Dendritic Catalysts

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Triarylphosphanes with Dendritically Arranged Tetraethylene Glycol Moieties at the Periphery: An Efficient Ligand for the Palladium-Catalyzed Suzuki–Miyaura Coupling Reaction**

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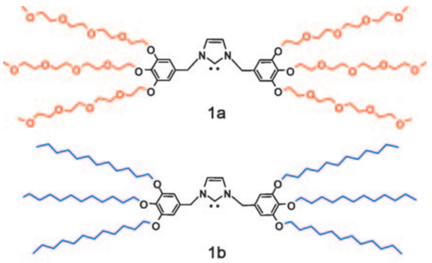
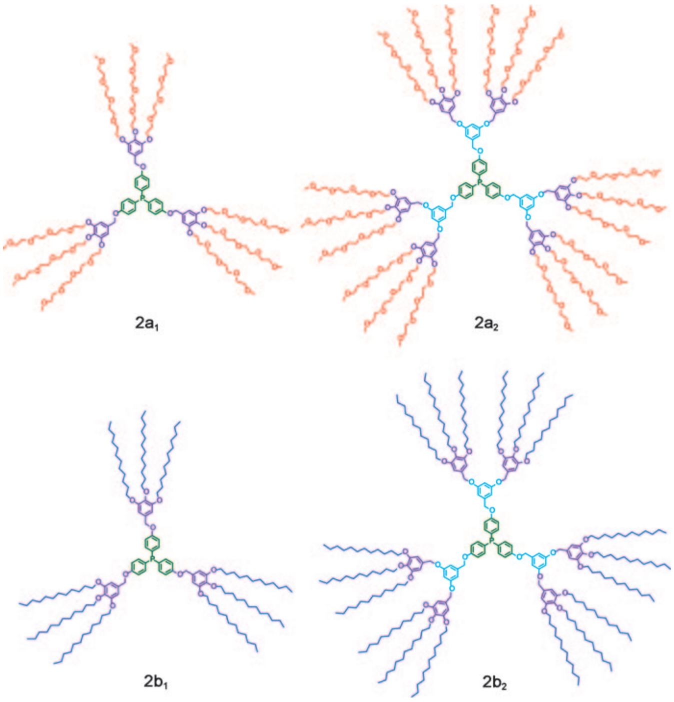
Development of a highly efficient catalyst systems is one of the most important tasks in organic chemistry. For homogeneous transition-metal catalysts,[1] modification within close proximity of the metal center (within a few angstroms) is a conventional way in which to develop efficient catalysts for various reactions, including C–C bond-formation.[2] Meanwhile, the catalytic surroundings can be expanded to the nano scale, and this unique environment has offered new prospects for homogeneous catalysis.[3] For constructing such an distinctive catalytic environment, phosphanes[1d,e] and *N*-heterocyclic carbene (NHC)[4] ligands are the most suitable components; this is because a wide variety of these ligands have been successfully utilized to realize high catalytic activity and selectivity.

Recently, our research group has designed novel NHC ligands (Scheme 1),[5] where **1a** bears tetraethylene glycol (TEG)[6] functionality and **1b** has n-C_{12} alkyl chains. With these ligands, the TEG moieties of **1a** considerably enhanced the catalytic activity of the palladium-catalyzed Suzuki–Miyaura coupling reaction[7] of aryl bromides, whereas the n-C_{12} alkyl chains of **1b** has no effect on the catalysis. Here, the TEG functionality of **1a** is folded in a particular manner around the catalyst center to enhance the catalytic activity. However, the catalytic activity of these NHC ligands was not good enough to activate the less reactive aryl chlorides during coupling reactions. Recently, highly active catalyst systems have been developed for the Suzuki–Miyaura coupling reaction of aryl chlorides. These systems mainly employ a basic, bulky phosphane derivative as a ligand.[8] Herein, we design and prepare a series of new triarylphosphanes in which the TEG or n-C_{12} moieties are arranged dendritically[9] at the periphery of the phosphanes. Among them, the second generation dendritic derivative, with the TEG chains, is distinctly effective as a ligand and provides a highly active Pd catalyst system for the Suzuki–Miyaura coupling reaction.



Scheme 1. *N*-Heterocyclic carbene ligands bearing tetraethylene glycol or n-C_{12} moieties.

The novel phosphanes with TEG (**2a$_1$** and **2a$_2$**) or n-C_{12} (**2b$_1$** and **2b$_2$**) moieties are shown in Scheme 2. These long chains are arranged dendritically at the periphery of the phosphanes: **2a$_2$** and **2b$_2$** are higher dendritic analogues of **2a$_1$** and **2b$_1$**, respectively. These phosphanes were prepared in a high yielding and straightforward manner by the reaction of tri(4-hydroxyphenyl)phosphane oxide with the corresponding



Scheme 2. Novel phosphane ligands bearing tetraethylene glycol or n-C_{12} moieties.

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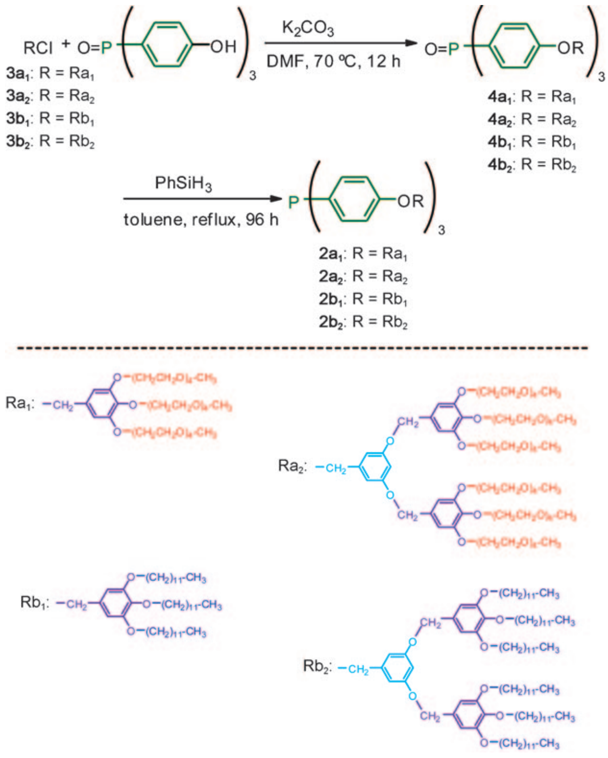
benzyl chlorides ($\mathbf{3a_1}$,[10a] $\mathbf{3a_2}$, $\mathbf{3b_1}$,[10b] and $\mathbf{3b_2}$[10c]) and subsequent reduction of the phosphane oxides (**4**)[11] with $PhSiH_3$ (Scheme 3). These new phosphanes have been fully characterized (see the Supporting Information), and the MALDI-TOF mass spectra show the molecular ion peaks at m/z 2438 ($\mathbf{2a_1}$), 4930 ($\mathbf{2a_2}$), 2240 ($\mathbf{2b_1}$), and 4535 ($\mathbf{2b_2}$), respectively.

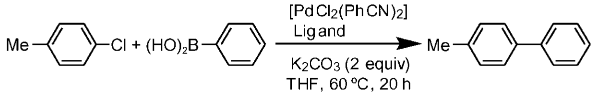


Scheme 3. Preparation of phosphanes $\mathbf{2a_1}$, $\mathbf{2a_2}$, $\mathbf{2b_1}$, and $\mathbf{2b_2}$.

The phosphanes $\mathbf{2a}_n$ and $\mathbf{2b}_n$ ($n = 1$ and 2) were employed as ligands in the Suzuki–Miyaura coupling of 4-chlorotoluene with phenylboronic acid in the presence of a catalytic amount of $[PdCl_2(PhCN)_2]$ with K_2CO_3 in THF at 60 °C (Table 1). As a ligand, the addition of $\mathbf{2a_1}$ bearing the TEG moieties afforded 4-phenyltoluene in 36 % yield (Table 1, entry 1). Remarkably, the higher dendritic analogue $\mathbf{2a_2}$ is a much more efficient ligand and afforded the product in 93 % yield, even with a low catalyst loading (0.1 mol %; Table 1, entry 2). In contrast, $\mathbf{2b_1}$ with n-C_{12} alkyl chains gave the product in only 2 % yield under the same reaction conditions (Table 1, entry 3). Unlike $\mathbf{2a_2}$, $\mathbf{2b_2}$ (the higher dendritic analogue of $\mathbf{2b_1}$) did not show a positive dendrimer effect[12] and afforded the product in only 4 % yield (Table 1, entry 4). Moreover, even with phosphane ligand PPh_3 (the common core of $\mathbf{2a_1}$, $\mathbf{2a_2}$, $\mathbf{2b_1}$, and $\mathbf{2b_2}$) or without it, no conversion of 4-chlorotoluene was observed (Table 1, entries 5 and 6). The use of NHC ligands **1a** and **1b** in the reaction was not successful under the same reaction conditions (Table 1, entries 7 and 8). Overall, the higher dendritic phosphane $\mathbf{2a_2}$ had particular efficiency with aryl chloride in the Suzuki–Miyaura coupling reaction.

The efficiency of $\mathbf{2a_2}$ as the ligand is effected considerably by the type of solvent and base used in the reaction (Table 2). In THF, the catalyst system with $\mathbf{2a_2}$ afforded the product in high yield (Table 2, entry 1). However, 1,4-dioxane and toluene, very common solvents for the Suzuki–Miyaura coupling reaction, were not suitable for the present system (Table 2, entries 2 and 3). In the solvents DME, DMF, 2-propanol, and water,[13] the products were obtained in only low to moderate yields (Table 2, entries 4–7). Thus, THF seems to play an important role in the catalysis. Actually, upon addition of a small amount of THF to the reaction described by entry 3 (with 0.1 mL of THF and 0.9 mL of toluene as the solvent), the yield of the product increased noticeably to 24 %. It is well known that the Suzuki–Miyaura coupling reaction is affected by the type of base used. Potassium salts have been frequently employed in the

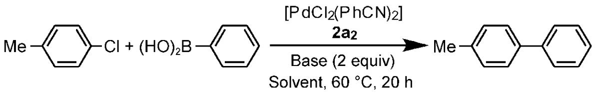
Table 1: Effect of a phosphane and related ligand on the coupling reaction.[a]



Entry	Ligand	Yield [%][b]
1	$\mathbf{2a_1}$	36
2	$\mathbf{2a_2}$	93 (92)[c]
3	$\mathbf{2b_1}$	2
4	$\mathbf{2b_2}$	4
5	PPh_3	0
6	none	0
7	**1a**	9
8	**1b**	< 1

[a] 4-Chlorotoluene (2.0 mmol), phenylboronic acid (4.0 mmol), $[PdCl_2(PhCN)_2]$ (0.0020 mmol, 0.10 mol %), phosphane (0.0040 mmol, 0.20 mol %), and K_2CO_3 (4.0 mmol) in THF (1.0 mL) at 60 °C for 20 h. [b] Yield based on the GC internal standard technique. [c] Yield of isolated product.

Table 2: Effect of solvent and base on the coupling reaction.[a]



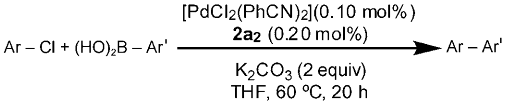
Entry	Solvent	Base	Yield [%][b]
1	THF	K_2CO_3	93
2	1,4-dioxane	K_2CO_3	15
3	toluene	K_2CO_3	7
4	DME	K_2CO_3	33
5	DMF	K_2CO_3	10
6	2-propanol	K_2CO_3	43
7	H_2O	K_2CO_3	9
8	THF	KF	78
9	THF	K_3PO_4	43
10	THF	Rb_2CO_3	75
11	THF	Na_2CO_3	33
12	THF	Cs_2CO_3	25
13	THF	Li_2CO_3	3

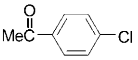
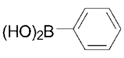
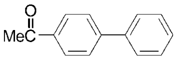
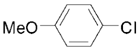
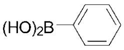
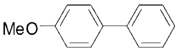
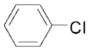
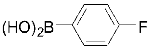
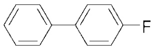
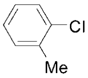
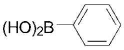
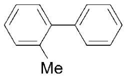
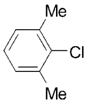
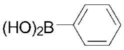
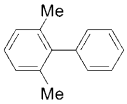
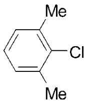
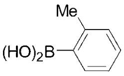
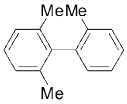
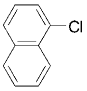
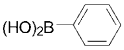
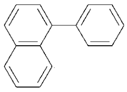
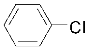
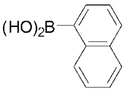
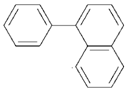
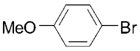
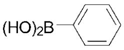
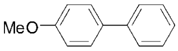
[a] 4-Chlorotoluene (2.0 mmol), phenylboronic acid (4.0 mmol), $[PdCl_2(PhCN)_2]$ (0.0020 mmol, 0.10 mol %), $\mathbf{2a_2}$ (0.0040 mmol, 0.20 mol %), base (4.0 mmol), and solvent (1.0 mL) at 60 °C for 20 h. [b] Yield based on the GC internal standard technique. DME = 1,2-dimethoxyethane, DMF = N,N-dimethylformamide.

reaction. In fact, K_2CO_3 afforded the best result (93 % yield; Table 2, entry 1), whereas KF and K_3PO_4 afforded the product in 78 % and 43 % yields, respectively (Table 2, entries 8 and 9). Rb_2CO_3 may also be a suitable base (Table 2, entry 10), however, only low yields were obtained with Na_2CO_3, Cs_2CO_3, and Li_2CO_3 (Table 2, entries 11–13).

The efficacy of **2a** as the ligand was further confirmed by using various aryl chloride and arylboronic acid substrates under the optimum reaction conditions in THF with K_2CO_3 (Table 3). The electron-poor aryl chloride was smoothly converted into the corresponding biphenyl compound in 95 % yield (Table 3, entry 1). In the case of an electron-rich substrate, the desired product was obtained in 92 % yield by using a higher catalyst loading (0.50 mol %; Table 3, entry 2). 4-Fluorophenylboronic acid afforded the product in 93 % yield (Table 3, entry 3). In the reaction of 2-chlorotoluene with phenylboronic acid, the product was obtained in high yield (Table 3, entry 4). The coupling reaction of 2-chloro-1,3-dimethylbenzene with phenylboronic acid also provided the product in 93 % yield (Table 3, entry 5). In the more sterically demanding coupling reaction of 2-chloro-1,3-dimethylbenzene with 2-methylphenylboronic acid, the product was obtained in moderate yield (Table 3, entry 6). Unfortunately, 2,2′,6,6′-biphenyl derivatives could not be obtained from the present coupling reaction. The substrates 1-chloronathpharene or 1-naphthylboronic acid gave the corresponding products in high yields (Table 3, entries 7 and 8). More reactive aryl bromides were also smoothly coupled to give the corresponding products as exemplified by entry 9 of Table 3.

Table 3: The reaction of various substrates under the optimum reaction conditions.[a]

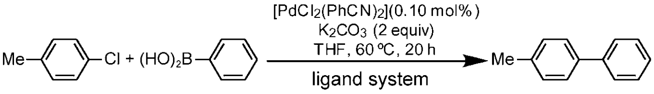


Entry	Aryl chloride	Arylboronic acid	Product	Yield [%][b]
1				95
2[c]				92
3				93
4				83 (99)
5				93
6				(55)
7				87 (96)
8				86 (93)
9				93

[a] Aryl chloride (2.0 mmol), arylboronic acid (4.0 mmol), $[PdCl_2(PhCN)_2]$ (0.0020 mmol, 0.10 mol %), **2a₂** (0.0040 mmol, 0.20 mol %), K_2CO_3 (4.0 mmol), and THF (1.0 mL) at 60 °C for 20 h. [b] Yield of isolated product. The data in parentheses show yields based on the GC internal standard technique. [c] $[PdCl_2(PhCN)_2]$ (0.010 mmol, 0.50 mol %) and **2a₂** (0.020 mmol, 1.0 mol %) were used.

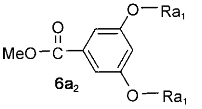
To clarify the unique role of the TEG moieties of **$2a_2$** in the catalysis (vide supra), control experiments were carried out with several ligand systems in the presence of $[PdCl_2(PhCN)_2]$ (Table 4). The ligand system, consisting of a mixture of PPh_3 and tetraethylene glycol dimethyl ether (**5**) in place of **$2a_2$** (molar ratio of **5**/PPh_3 18:1), did not afford any product (Table 4, entry 1). Two other ligand systems were examined: one was a combination of PPh_3 and the ester **$6a_2$** having two Ra_1 groups (Table 4, entry 2), and the other was a mixture of PPh_3 and **$4a_2$** (the oxide of **$2a_2$**; Table 4, entry 3). Both ligand systems did not afford the product. These results clearly indicate that the TEG moieties linked to the phosphane framework are indispensable in causing the high catalytic activity. On the other hand, dendrimers are known to stabilize nanoparticles.[14] Therefore, to examine a possibility of nanoparticles acting as active catalyst species, the mercury test[15] was performed. Since the product was obtained in significant yield (55 %), even in the presence of 25 mol % mercury (Table 4, entry 4), it is unlikely that nanoparticles acted as the active catalyst species.

Table 4: Effect of several ligand systems of relevance on the effectiveness of **2a₂**.[a]



Entry	Ligand system	Yield [%][b]
1	PPh_3 (0.20 mol %) + **5** (3.6 mol %)	0
2[c]	PPh_3 (0.2 mol %) + **6a₂** (0.60 mol %)	0
3	PPh_3 (0.2 mol %) + **4a₂** (0.20 mol %)	0
4	**2a₂** (0.2 mol %) + Hg (25 mol %)	55

[a] 4-Chlorotoluene (2.0 mmol), phenylboronic acid (4.0 mmol), $[PdCl_2(PhCN)_2]$ (0.0020 mmol, 0.10 mol %), and K_2CO_3 (4.0 mmol) in THF (1.0 mL) at 60 °C for 20 h. [b] Yield based on the GC internal standard technique. [c] For Ra_1, see Scheme 3.



6a₂

The basicity of these new phosphanes was evaluated by looking at the $^1J_{P-Se}$ coupling constants of the corresponding phosphane selenides Se=PR₃. It is well known that small $^1J_{P\text{-}Se}$ values for phosphane selenides correspond to a higher basicity of the parent phosphanes.[16] The coupling constants (hence basicity) of **$2a_1$** ($J = 714$ Hz), **$2a_2$** ($J = 715$ Hz), **$2b_1$** ($J = 707$ Hz), and **$2b_2$** ($J = 715$ Hz) were all very similar and comparable to that of PPh_3 ($J = 730$ Hz), but much larger (therefore a weaker base) than those of basic phosphanes such as $P(tBu)_3$ ($J = 686$ Hz) and tricyclohexylphosphane ($J = 674$ Hz). The $^{31}P\{^1H\}$ NMR spectra of **$2a_n$** and **$2b_n$** ($n = 1$ or 2) show that ^{31}P resonances are very similar when recorded in [D$_8$]THF and CDCl$_3$.[17] Thus, the environment close of the phosphorus atoms of **2a**$_n$ and **2b**$_n$ ($n=1$ or 2) seem to resemble each other. This observation may be a result of the intrinsic dendritic structures. The TEG and n-C$_{12}$ moieties are at the periphery of the phosphanes, which have the common triarylphosphane cores.

The reasons for the distinct efficacy of **2a$_2$** as a ligand (vide supra) are not obvious. Figure 1 shows an optimized structure of **2a$_2$** calculated by ONIOM[18] (B3LYP/LANL2DZ:UFF)-CONFLEX[19] methods. The TEG moieties are very flexible, and are folded in a particular manner around the triarylphosphane core in the optimized structure (the triphenylphosphane core is represented by the space-filling model shown in Figure 1). The density of the TEG moieties of **2a$_2$** around the core is much higher than that of **1a**.[5] Phosphanes of this massive shape may exclude other massive phosphanes in the coordination sphere to generate a highly unsaturated and hence extremely active catalyst species, which can successfully accelerate the oxidative addition step of strong aryl–Cl bonds. We have previously shown that large, but sterically well-designed phosphanes effectively furnish highly unsaturated and active catalyst species,[20] and even they have comparable basicity to PPh$_3$. Such highly unsaturated species may be unfavorable upon increasing the amount of **2a$_2$** used in the reaction. When the amount of **2a$_2$** was doubled to P/Pd 4:1, as shown in entry 2 in Table 1, the initial reaction rate decreased to one-thirtieth of the rate for P/Pd 2:1. Recently, a hexacationic triarylphosphane was reported to accelerate the Suzuki–Miyaura coupling of aryl bromides by generating an unsaturated catalytic species.[21] In the present reaction, however, the strong effects of the solvent and the base on the catalytic activity were observed (Table 2). The oxygen atoms of the TEG moieties could coordinate onto the K$^+$ ion (in the case where K$_2$CO$_3$ is the base) and/or the arylboronic acids during the coupling reaction. Therefore, it is conceivable that both the transmetalation and the oxidative addition steps would be accelerated cooperatively because of the strong interaction of the TEG moieties surrounding the active catalyst center.

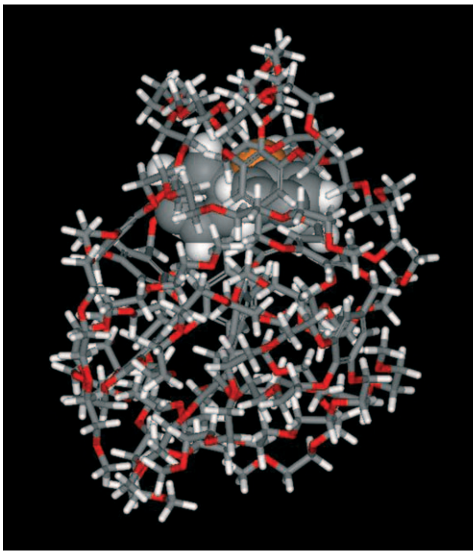


Figure 1. Optimized structure of **2a$_2$** calculated by ONIOM (B3LYP/LANL2DZ:UFF)-CONFLEX method. The space-filling diagram shows the triphenylphosphane core.

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