Synthesis, Characterization and Catalytic Applications of Palladium Nanoparticle-Cored Dendrimers Stabilized by Metal–Carbon Bonds

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The synthesis and characterization of four generations of palladium nanoparticle-cored Fréchet-type dendrimers (**Pd-G**$_n$) possessing direct palladium–carbon bonds are reported. These core–shell materials have been synthesized by the simultaneous reduction of different generation diazodendrons and Pd^{II} in an organic medium. The resulting organic–inorganic hybrid materials were characterized by IR, NMR and UV/Vis spectroscopic techniques. The formation of nearly spherical particles of 2–4 nm diameter was confirmed by TEM studies. The efficiency of one member of this series, **Pd-G$_1$**, in catalysing important C–C bond-forming reactions such as Suzuki, Stille and Hiyama coupling reactions was investigated. The results clearly show that **Pd-G$_1$** can efficiently catalyse the cross-coupling of arylboronic acids, aryl stannanes and organosilicon compounds with differently substituted aryl halides in addition to efficiently catalysing hydrogenation reactions. The catalyst exhibited good recovery and recyclability in Suzuki coupling reactions. The study suggests that a single catalyst capable of catalysing several reactions can be designed.

Introduction

The ever growing quest for new frontiers in nanoscience and technology makes nanoparticle research an active area of interest. Whereas the emergence of novel optic and electronic properties makes noble metal nanoparticles attractive, the interest in transition-metal nanoparticles is essentially due to their enhanced catalytic efficiency, attributable to their large surface-to-volume ratio.[1–6] Nanoparticles of various metals stabilized by a variety of stabilizing ligands such as polymers, surfactants and dendrimers have been synthesized to study their catalytic activity.[7] On the other hand, polyelectrolyte shells with trapped metal particles have also been studied for their catalytic activity.[8] Nanoparticle-cored dendrimers (NCD), which are core–shell materials possessing a nanometre-sized metal cluster at the core and a shell made of dendrons radially connected to the core, is a relatively new entrant in this field.[9–12] The different types of NCDs and strategies for their synthesis have been reviewed recently.[13] Because of the conical shape and large steric requirements of the dendrons, the assembly of dendrons on the metal surface is decided by a sterically induced stoichiometry (SIS) that leaves large numbers of

voids on the metal surface, as shown in Figure 1. The unpassivated metal surfaces in the voids can function as catalytic sites in reactions.
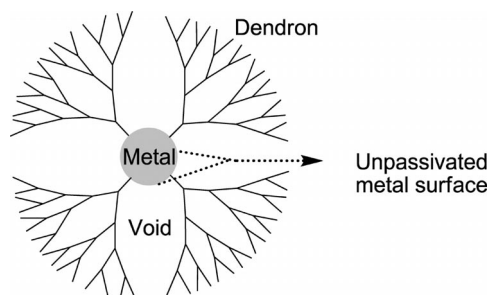

Figure 1. Idealized structure of a NCD.

The synthesis of a catalytically active palladium NCD was reported for the first time by Fox and co-workers.[11] The authors prepared a third-generation Pd NCD by the Brust reaction[14] in which potassium tetrachloropalladate(II) (K$_2$[PdCl$_4$]) was phase-transferred into toluene and reduced by using sodium borohydride (NaBH$_4$) in the presence of a thiol-terminated Fréchet-type G$_3$ dendron. The Pd–G$_3$ NCDs thus obtained catalysed Suzuki and Heck reactions, but disintegrated during catalytic hydrogenation reactions due to hydrogenolysis of the C–S bond. Fan and co-workers later reported the synthesis and characterization of Pd NCDs by using phosphane-terminated dendrons and these were capable of catalysing hydrogenation reactions.[15,16] However, these catalysts could not be recycled, most probably due to the poor stability arising from the labile nature of the metal–heteroatom bond. We reasoned that the stability would be greater if the metal–heteroatom

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bond is replaced by a metal–carbon bond. As part of our continuing interest in the chemistry of NCDs, we have recently reported the synthesis and characterization of Au NCDs stabilized by direct metal–carbon bonds.[17] The synthesis of these NCDs made use of the propensity of aryl radicals generated by the one-electron reduction of diazonium salts to form covalent bonds with metal/solid surfaces.[18–21] We synthesized dendrons of different generations with diazophenyl groups at the focal point and these were subjected to one-electron reduction in the presence of Au^{III} phase-transferred into toluene.[17] The resulting core–shell materials were found to be highly stable when compared with the previously reported thiol-stabilized NCDs. In a very recent communication[22] we reported an extension of this diazonium chemistry to the synthesis of a first-generation Fréchet-type dendron-stabilized Pd NCD (designated here as **Pd-G$_1$**). We were interested in developing palladium catalysts capable of promoting several reactions under phosphane-free reaction conditions. The **Pd-G$_1$** thus prepared could efficiently promote the chemoselective hydrogenation of multifunctional organic substrates with high recyclability.[22] In this paper we show that in addition to hydrogenation reactions, this Pd NCD can efficiently catalyse Suzuki, Stille and Hiyama coupling reactions under phosphane-free reaction conditions. We also report the synthesis of higher-generation Pd NCDs (abbreviated here as **Pd-G$_n$**, n = 1–4).[22] Higher-generation Pd NCDs show slightly higher catalytic efficiency than **Pd-G$_1$**.

Results and Discussion

Synthesis and Characterization of Pd-G$_n$

Fréchet-type poly(aryl ether) dendritic bromides of different generations (**G$_1$**–**G$_4$**) required for the synthesis of **Pd-G$_n$** were prepared according to previously reported procedures.[23,24] These were converted into diazophenyl-terminated dendrons (designated as **G$_1$**–**G$_4$** diazodendrons) following a procedure recently developed by us.[17] The **Pd-G$_n$** NCDs were synthesized in the following manner. An aqueous solution of K$_2$[PdCl$_4$] was stirred with a solution of diazodendron and tetra-n-octylammonium bromide (TOAB) in toluene. After the complete transfer of Pd^{II} from the aqueous to the toluene phase, the latter was separated and reduced with a solution of NaBH$_4$ in water. During the reaction Pd^{II} is reduced by electron transfer from BH$_4^-$ to give Pd atoms, which undergo nucleation and growth to form small clusters. The dendritic diazonium salt, upon receiving an electron from the reducing agent, decomposes into nitrogen and the dendron with a phenyl radical at the focal point.[17–22] At some stage in the growth of the Pd cluster, the dendron radicals are attached to the Pd surface, thereby arresting its growth and leading to the formation

of **Pd-G$_n$** (Scheme 1). After the reaction the organic layer was washed twice with 0.5 M H$_2$SO$_4$, 0.5 M Na$_2$CO$_3$ and finally with water. The solvent was then removed and the residue was further purified by column chromatography.
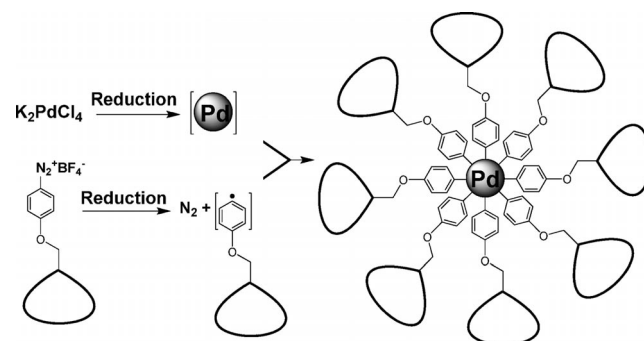
Scheme 1. Synthesis of **Pd-G$_n$**.

The **Pd-G$_n$** NCDs thus prepared were black powders, stable in the solid form and in solution for several months, freely soluble in dichloromethane, chloroform, tetrahydrofuran and toluene, and insoluble in methanol, ethanol and diethyl ether. Dilute solutions of **Pd-G$_n$** were a deep-brown colour. We observed that the **Pd-G$_n$** incorporate a small percentage of TOAB (used as the phase-transfer agent) in the dendritic shell. **Pd-G$_n$** could be purified by chromatography over silica gel without undergoing decomposition but this procedure could not remove the TOAB. Soxhlet extraction with ethanol also could not remove the residual TOAB. The **Pd-G$_n$** synthesized were analysed by IR, UV and NMR spectroscopy. Information about the size of the Pd cores were obtained by TEM. We have recently reported the characterization data for **Pd-G$_1$**.[22] The data for the other systems are presented herein.

Characterization of Pd-G$_n$

FTIR Spectra

In the case of the Pd NCD stabilized by Pd–S bonds, the FTIR spectra of the NCD and precursor disulfide dendron were nearly identical.[11] In the present case, the IR spectra of the precursor diazodendrons are different to those of the NCDs. The FTIR spectra of the diazodendrons shown in Figure 2 (a) clearly indicate the vibrational stretching of a diazo group at around 2245 cm^{-1}.[17–22] The FTIR spectra of **Pd-G$_n$** are presented in part b of Figure 2. The diazo group decomposes during the synthesis of the NCDs and hence this peak is absent in their IR spectra. This also shows the absence of any diazo precursor in the NCDs. The IR spectra of the diazodendrons and NCDs feature methylene C–H stretching modes at v_s = 2870 and v_{as} = 2927 cm^{-1} and aromatic C–H vibration modes at v_s = 3030 and v_{as} = 3061 cm^{-1}.
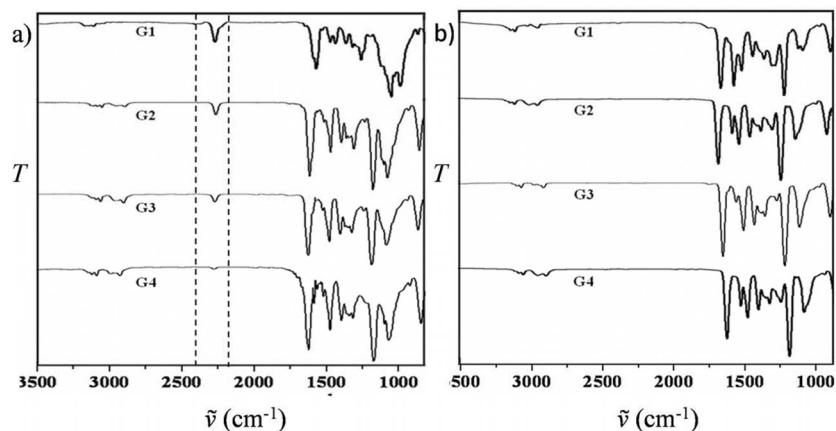
Figure 2. FTIR spectra of a) diazodendrons and b) **Pd-G$_n$**.

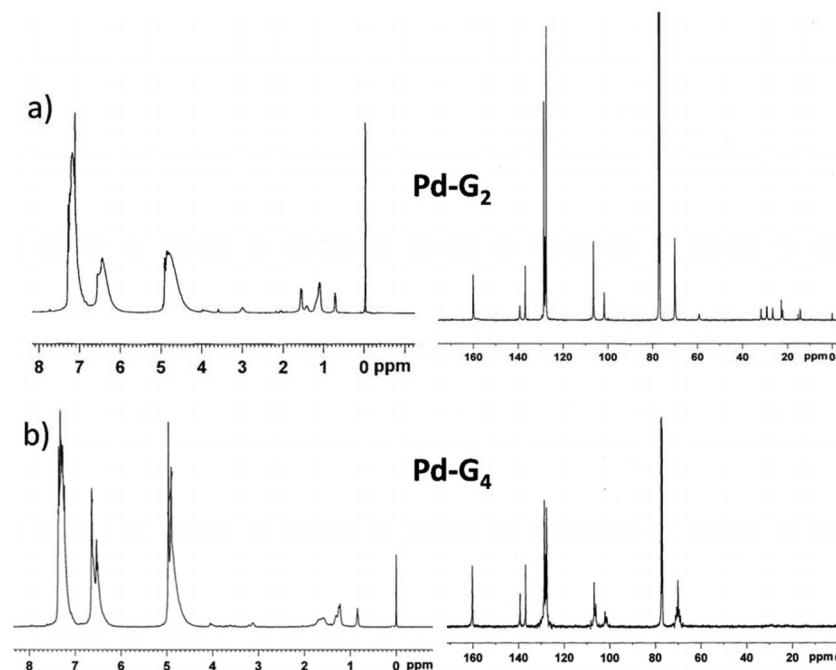
Figure 3. ^{1}H and ^{13}C NMR spectra of a) **Pd-G$_2$** and b) **Pd-G$_4$**.

^{1}H and ^{13}C NMR Spectra

In the case of Au NCDs, we observed that the ^{1}H and ^{13}C NMR signals of the phenyl groups linked to the metal core were broadened considerably.[17] Similar line-broadening was also observed in the case of **Pd-G$_n$**. Figure 3 shows the ^{1}H and ^{13}C NMR spectra of **Pd-G$_2$** and **Pd-G$_4$**.

The proton signals corresponding to the diazophenyl group normally appear at δ = 8.2 and 7.0 ppm[17,22] but these have broadened so much that they are not observable in the ^{1}H NMR spectra. The ^{13}C NMR signals due to the diazophenyl group resonate at 168, 135 and 118 ppm.[17,22] However, these signals are absent in the ^{13}C NMR spectra of **Pd-G$_n$**, which indicates that they have broadened con-

siderably and disappeared into the base line. These observations are consistent with earlier reports and the NMR data further confirm the formation of **Pd-G$_n$** with core–shell structures.[22,25–28]

Absorption Spectroscopy

The absorption spectra of **Pd-G$_1$** and **Pd-G$_2$** in dichloromethane are shown in Figure 4. The spectra show a smooth increase in absorption with increasing energy with no characteristic surface plasmon absorption, which is in accord with literature reports.[11,25]
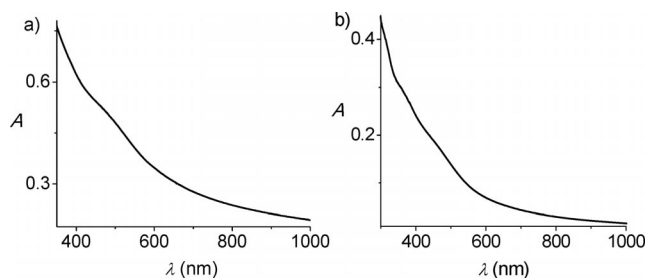
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Figure 4. Absorption spectra of a) **Pd-G$_1$** and b) **Pd-G$_2$** in dichloromethane.

Transmission Electron Microscopic Studies

TEM images of **Pd-G$_n$** (n = 1–4) are shown in Figure 5 (a). The TEM images, taken by drop-casting the NCD solution in toluene, show dispersed metal particles of non-uniform size. TEM shows only the images of the metal cores. In the case of several alkanethiolate monolayer-protected clusters (MPCs), the core–core separation corresponds to the length of the alkyl chain.[28] In the present case, similar core–core separations are rare in the TEM images and hence the thickness of the dendritic shell could not be estimated. The core-size histograms of **Pd-G$_n$** are shown in Figure 5 (b) and indicate the formation of nearly monodisperse particles with an average core diameter of around 2–4 nm. Unlike earlier reports,[15,16] these studies did not give any
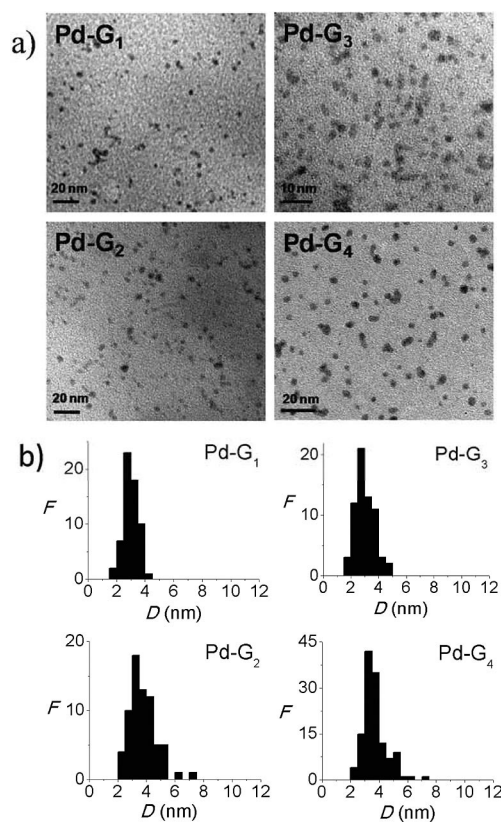

Figure 5. a) TEM images and b) core-size histograms of **Pd-G$_n$** (n = 1–4).

indication regarding the size dependency of palladium metal nanocluster formation with a change in the dendrimer generation.

Control Experiments

In our earlier work with Au NCDs with gold–carbon bonds, several control experiments were carried out to show that the NCDs are stabilized by gold–carbon bonds and not by the stabilization offered by the phase-transfer catalyst TOAB.[17] Control experiments were also carried out in the present case to show that the **Pd-G$_n$** are not stabilized by TOAB. For example, when Pd^{II} was reduced in the absence of diazodendrons, we observed precipitation of palladium black during the reaction. This clearly indicates that the phase-transfer catalyst alone is not capable of stabilizing the palladium nanoparticles and the signals due to TOAB observed in the NMR spectra are due to TOAB trapped inside the NCD.

Catalytic Studies of Pd-G$_1$

The vital role of palladium in organic synthesis stems from its ability to promote carbon–carbon bond-forming reactions with different substrates. Along with the use of simple heterogeneous palladium catalysts,[29] the development of homogeneous palladium systems capable of catalysing reactions in air is an active area of research in organic synthesis.[30] We observed that **Pd-G$_n$** can catalyse several important carbon–carbon bond-forming reactions. Among the four **Pd-G$_n$** systems developed, the synthesis of **Pd-G$_1$** involved fewer steps and it could be synthesized in larger amounts. Hence, in most of the reactions reported herein, we used **Pd-G$_1$** as the catalyst. Recently we reported that **Pd-G$_1$** can efficiently catalyse the chemoselective hydrogenation of multifunctional organic substrates under mild conditions with good recyclability of the catalyst.[22] Here we report the catalytic activity of **Pd-G$_1$** in important C–C bond-forming reactions like Suzuki, Stille and Hiyama coupling reactions. We observed that **Pd-G$_1$** can also catalyse Heck reactions, but the yields are less than 50% and hence these results are not reported here. For a few reactions we also compared the efficiencies of the four **Pd-G$_n$** systems and present the results here.

Catalysis of Suzuki Reactions by Pd-G$_1$

The Suzuki reaction involves the coupling of an arylboronic acid with an aryl halide in the presence of a palladium catalyst and an added base, as shown in Scheme 2.[31–33] We observed that **Pd-G$_1$** can efficiently catalyse Suzuki reactions. As the reaction involves the use of a base, an attempt was made to find out the most suitable base for **Pd-G$_1$**-catalysed Suzuki coupling reactions. For this purpose we studied the reaction between phenylboronic acid and 4-iodoanisole using **Pd-G$_1$** and the different bases shown in Table 1. The reactions were carried out in water/

tetrahydrofuran (50%, v/v). It is evident from Table 1 that the reaction times and yields varied significantly with the type of base employed. For example, with triethylamine, the product yield was very poor even after 24 h.

$$Ar'\text{-}X \quad + \quad ArB(OH)_2 \quad \xrightarrow[\text{Base}]{\text{Pd catalyst}} \quad Ar'\text{-}Ar$$

$$X = I, Br$$
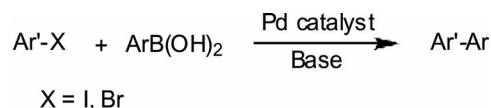
Scheme 2. General scheme for the Suzuki coupling reaction.

Table 1. Effect of base on Suzuki coupling between phenylboronic acid and 4-iodoanisole catalysed by **Pd-G$_1$**.[a]

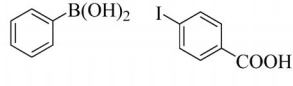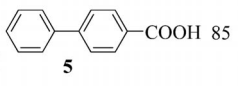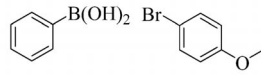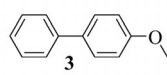| Entry	Base	Yield (%)[b]	Time (h)
1	NaHCO$_3$	94	24
2	K$_2$CO$_3$	85	20
3	Na$_2$CO$_3$	94	24
4	NaOH	95	3
5	K$_3$PO$_4$	95	6
6	KOH	98	12
7	CH$_3$COONa	40	24
8	Et$_3$N	trace	24
9	CsF	55	24
10	CH$_3$ONa	60	20
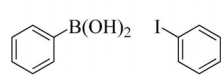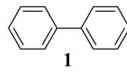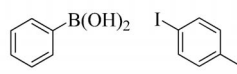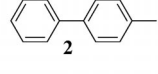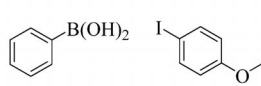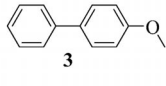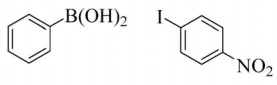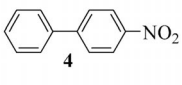
[a] Reagents: 4-iodoanisole (0.4 mmol), phenylboronic acid (0.4 mmol), **Pd-G$_1$** (1.0 mg) and base (1 mmol) in THF/water (10.0 mL). [b] Isolated yield.

Even though sodium hydroxide catalysed the reaction with near quantitative yields in a short reaction time, some palladium black was formed in this reaction. On the basis of the results in Table 1, we concluded that K$_3$PO$_4$ (95% yield in 6 h) is the most suitable base for this reaction and hence we have used it in all the Suzuki reactions reported here.

Tables 2–6 show the results of the Suzuki reactions with the **Pd-G$_1$** catalyst and in all cases the products were unambiguously characterized by ^{1}H NMR spectroscopy and GC–MS (see the Exp. Sect. for reaction conditions). We observed no interference by oxygen in any of the reactions, which were conducted without any special precautions for maintaining a dry or inert atmosphere as is required for conventional palladium-catalysed Suzuki coupling reactions. We also did not observe the formation of any boronic acid homocoupling products in these reactions. Table 2 shows the results of the Suzuki reactions of phenylboronic acid with different aryl halides. The aryl iodides selected for these studies included substrates possessing different electroactive groups like electron-withdrawing nitro and carboxylic acid groups as well as electron-donating methoxy and methyl substituents. It can be seen that regardless of

the electroactive nature of the substituent present on the aryl halide, all the reactions proceeded smoothly to give nearly quantitative product yields. Aryl bromides were also found to be reactive in Suzuki reactions with **Pd-G$_1$** as catalyst.

Table 2. Suzuki coupling of phenylboronic acid catalysed by **Pd-G$_1$**.[a]

Entry	Substrates	Products	Yield (%)[b]
1		1	97
2		2	95
3		3	95
4		4	96
5		5	85
6		3	89
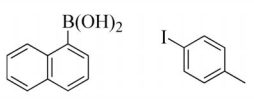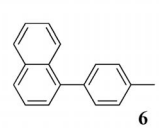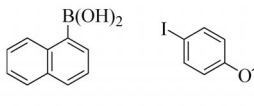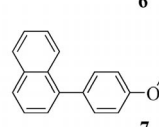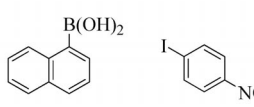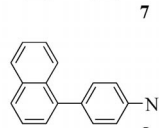
[a] Reagents and conditions: aryl halide (0.4 mmol), **Pd-G$_1$** (1.0 mg) and K$_3$PO$_4$·3H$_2$O (1 mmol) in THF/water (10.0 mL), reflux for 6 h. [b] Isolated yield.

1-Naphthylboronic acid showed similar reactivity to phenylboronic acid in the **Pd-G$_1$**-catalysed Suzuki coupling reaction. The results summarized in Table 3 show that the nature of the substituents do not influence the product yields and that both iodides and bromides are reactive.
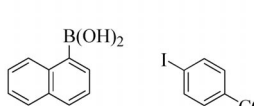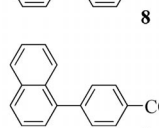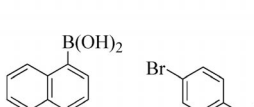
Table 4 presents the results of the reactions of 4-cyanophenylboronic acid with different aryl iodides. It can be seen that the product yields obtained here are lower than those obtained with phenyl- and naphthylboronic acids. However, when a nitro group was present in the aryl iodide, the yield was high.
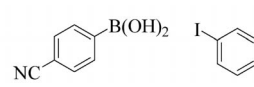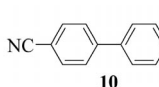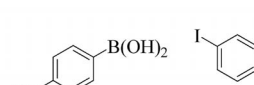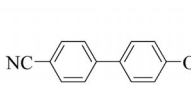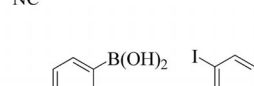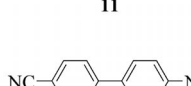
We also studied the Suzuki reactions between heteroaromatics and boronic acids using **Pd-G$_1$** as the catalyst. 3-Iodopyridine was used as the heteroaromatic component in these reactions and the results obtained are shown in Table 5. The general procedure described earlier was also used in this set of experiments and the product yields were in the range of 60–75%. It is evident from these studies that **Pd-G$_1$** can act as a good catalyst for the coupling of heteroaryl halides with different boronic acids, however, the product yields were found to be lower than those obtained with simple aryl halides. The formation of small amounts

Table 3. Suzuki coupling of 1-naphthylboronic acid catalysed by **Pd-G₁**.[a]

Entry	Substrates	Product	Yield (%)[b]
1		6	94
2		7	93
3		8	95
4		9	88
5		7	82

[a] For the reaction conditions, see Table 2. [b] Isolated yield.

Table 4. Suzuki coupling of 4-cyanophenylboronic acid catalysed by **Pd-G₁**.[a]
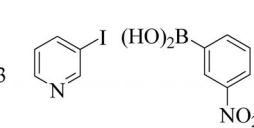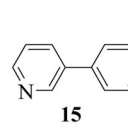
Entry	Substrates	Product	Yield (%)[b]
1		10	72
2		11	69
3		12	95

[a] For the reaction conditions, see Table 2. [b] Isolated yield.

(<10%) of homocoupled products (coupling occurs at the position occupied by the boronic acid group) was also observed in these reactions, which may be a reason for the low yields.

Some of the Pd NCDs previously reported can catalyse Suzuki reactions between aryl chlorides and boronic acids,[16] however, **Pd-G₁** did not even when 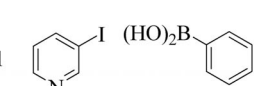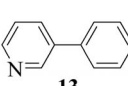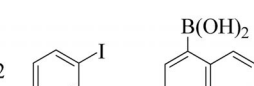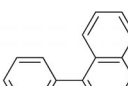the halide component contained an activating substituent such as a nitro or carbonyl group. When the aryl halide contained both chloro and iodo groups, the **Pd-G₁**-catalysed Suzuki reaction occurred only with the iodo substituent, as shown in Table 6.
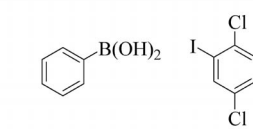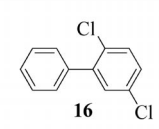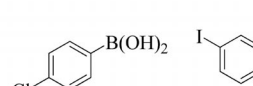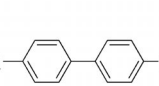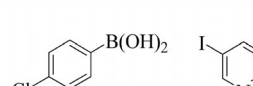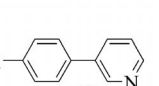
Table 5. Suzuki coupling of 3-iodopyridine catalysed by **Pd-G₁**.[a]

Entry	Substrates	Product	Yield (%)[b]
1		13	75
2		14	61
3		15	60

[a] Reagents and conditions: 3-iodopyridine (0.4 mmol), boronic acid (0.4 mmol), **Pd-G₁** (1.0 mg) and $K_3PO_4 \cdot 3H_2O$ (1 mmol) in THF/water (10.0 mL), reflux for 6 h. [b] Isolated yield.

A more detailed mechanistic study of these reactions, including the use of halogen-exchange reactions[32] as well as catalyst activators,[34] is under investigation.

Table 6. Substrate selectivity for Suzuki coupling catalysed by **Pd-G₁**.[a]

Entry	Substrates	Product	Yield (%)[b]
1		16	75
3		17	60
4		18	60

[a] For the reaction conditions, see Table 2. [b] Isolated yield.

Cross-coupling reactions between aryl iodides and arylboronic acids can be catalysed by several forms of Pd catalysts including Pd on carbon (Pd/C).[29] The performance of most of the new catalysts have only been studied for cross-coupling reactions of phenylboronic acid with substituted halobenzenes, as in Table 2, and for these systems the yields in general are comparable (or even better in some cases) to those we have reported here. Some of these reactions require high temperatures (>100 °C),[29c–29e] but reactions at room temperature have also been reported.[29f] For reac-

tions involving cyano-substituted boronic acids or naphthylboronic acids, simple Pd/C-type catalysts have not been used. For these and more complex systems, Pd catalysts in the presence of phosphanes as co-catalyst are generally employed.[29g–29i] We have also noted that simple Pd catalysts seem to be ineffective for cross-coupling reactions between halobenzoic acids and arylboronic acids. Pd/PANI (PANI = polyaniline) nanocomposites or hydrogel-supported Pd catalysts have been reported to catalyse these reactions.[29j–29l] Thus, for the reactions reported in Table 3 and Table 4 and also for Suzuki reactions involving iodobenzoic acid, **Pd-G$_1$** catalysis seems to have the advantage of achieving good yields under phosphane-free conditions.

The reusability of **Pd-G$_1$** in Suzuki coupling reactions was evaluated by using phenylboronic acid and 4-iodoanisole as substrates. After the reaction, the solvent was removed and the product extracted into diethyl ether. **Pd-G$_1$** being insoluble in diethyl ether adheres to the walls of the flask. The ether solution was decanted and the product isolated. Fresh amounts of reactants were added to the flask containing the **Pd-G$_1$** and the reaction was repeated. Each reaction was carried out for the same time (6 h). The isolated yields of the product **3** obtained for five cycles are summarized in Table 7 and plotted in Figure 6. The data in Table 7 show that the yield of the product is high even in the fifth cycle, which suggests good recyclability of the **Pd-G$_1$** catalyst.

Table 7. Recyclability of **Pd-G$_1$** in the catalysed Suzuki coupling reaction between phenylboronic acid and 4-iodoanisole.

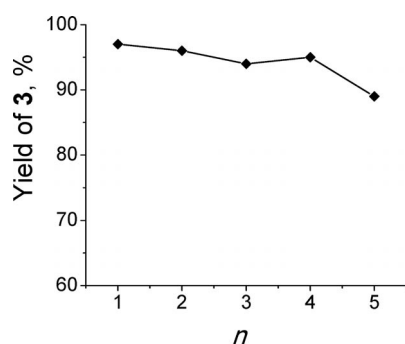| Cycle	1st	2nd	3rd	4th	5th
Yield (%) of **3**[a]	97	96	94	95	89

[a] Isolated yield.

Figure 6. Plot of the yield of **3** vs. the number of cycles of the **Pd-G$_1$**-catalysed Suzuki coupling reaction between phenylboronic acid and 4-iodoanisole.

The accepted mechanism for the Suzuki reaction involves oxidative addition of the aryl halide to the metal as the first step and an aryl–aryl bond-forming reductive elimination as the final step. Because the NCDs have metal–dendron covalent bonds, aryl–dendron and dendron–dendron bond-forming reductive elimination side-reactions are also possible. We have, however, not observed products arising from these reactions. In an attempt to further confirm this issue, a control experiment was performed with 4-iodotoluene and **Pd-G$_1$** in the absence of any added arylboronic acid. After the reaction time, no new product was identified and most of the aryl halide was recovered, which suggests the absence of dendron–dendron or aryl–dendron coupling in these reactions. Note, however, that the amount of catalyst used in the reaction is only 1.0 mg and the dendron content in 1.0 mg of **Pd-G$_1$** is only 0.41 mg. So even if the dendrons undergo dendron–dendron coupling, the maximum amount of coupled product would be 0.41 mg and this may have escaped isolation.

Because we observed the formation of palladium black in some of these reactions, we carried out a TEM analysis of **Pd-G$_1$** after the Suzuki reaction between phenylboronic acid and 4-iodoanisole (see the Supporting Information for images). Our studies showed that as the reaction progresses, the nanoparticle size increases with the formation of more aggregates. The formation of palladium black may be due either to the decomposition of partially protected NCDs present in the catalyst or to Ostwald ripening. It has been reported in the literature that the harsh conditions employed in nanocatalysis can induce Ostwald ripening of the nanoparticles, which ultimately leads to precipitation of the metal nanoparticle.[35–39] Ostwald ripening is a mechanism for cluster growth involving the detachment of atoms from smaller clusters possessing higher surface energy followed by their reattachment to more stable larger clusters with lower surface energy. This leads to a progressive growth in the size of the larger clusters while the smaller ones dissolve into solution.[40,41] The extent of the ripening process depends upon the nature of the capping ligands used. El-Sayed and co-workers carried out systematic studies in this regard and observed that an increase in the number of capping ligands on the nanoparticle surface lowers the rate of Ostwald ripening due to the unavailability of free surfaces/defective sites on the nanoparticle surface.[35–39,42] However, in such cases the observed catalytic activity will be lower owing to the blocking of active sites on the nanoparticle surface. In the present case, the fraction of nanoparticle surface occupied by the dendron ligand is lower and the chances of Ostwald ripening taking place is greater.

A comparative study of the rate of leaching for dendrimer- and polymer-stabilized palladium nanoparticles has been carried out by El-Sayed[43] and de Jesús[44] and their co-workers. These studies indicated that even though the leaching process occurs almost equally with both capping ligands, the possibility of leached-out metal atoms leaving the palladium core is smaller for the dendron ligands due to the steric congestion provided by the dendrons. As a result, a major fraction of the metal atoms will be preserved inside the dendron itself and these atoms can reattach to the parent metal core. This fact is reflected in the good recyclability of the dendrimer-protected metal nanoparticles. On the other hand, polymer ligands will not be able to pro-

vide the steric covering thus allowing the leached-out atoms to escape from the initial palladium core and to reattach to growing nanoclusters leading to the eventual precipitation of palladium black. The leaching followed by precipitation results in a decrease in the amount of colloidal palladium present in the system and this will have direct consequences on the product yield in subsequent reaction cycles.

The formation of small amounts of palladium black in the present system can mainly be attributed to Ostwald ripening. It was stated previously that nearly 50% of surface atoms in **Pd-G$_1$** are not linked to ligands.[22] Palladium atoms can detach from these sites, as suggested by Narayanan and El-Sayed.[43] Because the G$_1$ ligand is relatively small, the G$_1$ shell surrounding the palladium nanoparticle may not provide sufficient protection to the detached atoms. These atoms enter into solution and later are attached to partially protected NCDs that eventually precipitate out of solution. The high product yield even in the fifth cycle (Table 7) reveals a lower rate of activity loss for **Pd-G$_1$** due to palladium black formation.

It is known that ligand-free Pd in small amounts can catalyse these reactions.[2,45] One may then ask the question as to whether the leached out Pd is responsible for the catalytic action? Because the reaction medium contains both leached out Pd and dendron-linked Pd, it is difficult to answer this question. We studied the catalytic ability of higher-generation dendrons in some of these reactions (see below). The extent of leaching is low for higher-generation NCDs and if the leached out Pd is responsible for the reaction, the yield of product would be low when higher-generation NCDs are used as catalysts. We observed that the yields are higher with higher-generation NCDs (see below), which suggests that it is the NCDs that catalyse the reaction and not the leached out Pd. However, detailed studies are needed to confirm this issue.

Catalysis of Stille Reactions by Pd-G$_1$

The Stille reaction involves the palladium-catalysed coupling of substituted aryltin compounds with aryl halides leading to the formation of polyaryl compounds, as shown in Scheme 3.
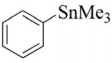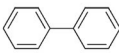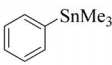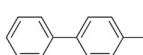
$$\text{Ar'-X} \quad + \quad \text{ArSnR}_3 \xrightarrow{\text{Pd catalyst}} \text{Ar'-Ar}$$

$$X = I$$
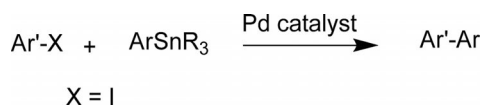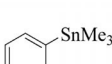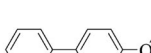
Scheme 3. General scheme for the Stille coupling reaction.

The widespread availability of organostannanes along with their compatibility with different organic functional groups makes these organotin intermediates attractive in organic synthesis even though they are toxic to the environment.[46–50] In this work we studied **Pd-G$_1$**-catalysed Stille reactions between trimethyl(phenyl)tin and aryl iodides. In

a typical reaction, equimolar amounts of trimethyl(phenyl)-tin and aryl iodide were heated in tetrahydrofuran at reflux for 4 h in the presence of **Pd-G$_1$** (see the Exp. Sect.). We attempted the reaction with differently substituted aryl iodides and the products and yields are given in Table 8. All the products in Table 8 were characterized by ^{1}H NMR spectroscopy and GC–MS. The yields shown in Table 8 are isolated yields. The aryl iodides used in this study contained both electron-withdrawing and -donating groups. It is evident from Table 8 that the reaction proceeded equally well with all substrates and we did not observe any influence of the nature of the substituent on the aryl halide on the **Pd-G$_1$**-catalysed Stille coupling reactions. As with the Suzuki coupling reactions, there was no observable interference by oxygen in these reactions. All the reactions were carried out under ordinary laboratory conditions without any special precautions such as inert or dry reaction conditions.

Table 8. Stille coupling reaction catalysed by **Pd-G$_1$**.[a]

Entry	Substrate	Product	Yield (%)[b]
1		**1**	85
2		**2**	73
3		**3**	80
4		**4**	96
5		**5**	81

[a] Reagents and conditions: aryl halide (1 mmol), trimethyl(phenyl)tin (1 mmol), **Pd-G$_1$** (1.0 mg) in THF (6.0 mL) at reflux for 4 h. [b] Isolated yield.

Catalysis of Hiyama Reactions by Pd-G$_1$

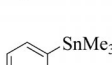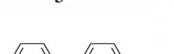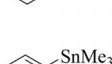The palladium-catalysed cross-coupling of organosilicon compounds with aryl halides is known as the Hiyama reaction (Scheme 4) and this is also an important method for achieving C–C bond formation in organic synthesis.

$$\text{Ar'-X} \quad + \quad \text{ArSi(OCH}_3)_3 \xrightarrow[\text{Base}]{\text{Pd catalyst}} \text{Ar'-Ar}$$

$$X = I$$
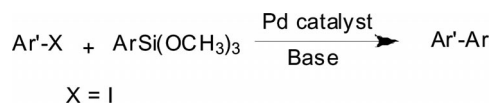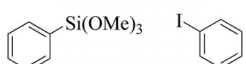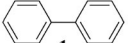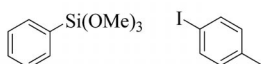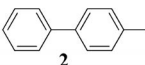
Scheme 4. General scheme for the Hiyama coupling reaction.

In the original report, 1-iodonaphthalene was treated with trimethyl(vinyl)silane with allylpalladium chloride dimer as catalyst and HMPA as solvent to produce 1-vinylnaphthalene. The presence of a base or fluoride ion source

is required for the coupling reaction. The inherently low toxic nature of these organosilicon reagents along with their high atom efficiencies in reactions makes them attractive over other coupling intermediates such as organoboron, organozinc and organotin compounds.[51–55] We observed that **Pd-G₁** can catalyse the Hiyama reaction between trimethoxy(phenyl)silane and aryl iodides in anhydrous tetrahydrofuran. We attempted the reaction with a few aryl iodides and the products and yields obtained are presented in Table 9.

Table 9. Hiyama coupling reactions catalysed by **Pd-G₁**.[a]

Entry	Substrates	Product	Yield (%)[b]
1	Si(OMe)₃ / I	**1**	75
2	Si(OMe)₃ / I	**2**	60
3	Si(OMe)₃ / I—O	**3**	60
4	Si(OMe)₃ / I—NO₂	**4**	82

[a] Reagents and conditions: aryl halide (1 mmol), trimethoxy-(phenyl)silane (2 mmol), tetrabutylammonium fluoride (1.0 M, 2.0 mL) and **Pd-G1** (1.0 mg) in anhydrous THF (5.0 mL) at reflux for 24 h. [b] Isolated yield.

All the products in Table 9 were characterized by ^{1}H NMR spectroscopy and GC–MS analysis. The isolated product yields are shown in Table 9 and are low when compared with those obtained in the Suzuki and Stille reactions. We used aryl iodides bearing different electroactive substituents and observed that the product yield was a maximum when a nitro substituent was present on the aryl halide substrate. Note that unlike the Suzuki and Stille coupling reactions, dry reaction conditions are required for the Hiyama coupling. However, the presence of oxygen did not interfere in the **Pd-G₁**-catalysed Hiyama coupling reactions. We also observed that product yields were low if only 1 equiv. of the silane was used.

Comparison of Pd-G*ₙ* Catalytic Activity

For **Pd-G₁**, the average diameter of the metal core is 2.7 nm.[22] By using this value and the results from a TGA analysis we determined the average number of dendrons attached to the core in **Pd-G₁** to be 131 (see the Supporting Information for calculation). As we proceed from one generation to the next higher generation, the molecular mass and size of the dendron nearly doubles[56,57] and hence the number of dendrons that can be accommodated becomes

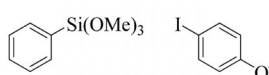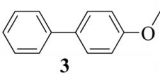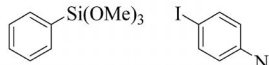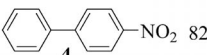half of that in the previous generation. Assuming that the higher-generation NCDs also have the same palladium core size as **Pd-G₁**, the average number of attached dendrons on **Pd-G₂**, **Pd-G₃** and **Pd-G₄** would be 66, 33 and around 17, respectively. A 2 nm Pd cluster would have around 50% of its atoms on its surface.[11] For a 2.7 nm NCD with 700 Pd atoms, if we assume that 35% of the palladium atoms are present on the surface of the metal cluster, there would be 245 Pd atoms on the surface to which dendrons can be attached. In **Pd-G₁**, 131 of these sites (53.5%) are attached to dendrons and the remaining surface sites (46.5%) are free. In this way we can show that the free surface sites would be 73, 86 and 93% in **Pd-G₂**, **Pd-G₃** and **Pd-G₄**, respectively. This suggests that **Pd-G₄** would be the best catalyst. However, whilst evaluating the catalytic ability of NCDs the accessibility of the surface to the reactants also needs to be considered. The steric crowding at the periphery of the dendrimer and the distance from the periphery to the core are important factors that determine the accessibility of the core to the reactants. In the case of dendrimers, it is known that steric crowding at the periphery increases with higher dendrimer generation.[9,11,56,57] This suggests that the accessibility of the reagents to the metal core would be a maximum for **Pd-G₁**. Thus, the catalytic efficiency of **Pd-G*ₙ*** is the result of two opposing factors.

In an attempt to compare the efficiency of **Pd-G*ₙ*** we carried out two reactions with all four **Pd-G*ₙ*** catalysts under identical conditions. The first reaction selected was the Suzuki reaction of 4-cyanophenylboronic acid with 4-iodoanisole. The isolated yields of the product obtained with the different NCD generations are also shown in Scheme 5.
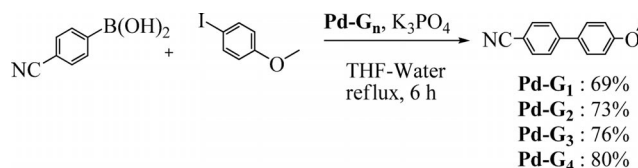
Scheme 5. Suzuki coupling reactions catalysed by different generation Pd NCDs.

The results clearly show that the catalytic efficiency increases with increasing generation of the NCDs. We obtained similar results in the Hiyama reaction between trimethoxy(phenyl)silane and 4-iodoanisole (Scheme 6), the isolated product yield increasing from 60% for **Pd-G₁** to 76% for **Pd-G₄**. Schemes 5 and 6 show that the yields of the products increased only moderately with NCD generation, which suggests that the increased unpassivated or free surface area on **Pd-G₄** predominates over the reduced accessibility of the **Pd-G₄** core to the reactants. Thus, the low yields obtained in the Hiyama reactions (Table 9) can be improved by employing **Pd-G₄** as catalyst. However, the synthesis of **Pd-G₄** requires several steps and the moderate increase in yields that may be achieved may not justify the use of higher-generation NCDs as catalysts in the above reactions.
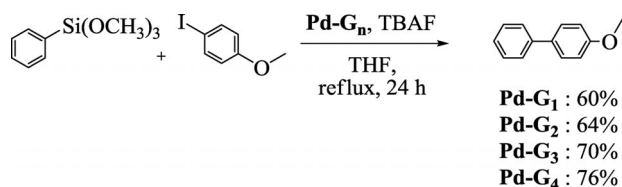
Scheme 6. Hiyama coupling reaction catalysed by different generation Pd NCDs.

Conclusions

In this report we have described the synthesis and characterization of the first four generations of palladium nanoparticle-cored poly(aryl ether) dendrimers stabilized by a direct carbon–palladium bond. These core–shell materials were synthesized by the simultaneous reduction of Pd^{II} and the corresponding diazodendron precursor. The resulting NCDs were characterized by IR, NMR and UV/Vis spectroscopic techniques. TEM analysis of the NCDs confirmed the formation of palladium nanoparticles with an average core diameter of 2–4 nm. The catalytic activity of the NCDs for important C–C bond-forming reactions, for example, the Suzuki, Stille and Hiyama coupling reactions, were studied by using the first-generation Pd-NCD. Our studies showed that **Pd-G$_1$** can efficiently catalyse the Suzuki, Stille and Hiyama couplings of different aryl iodides and bromides under mild reaction conditions. The recyclability of **Pd-G$_1$** was found to be excellent for Suzuki reactions. Preliminary studies showed that the reaction yields increase with increasing NCD generation. Our results clearly suggest that **Pd-G$_1$** can act as a single catalyst system capable of promoting several reactions. Although the yields of **Pd-G$_1$**-catalysed Heck reactions were low, we are hopeful that reaction conditions can be optimized to obtain better yields. Studies in this regard are progressing in our laboratory.

Experimental Section

Materials and Methods: ^{1}H NMR spectra were recorded with a 300 MHz Bruker Avance DPX spectrometer. ^{13}C NMR spectra were recorded by using a 500 MHz Bruker Avance DPX spectrometer. FTIR spectra were recorded with a Shimadzu IR Prestige 21 spectrometer. HRMS were obtained by using a JEOL JMS600 mass spectrometer. Absorption spectra were obtained by using a Shimadzu 3101PC UV/Vis/NIR scanning spectrophotometer. TEM images of **Pd-G$_n$** were obtained with a 200 kV FEI-Tecnai 30G^{2}S-Twin transmission electron microscope. Samples for TEM were prepared by drop-casting one drop of an approx. 1 mg/mL solution in toluene onto standard carbon-coated copper grids (300 mesh) and drying in air for 2 d.

Synthesis of the Diazodendrons: The diazodendrons were synthesized as reported earlier.[17]

Synthesis of Pd-G$_n$: An aqueous solution of K$_2$[PdCl$_4$] (110.0 mg, 0.34 mmol) was stirred with G$_n$N$_2^+$BF$_4^-$ (1 equiv.) in a 1:1 toluene/dichloromethane mixture (50.0 mL). Tetra-n-octylammonium bromide (1.5 equiv.) was added and stirring was continued until the aqueous phase became colourless. The organic phase was separated, washed twice with water and cooled to –30 °C. NaBH$_4$

(10 equiv.) in methanol (10.0 mL) was added dropwise and the reaction mixture was stirred for 4 h at –30 °C and 20 h at room temperature. The organic phase was separated and washed twice with 0.5 M H$_2$SO$_4$, 0.5 M Na$_2$CO$_3$ and finally with water. The organic layer was concentrated and the residue obtained was dried. The black powder was then dissolved in dichloromethane and stirred overnight with 10% aqueous sodium citrate. Further purification was carried out by column chromatography (silica gel). The NCD band was eluted by using ethyl acetate as eluent.

Spectroscopic Data for Pd-G$_1$: The data for **Pd-G$_1$** has previously been reported.[22]

Spectroscopic Data for Pd-G$_2$: IR (KBr): $\tilde{\nu}_{max}$ = 3030.17, 2932.21, 2245.36, 1595.13, 1506.41, 1450.47, 1373.32, 1319.31, 1296.16, 1244.09, 1217.08, 1157.29, 1055.06, 833.25, 736.81, 698.21, 418.55 cm^{-1}. ^{1}H NMR (500 MHz, TMS, CDCl$_3$): δ = 4.97–5.02 (m, 14 H), 6.57–6.65 (m, 10 H), 7.26 (s, 23 H) ppm. ^{13}C NMR (125 MHz, TMS, CDCl$_3$): δ = 69.9, 70.0, 101.6, 106.3, 127.5, 127.9, 128.2, 128.5, 136.7, 139.2, 160.0 ppm.

Spectroscopic Data for Pd-G$_3$: IR (KBr): $\tilde{\nu}_{max}$ = 3030.17, 2929.87, 2914.44, 2872.01, 1595.13, 1498.69, 1448.54, 1373.32, 1321.24, 1296.16, 1215.15, 1157.29, 1055.06, 910.40, 833.25, 738.74, 698.23, 632.65, 460.99 cm^{-1}. ^{1}H NMR (300 MHz, TMS, CDCl$_3$): δ = 4.95–5.00 (br.), 6.53–6.64 (br.), 7.25–7.31 (br.) ppm. ^{13}C NMR (125 MHz, TMS, CDCl$_3$): δ = 69.9, 70.1, 101.5, 106.3, 127.5, 128.5, 136.7, 139.2, 143.5, 160.0, 160.1 ppm.

Spectroscopic Data for Pd-G$_4$: IR (KBr): $\tilde{\nu}_{max}$ = 3061.03, 3030.17, 2927.94, 2870.08, 1595.13, 1496.76, 1452.40, 1373.32, 1321.20, 1296.16, 1263.37, 1155.36, 1053.13, 833.25, 736.81, 696.30 cm^{-1}. ^{1}H NMR (500 MHz, TMS, CDCl$_3$): δ = 4.90–4.61 (br.), 6.51–6.63 (br.), 7.23–7.36 (br.) ppm. ^{13}C NMR (125 MHz, TMS, CDCl$_3$): δ = 70.1, 70.5, 71.2, 101.4, 101.9, 102.1, 106.6, 106.8, 127.6, 128.6, 129.5, 136.8, 139.3, 160.2 ppm.

General Procedure for the Suzuki Reactions: The arylboronic acid (0.4 mmol) and aryl halide (0.4 mmol) were dissolved in tetrahydrofuran (5.0 mL) added to a dry round-bottomed flask containing **Pd-G$_1$** (1.0 mg). The mixture was heated at reflux with an aqueous solution (5.0 mL) of K$_3$PO$_4$ (1 mmol) for 6 h. The organic layer was separated, washed with distilled water and concentrated. The products were purified by column chromatography over silica gel using 1–50% chloroform/hexane as eluent.

Catalyst Recovery Studies with Pd-G$_1$: Phenylboronic acid (0.4 mmol) and 4-iodoanisole (0.4 mmol) were heated at reflux in THF (5.0 mL) containing **Pd-G$_1$** (5.0 mg) and aqueous K$_3$PO$_4$ (1 mmol, 5.0 mL) for 6 h. THF was removed and the product extracted into diethyl ether. **Pd-G$_1$** being insoluble in ether adheres to the walls of the flask. The ether solution was decanted to recover the catalyst and the product was isolated from the ether layer. Fresh amounts of reactants were added to the flask containing the recovered **Pd-G$_1$** and the reaction was repeated.

General Procedure for the Stille Reaction: Trimethyl(phenyl)tin (1 mmol), aryl iodides (1 mmol) and **Pd-G$_1$** (1.0 mg) were added to THF (6.0 mL) and the mixture heated at reflux for 4 h. The reaction mixture was then worked up to yield the product, which was further purified by column chromatography over silica gel using 1–50% chloroform/hexane as eluent.

Procedure for the Hiyama Reaction: Trimethoxy(phenyl)silane (2 mmol), aryl iodide (1 mmol), **Pd-G$_1$** (1.0 mg) and a solution of tetrabutylammonium fluoride (1.0 M, 2.0 mL) were added to dry THF (5.0 mL) and heated at reflux for 24 h. The reaction mixture was then extracted with distilled water and the organic layer was

concentrated to give the products. The products were purified by column chromatography over silica gel using hexane as eluent.

Comparison of the Activities of Pd-G$_1$–Pd-G$_4$

Suzuki Coupling: The reaction was carried out with 4-cyanophenylboronic acid (0.4 mmol) and 4-iodoanisole (0.4 mmol) in THF (5.0 mL) in the presence of aqueous K$_3$PO$_4$ (1 mmol) under reflux conditions for 6 h. The catalyst loading was 1 mg for each generation. After the reaction time, the reaction mixture was worked up and the products were isolated by column chromatography over silica gel.

Hiyama Coupling: Trimethoxy(phenyl)silane (2 mmol), 4-iodoanisole (1 mmol) and a solution of tetrabutylammonium fluoride (1.0 M, 2.0 mL) were added to dry THF (5.0 mL) and heated at reflux for 24 h. The catalyst loading was 1.0 mg for each generation. After the reaction time, the reaction mixture was extracted with distilled water and the organic layer was concentrated to obtain the product, which was further purified by column chromatography over silica gel using hexane as eluent.

Supporting Information (see footnote on the first page of this article): NMR spectra of **Pd-G$_1$** and **Pd-G$_3$**, TEM image of **Pd-G$_1$** after the Suzuki reaction and characterization data of the products formed from **Pd-G$_n$**-catalysed reactions.

Acknowledgments

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