxyphenyl)phosphine oxide and poly(aryl ether) dendron. In particular, when an amphiphilic dendritic phosphine–palladium complex was used as a catalyst, the aqueous media Suzuki–Miyaura reaction proceeded smoothly to provide the corresponding cross-coupling product at 50 °C. A positive dendritic effect on chemical yields was observed.

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1. Introduction

Dendrimers are fascinating man-made macromolecules with their unique physical and chemical properties, and have been widely used as a new class of catalyst supports.¹ Metallo-dendrimers, which have a catalytic site at their core, have received considerable attention because of their unique selectivity and reactivity, which are caused by a specific reaction field constructed by the dendron.² Moreover, their solubilities and physical properties can be altered by peripheral modification.³ For example, by the introduction of hydrophilic groups to the peripheral layer of a hydrophobic dendritic ligand, the corresponding metal core dendrimers as catalysts can become water-soluble and afford unique catalytic activity.⁴

Recently, several examples of a positive dendritic effect on chemical yields—that is, an enhanced reactivity via an increase in the generation number of the dendrimers—have been reported by us⁵ and by other groups.⁶ In our previous study, it was found that a hydrophobic dendron was effective as a reaction field in aqueous media organic syntheses.^{5a,b} In this paper, we report the synthesis of novel phosphine core dendrimers having poly(benzyl ether) dendrons with the modification of the peripheral layer **1Gn[X]** (X=H, CO₂K, *n*=0–3; Fig. 1),⁷ and their application as phosphine ligands to the Suzuki–Miyaura coupling reaction catalyzed by the phosphine–palladium complex.⁸ In particular, by employing amphiphilic dendritic phosphine–palladium complexes having

potassium carboxylate units at the peripheral layer as catalysts, an aqueous media Suzuki–Miyaura reaction proceeded smoothly to provide the corresponding coupling product, and a positive dendritic effect on chemical yields was observed. Suzuki–Miyaura reaction between a boronic acid and an aryl or vinyl halide has become one of the most powerful carbon–carbon coupling methods.⁹ This coupling reaction has been widely used in the synthesis of a variety of fine chemicals and pharmaceutical products, as well as in material science. From the perspective of green chemistry, the development of an aqueous media Suzuki–Miyaura reaction is a very attractive field,¹⁰ as water is an environmentally benign solvent.¹¹

2. Results and discussion

Novel phosphine core dendrimers **1Gn[H]** (*n*=0–3), which are shown in Fig. 1, were synthesized as follows (Scheme 1). An *N,N*-dimethylformamide (DMF) solution of tris(4-hydroxyphenyl) phosphine oxide **2** and poly(benzyl ether) dendritic bromide **3Gn[H]** was stirred at 70 °C in the presence of potassium carbonate and a catalytic amount of 18-crown-6 under an argon atmosphere. The obtained dendritic phosphine oxide **4Gn[H]** was reduced by trichlorosilane in degassed xylene at 120 °C to afford the dendritic phosphine **1Gn[H]**. All transformations were carried out in good chemical yields in all generations.

We examined the utility of the dendrimer **1Gn[H]** (*n*=0–3) as a phosphine ligand by performing the Suzuki–Miyaura reaction using the corresponding **1Gn[H]**–palladium catalyst (Table 1).

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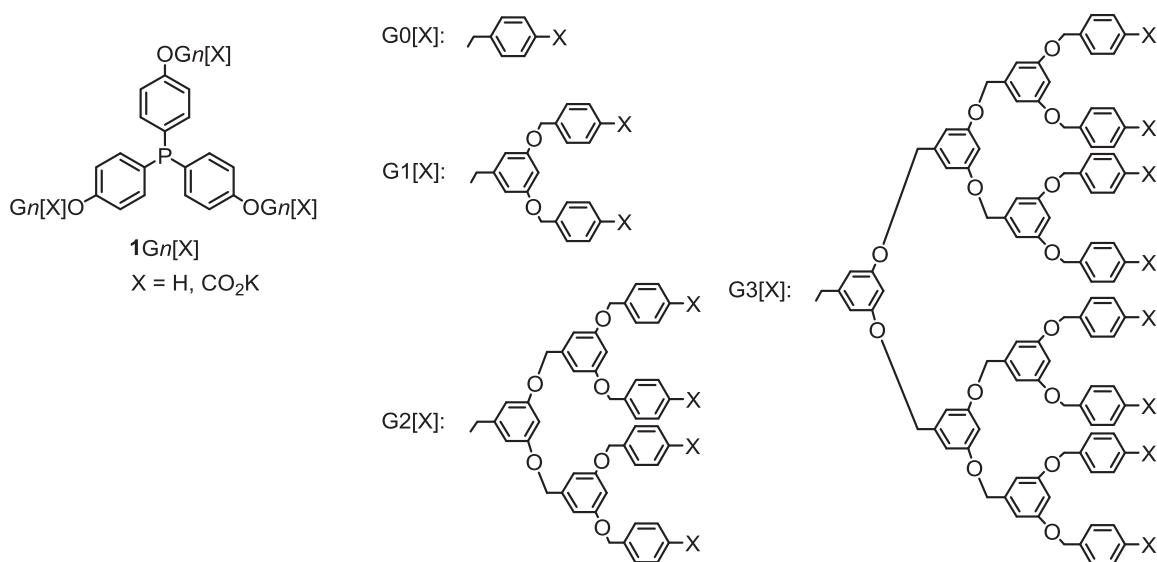
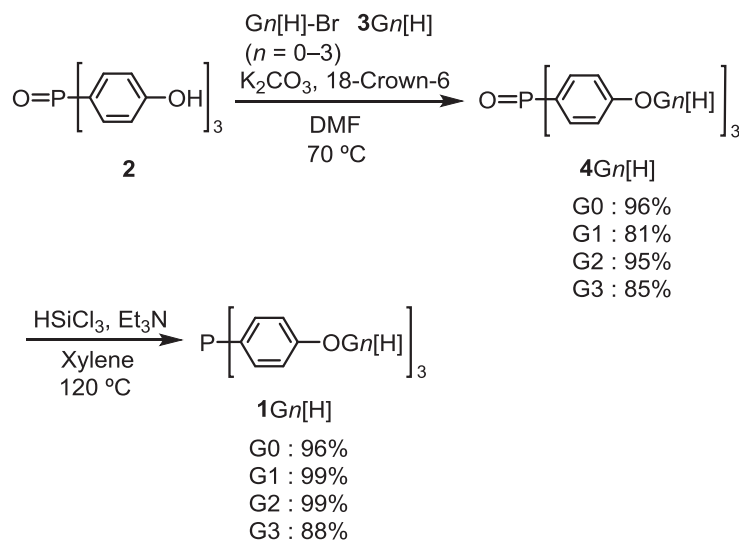


Fig. 1. Structural formulas of $1G_n[X]$ and $G_n[X]$ dendrons ($n=0-3$).



Scheme 1. Preparation of $1G_n[H]$ ($n=0-3$).

Table 1
Suzuki–Miyaura reaction in 1,4-dioxane catalyzed by the $1G_n[H]$ –palladium complex^a

The reaction scheme shows the Suzuki–Miyaura cross-coupling of 4-iodotoluene (**5a**) and phenylboronic acid (**6a**) to form 4-methylbiphenyl (**7a**). The reaction conditions are: $1G_n[H]$ + $[PdCl(\eta^3-C_3H_5)]_2$ (0.5 mol% Pd, P/Pd = 1/1), Cs_2CO_3 , 1,4-Dioxane, $50^\circ C$, 4 h.

	G_0	G_1	G_2	G_3
Yield (%) ^b	78	76	84 (75) ^c	77

^a Reaction Conditions: $1G_n[H]$ (0.0055 equiv), $[PdCl(\eta^3-C_3H_5)]_2$ (0.0025 equiv, 0.5 mol% Pd), **5a** (1 equiv), **6a** (1.5 equiv), Cs_2CO_3 (4.5 equiv), 1,4-dioxane (0.5 M based on **5a**), carried out at $50^\circ C$ for 4 h.

^b Isolated yield.

^c P/Pd=2/1.

The coupling reactions were carried out by using 4-iodotoluene **5a** and phenylboronic acid **6a** with 0.5 mol % of various generations of $1G_n[H]$ –palladium catalysts, which were prepared from $1G_n[H]$ and $[PdCl(\eta^3-C_3H_5)]_2$ in situ (P/Pd=1/1), in 1,4-dioxane at $50^\circ C$ for 4 h. As a result, the corresponding cross-coupling product **7a** was obtained in comparable yields in all generations, contrary to our expectations. In addition, the second-generation $1G_2[H]$ –palladium catalyst prepared at a P/Pd ratio of 2/1 afforded a slightly lower chemical yield of **7a** than the catalyst prepared at P/Pd=1/1, as shown in Table 1, column G2.

Next, we synthesized the dendritic phosphine having carboxylic groups at the peripheral layer $1G_n[CO_2H]$, which was suitable for an aqueous media Suzuki–Miyaura reaction (Scheme 2). Phosphine core dendrimers $1G_n[CO_2Me]$ were synthesized according to a procedure similar to that used for $1G_n[H]$. Phosphine core dendrimers having carboxylic groups $1G_n[CO_2H]$ were obtained by hydrolysis of $1G_n[CO_2Me]$ with potassium hydroxide in degassed aqueous solution (THF–methanol– H_2O) at $50^\circ C$, followed by protonation of the product with hydrochloric acid. All

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