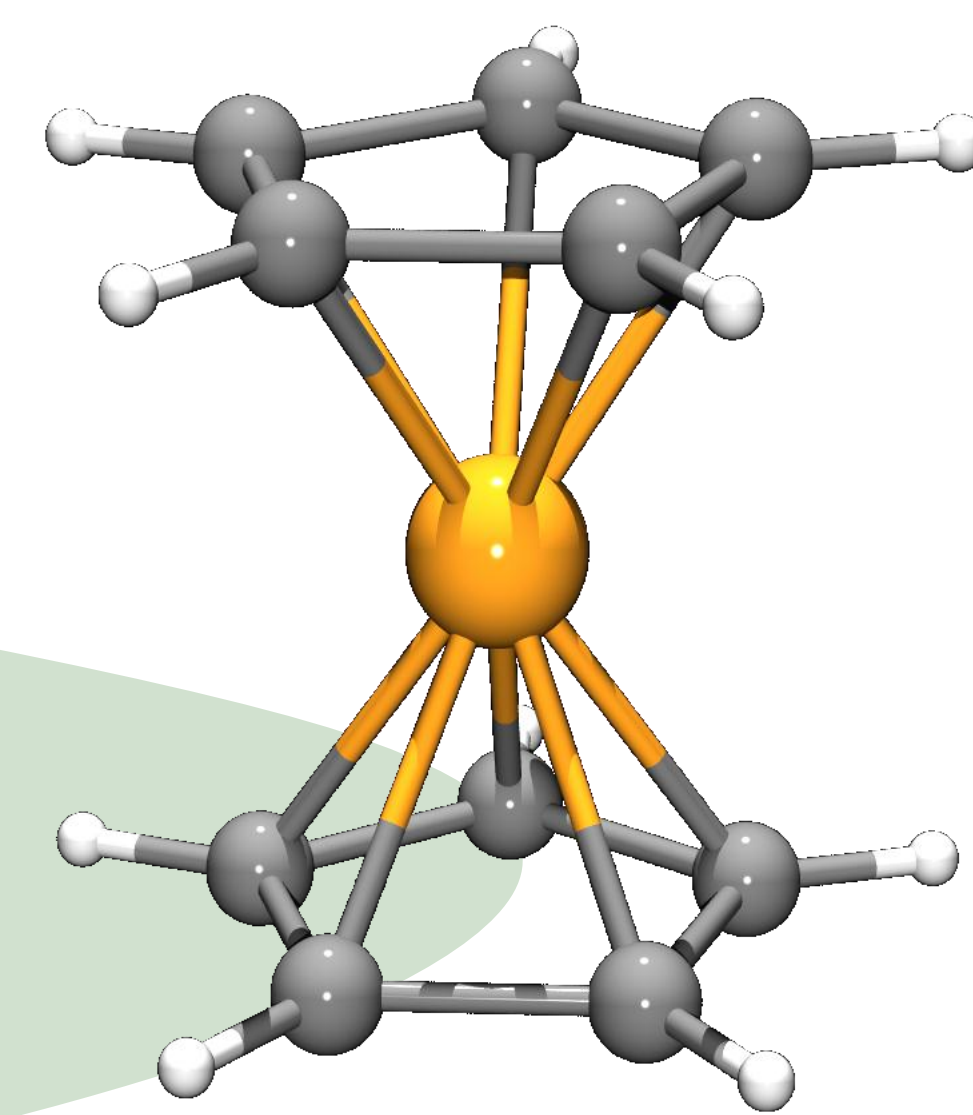


# Catalytic Performance of Palladium Nanoparticles Stabilised by PEGylated Dendrimers in the Suzuki Reaction

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## Introduction

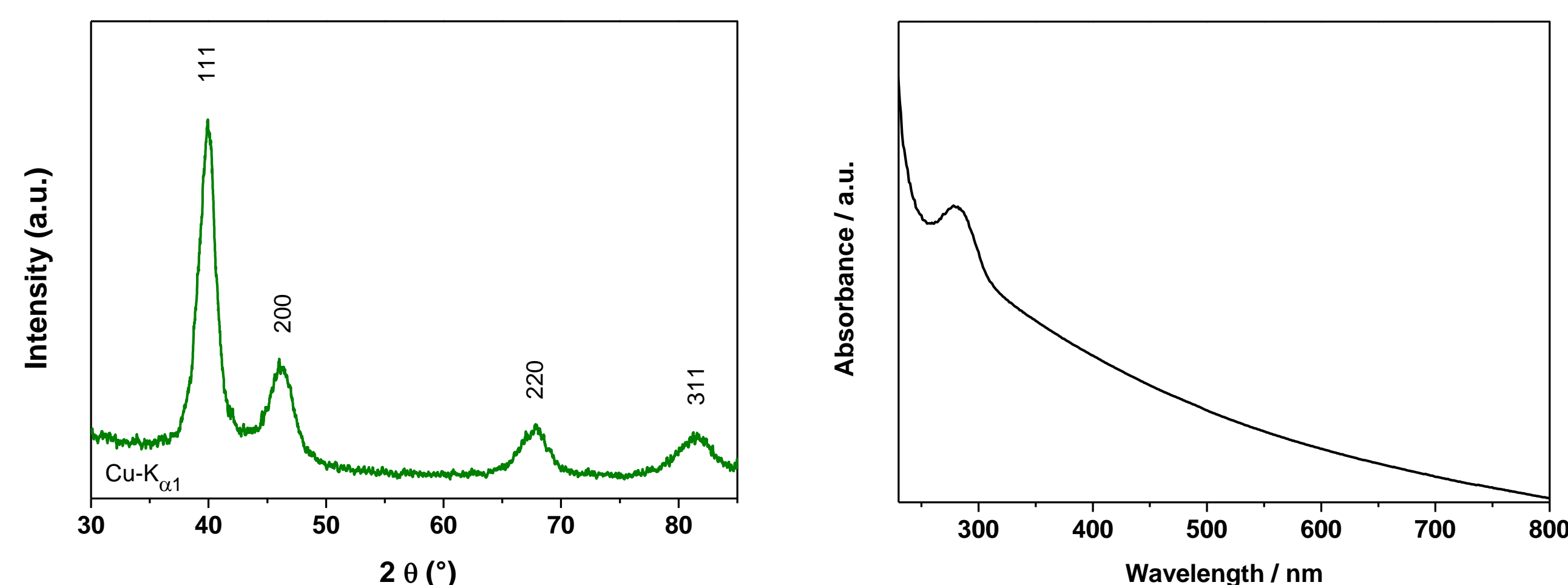
Nanosized metallic particles (= NPs) exhibiting a large surface-to-volume ratio gained considerable interest in the application as effective catalysts for a variety of chemical transformations, including C,C cross-coupling reactions. [1] Since metal NPs are thermodynamically unstable with respect to agglomeration and precipitation phenomena, stabilising agents have to be applied in order to preserve their unique characteristics. Therefore among others monodisperse, radial symmetric dendrimers have

been applied as surfactants for the generation of particles at nanometer dimensions. [2] However, their elaborate and time consuming syntheses as well as extensive purification make them less attractive for a wide variety of applications, due to economical reasons. In contrast, low-generation dendrimers possessing high donation capabilities are highly interesting, as these materials are accessible via straightforward, time efficient synthesis methodologies. [3]

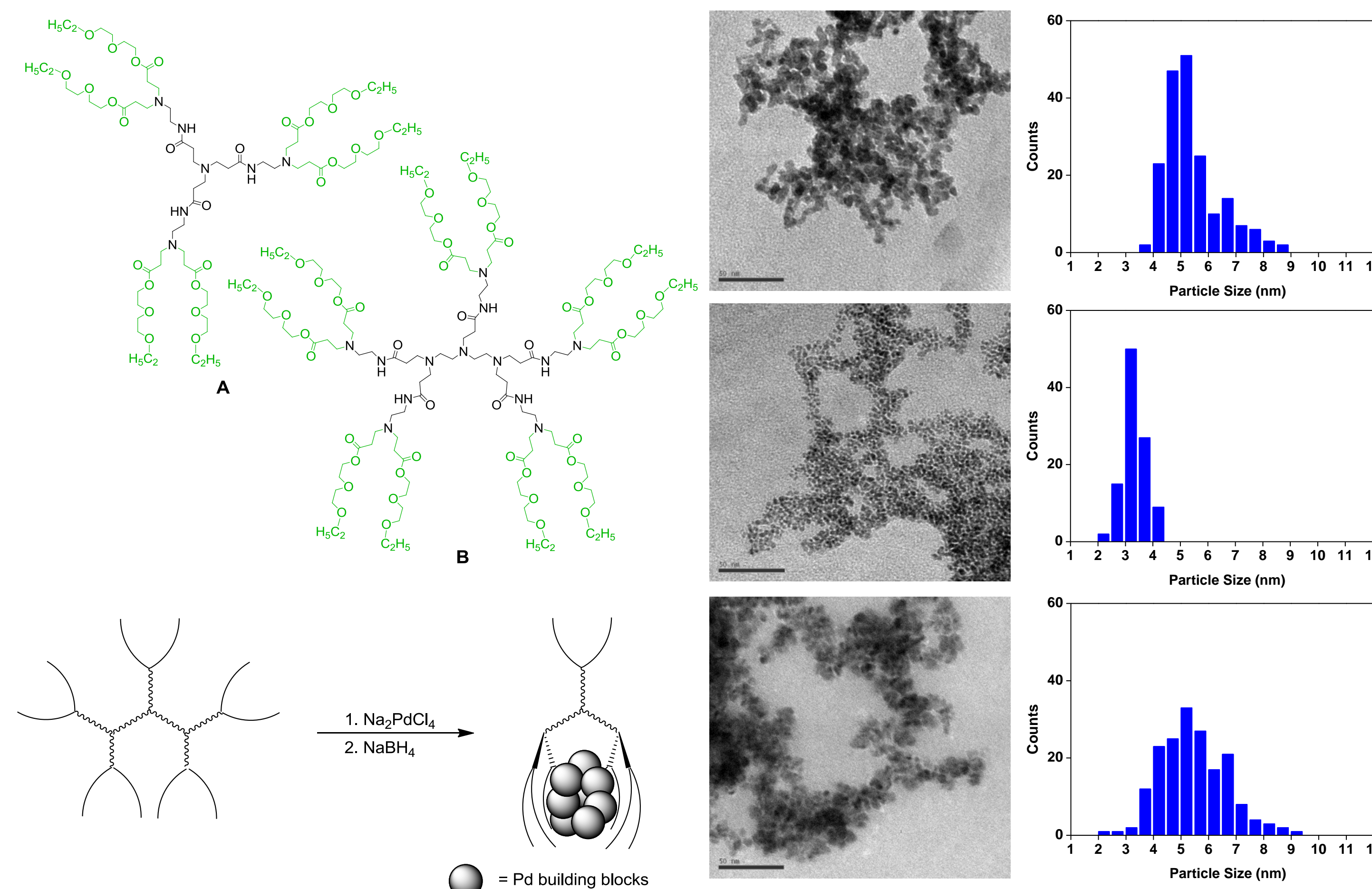
## Dendrimer-Stabilised Pd NPs

The low-generation amidoamine-based PEGylated dendrimers are accessible by exhaustive Michael addition of appropriate commercially available tri- (**A**) or penta- (**B**) amine-terminated PAMAM dendrimers with (poly)ethylene glycol ether ethyl acrylates in quantitative yield. These dendrimers are applied as surfactants within the wet-chemical borohydride reduction of Na<sub>2</sub>PdCl<sub>4</sub> (Scheme 1). In solution these colloids are stable for several weeks.

The dendrimer stabilised Pd NPs were identified by XRPD, as expected a surface plasmon resonance is observed in the UV-Vis spectrum (Figure 1). FT-IR measurements revealed the presence of the PEGylated surfactant. The size of the Pd colloids can be determined by TEM imaging and DLS experiments, respectively. (Figure 2).



**Figure 1.** left: XRPD derived from **B**-stabilised Pd NPs (**B**:Pd = 1:150); right: UV-Vis spectrum of **B**-stabilised Pd NPs (**B**:Pd = 1:150) in MeOH (25 °C, c = 1 mmol·L<sup>-1</sup>).



**Figure 2.** TEM images and particle size distributions of dendrimer coated Pd NPs: top: **A**:Pd = 1:150; Ø = 5.1 (± 1.2) nm; middle: **B**:Pd = 1:10; Ø = 2.9 (± 0.4) nm; bottom: **B**:Pd = 1:150; Ø = 5.7 (± 1.4) nm.

**Scheme 1.** top: Structure of dendrimers **A** and **B**; bottom: Synthesis of dendrimer-stabilised Pd NPs.

## Pd NPs in the Suzuki Reaction

The palladium nanoparticles stabilised by PEGylated dendrimers were applied as catalysts in the Suzuki cross-coupling reaction of aryl halides and aromatic boronic acids. The influence of the



The applied surfactant impacts the behaviour of the Pd colloids in two ways. On the one hand it acts as stabilizing agent preventing formation of catalytically inactive palladium black (entry 1). On the other hand it shields the active catalyst from the substrate molecules. Therefore the surfactant to palladium ratio has to be optimised (entries 9–14). Within this study a ratio of 1:150 for surfactant **A** provides the best results (entry 11). Consequently, increasing the number of ethylene glycol chains (surfactant **B**), the catalytic activity is considerably decreased (entry 4 vs 5). Regarding the catalyst loadings almost identical conversions are observed in the range of 0.1–1.0 mol-%.

**Table 1.** Optimization of reaction conditions.

Entry	Surfactant	Surfactant to Palladium	[Pd] / mol-%	Yield / % <sup>a</sup>
1	no	–	1.0	22
2	<b>A</b>	1:1	1.0	10
3	<b>A</b>	1:10	1.0	98
4	<b>A</b>	1:100	1.0	99
5	<b>B</b>	1:100	1.0	58
6	<b>B</b>	1:1000	1.0	26
7	<b>A</b>	1:100	0.5	92
8	<b>A</b>	1:150	0.25	98
9	<b>A</b>	1:50	0.1	30
10	<b>A</b>	1:100	0.1	61
11	<b>A</b>	1:150	0.1	93
12	<b>A</b>	1:200	0.1	87
13	<b>A</b>	1:250	0.1	82
14	<b>A</b>	1:500	0.1	28

<sup>a</sup> Conditions: 2-bromotoluene (2 mmol), phenylboronic acid (3 mmol), K<sub>2</sub>CO<sub>3</sub> (6 mmol), dioxan:water = 2:1 (7 mL), 100 °C, 3 h.

surfactant, the surfactant to palladium ratio as well as the catalyst concentration have been optimised on the example of the formation of 2-methylbiphenyl (equation 1).

**Table 2.** Suzuki reaction of various aryl halides with phenylboronic acid.

Entry	Aryl halide	Yield / % <sup>a</sup>	Entry	Aryl halide	Yield / % <sup>a</sup>
1		100	6		60
2		71	7		74
3		98	8		35
4		99	9		27
5		70	10		26

<sup>a</sup> Conditions: aryl halide (2 mmol), phenylboronic acid (3 mmol), K<sub>3</sub>PO<sub>4</sub> (6 mmol), dioxan:water = 2:1 (7 mL), A:Pd = 1:150, 0.25 mol-% [Pd], 100 °C, 3 h.

To screen the substrate scope of the dendrimer stabilised Pd NPs different aryl halides were reacted with phenylboronic acid under optimised reaction conditions. From Table 2 it can be seen that a wide range of activated, non-activated and deactivated bromo arenes can be coupled at a catalyst level of 0.25 mol-%, the respective biaryls are formed in good to excellent yields after only 3 hours (entries 1–6). However, a major drawback of the here presented Pd NPs is the lower catalytic activity towards the conversion of *ortho*-substituted substrates (entries 7–9) and chloro arenes (entry 10).

## Conclusion

Stable dendrimer-coated Pd NPs were synthesised using the wet-chemical borohydride reduction method of Pd(II) salts in the presence of low-generation amidoamine-based PEGylated dendrimers. The structural properties of the Pd colloids were analyzed by including but not limited to X-ray powder diffraction and transmission electron microscopy. Pd colloids with particle diameters in the range of 2.9 (± 0.4) to 7.1 (± 1.3) nm were obtained exerting this methodology.

The Pd NPs showed a high catalytic activity in the Suzuki reaction of activated, non-activated and deactivated bromo arenes, while being only moderately active for the conversion of *ortho*-substituted substrates and chloro arenes.

## References and Acknowledgement

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